INSTITUT FÜR VERFAHRENSTECHNIK DES INDUSTRIELLEN UMWELTSCHUTZES
Montanuniversität Leoben
Franz-Josef-Straße 18
www.vtiu.com
A-8700 Leoben

Masterarbeit

Mixed Alcohols from Biomass Steam Gasification

erstellt für

Bioenergy 2020+ GmbH

Vorgelegt von:
Gabriela Falk
0410892

Betreuer/Gutachter:
Ao.Univ.Prof.,Dipl.-Ing.,Dr.techn. **Christian Weiss**
Dipl.-Ing.,Dr.techn. **Reinhard Rauch**

Leoben, November 2011

EIDESSTATTLICHE ERKLÄRUNG

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.

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.

Datum	Unterschrift

DANKSAGUNG

Ich möchte mich an dieser Stelle bei allen bedanken, die mich während dieser Arbeit unterstützt haben.

Besonders bedanken möchte ich mich bei meinen beiden Betreuern, Herrn Ao. Univ. Prof. Dipl.-Ing. Dr. techn. Christian Weiss und Herrn Dipl.-Ing. Dr. techn. Reinhard Rauch.

Bei Herrn Christian Weiss möchte ich mich für die kritische Durchsicht meiner Arbeit sowie für die interessanten Beiträge und Änderungsvorschläge bedanken.

Herrn Reinhard Rauch möchte ich ganz besonders dafür danken, dass er mir die Möglichkeit gegeben hat, diese interessante Arbeit durchführen zu können. Er stand mir während meiner gesamten Zeit in Güssing mit Rat und Tat zur Seite. Durch sein außerordentliches Fachwissen und seine Bereitschaft zu Diskussionen hat er mich in jeder Hinsicht unterstützt und mir trotzdem die Freiheit gegeben, selbstständig zu arbeiten.
Vielen Dank für die hilfreichen Anregungen und deine Geduld!

Zudem möchte ich mich auch besonders bei Herrn DI (FH) Gerald Weber bedanken. Er ist mir während der gesamten Zeit in Güssing zur Seite gestanden und hat mich in jeder Beziehung tatkräftig unterstützt.

Bei meinen Kollegen in Güssing möchte ich mich für ihre Hilfsbereitschaft und das angenehme Arbeitsklima bedanken.

Weiters möchte ich mich bei den Mitarbeitern des Instituts für Verfahrenstechnik, Umwelttechnik und Technische Biowissenschaften der TU Wien bedanken, insbesondere bei Frau Dipl.-Ing. Angela Potetz, Frau Dipl.-Ing Anca Sauciuc und Herrn Dipl.-Ing. Alexander Weinert.

Auch möchte ich mich bei den Mitarbeitern des Biomassekraftwerks Güssing sowie denen der Güssing Energy Technologies bedanken. Besonderer Dank gilt hier Herrn DI (FH) Markus Goritschnig, der mich bei den elektrischen und steuertechnischen Arbeiten an meiner Anlage tatkräftig unterstützt hat.

Nicht zuletzt möchte ich mich ganz besonders bei meiner Familie bedanken, die mich während meiner gesamten Studienzeit immer unterstützt hat. Meine Eltern haben mich nicht nur finanziell unterstützt, sondern waren mir auch moralisch eine hilfreiche Stütze.
Vielen Dank!

Kurzfassung

Gemischte Alkohole aus der Biomasse-Dampfvergasung

Die Erzeugung von erneuerbaren Biotreibstoffen aus Biomasse mittels Synthese von gemischten Alkoholen (MAS) gewinnt zunehmend an Bedeutung aufgrund einer Reihe von Vorteilen verglichen mit reinem Methanol oder Ethanol. Die gemischten Alkohole haben unter anderem höhere Oktanzahlen als andere Biotreibstoffe. Auch die Möglichkeit, diese mit Methanol oder Ethanol zu mischen ist von Vorteil. Zusätzlich zu diesen Vorteilen sind die gemischten Alkohole umweltfreundlich aufgrund des Einsatzes von erneuerbaren Ressourcen, wie zum Beispiel Biomasse.

Gegenstand dieser Arbeit sind Untersuchungen eines thermochemischen Prozesses zur Umwandlung von Biomasse zu gemischten Alkoholen im Pilotmaßstab. Die produzierten Biotreibstoffe bestehen in erster Linie aus Ethanol, sowie auch Methanol, Propanol, Butanol und Pentanol. Dazu wurde eine Pilotanlage am Standort der Kraft-Wärme-Kopplungs (KWK) Anlage Güssing aufgebaut. Das verwendete Synthesegas wurde zu diesem Zweck direkt vom Vergaser der KWK Anlage entnommen. Sowohl die Alkoholsynthese als auch die Biomassevergasung werden in dieser Arbeit beschrieben und diskutiert. Besonders erwähnenswert ist hier, dass diese MAS Pilotanlage mit echtem Synthesegas aus Biomasse betrieben wird, im Gegensatz zu anderen Arbeiten, welche sich mit MAS beschäftigen.

Im Zuge dieser Arbeit wurde an der MAS Pilotanlage ein Testlauf mit zehn Experimenten durchgeführt. Während der Experimente wurden die Temperaturen und Drücke für die einzelnen Anlagenteile mit Hilfe eines Automatisierungs- und Visualisierungsprogrammes online gemessen. Es wurde eine Parametervariation von Temperatur und Druck durchgeführt. Darüber hinaus wurde sowohl die Gaszusammensetzung des Synthesegases als auch das MAS Produkt mit Hilfe eines Gaschromatographens analysiert.

Abstract

Mixed Alcohols from Biomass Steam Gasification

The conversion of biomass to renewable biofuels by mixed alcohol synthesis (MAS) becomes more and more important because of its benefits compared with other fuels like pure methanol or ethanol. Mixed alcohol fuels have for example higher octane numbers than other biofuels. Advantageous is also the possibility to blend them with methanol or ethanol due to their ability to act as a solvent. In addition to these benefits, mixed alcohol fuels are environmentally beneficial as a result of the use of renewable resources as feedstock, like biomass.

The master thesis investigates a thermo-chemical process for the conversion of biomass to a renewable biofuel mixture in pilot plant scale. The produced biofuels are primarily ethanol as well as methanol, propanol, butanol and pentanol. For this purpose a pilot plant was built at the location of the combined heat and power (CHP) plant Güssing to produce mixed alcohols. The synthesis gas was taken directly from the gasifier installed at the CHP plant. The mixed alcohol synthesis as well as the biomass gasification are described and discussed in this work. It should be noted that in this MAS pilot plant real synthesis gas from biomass is used in contrast to other work on MAS.

In the course of this work, a test run with ten experiments was carried out on the MAS pilot plant. During this test run temperatures and pressures of the several plant sections were measured online via an automation and visualisation program. A parameter variation of temperatures and pressures was made too. Furthermore, the gas composition of the synthesis gas and the MAS product was analysed by means of gas chromatography.

Contents

1 Introduction

1.1 Background

In consideration of the fact, that the consumption of conventional fuels - both gasoline and diesel - is extremely increasing, the investigation in different pathways for the production of biofuels is inevitable. In Figure 1.1 the trend for vehicle penetration as well as the fleet of vehicles by engine types is shown. On the left you can see the huge growth of cars relating to population, especially in China. In the illustration pictured right the rising amount of cars from 2000 till 2030 is shown. With a view to reducing the consumption of crude oil renewable energy technologies has to be established, mainly in the biofuels sector.

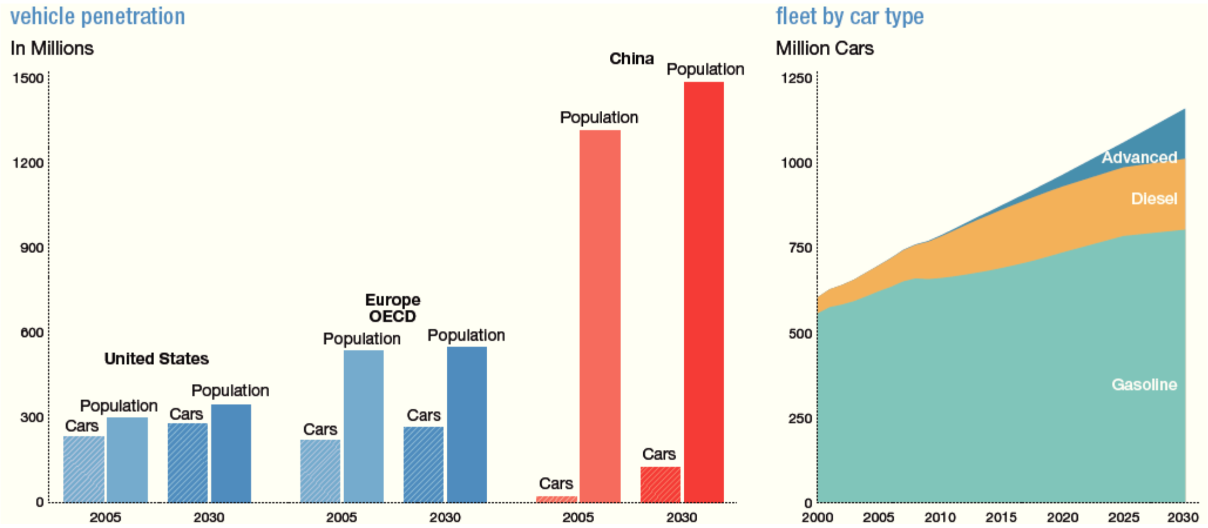


Figure 1.1: Vehicle penetration and fleet of vehicles by engine type [1]

A further reason for the need of biofuel investigations is the decreasing world discovery of crude oil in comparison with increasing production (see Figure 1.2). Therefore alternatives for crude oil have to be investigated necessarily.

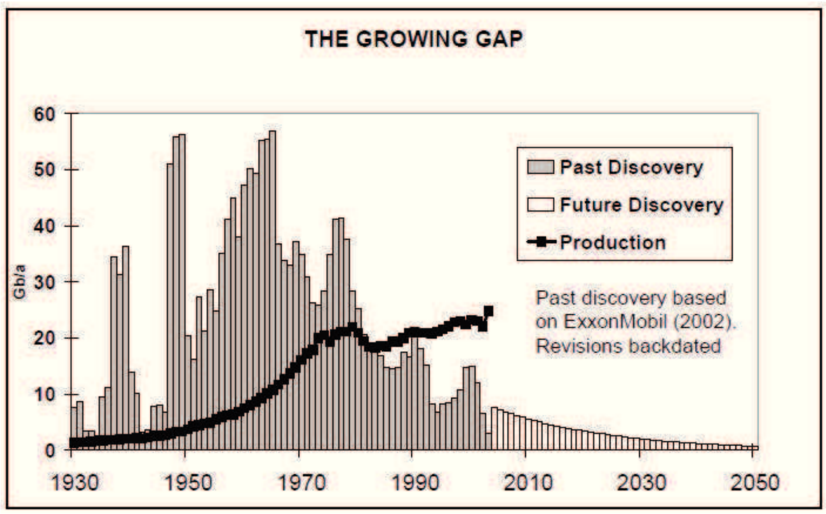


Figure 1.2: World discovery of crude oil versus production [2]

1.2 Research Issue

At the Güssing biomass combined heat and power plant synthesis gas from wood is produced throughout the whole year to supply the commune of Güssing with electricity and heat. Therefore a gas engine is operating, which produces approximately 13,000 MWh electrical power annually. The rejected heat is fed in the district heating grid of Güssing.

The CHP Güssing is based on a dual fluidized bed steam blown biomass gasifier, wherein wood chips are gasified under atmospheric pressure with steam. The thereby produced synthesis gas has a H_2/CO ratio of about 1.6 to 2.0 and is well suited for diverse synthesis applications hence. There are already different synthesis operations, which are using the biomass syngas from the CHP Güssing. Examples are the Fischer-Tropsch synthesis for producing diesel, petrol and waxes and the methanation for producing SNG (synthetic natural gas). The huge disadvantage of these syntheses is the high sensibility to sulphur poisoning, which causes extremely high investment and operation costs. For this reason, a synthesis should be investigated, which is non-sensible to sulphur.

At present, miscellaneous technologies for the production of fuels from biomass are investigated, e.g. ethanol from lignocelluloses or FT-Diesel. In the field of mixed alcohols from synthesis gas, there was no research work in Europe in the past, as opposed to the US. The main advantage of this synthesis compared with the other procedures is the simple gas cleaning because of its resistance against sulphur poisoning. The possibility to convert the mixed alcohols to high quality fuels over dehydration and oligomerisation is an additional advantage.

1.3 Objective

The objective of this master thesis is the investigation of a thermochemical process to produce mixed alcohols (primary ethanol as soon as methanol, propanol, butanol and pentanol) from biomass.

The technology to convert a renewable mixed alcohol fuel out from biomass is predicated on a three-stage process. In the first stage the biomass is gasified, afterward the produced gas is reformed to a high quality syngas and finally the syngas is converted into mixed alcohols.

For the investigation on the synthesis in kg/day scale a pilot plant for mixed alcohols synthesis has been constructed and operated. The purpose is to record the mass and energy balances with the synthesis gas from the CHP Güssing. A further purpose is the production of larger quantities of mixed alcohols which will be collected and analysed.

Areas of interest which were investigated in the course of this work consisted of:

- Plant engineering and construction
- Selection and ordering of all technical components
- Development and supervision of the electrical installation
- Development and supervision of the process measuring and control technology
- Testing of the pilot plant
- Pilot operation
- Interpretation of the experimental results

2 Theory

2.1 Fuels from biomass

2.1.1 Introduction

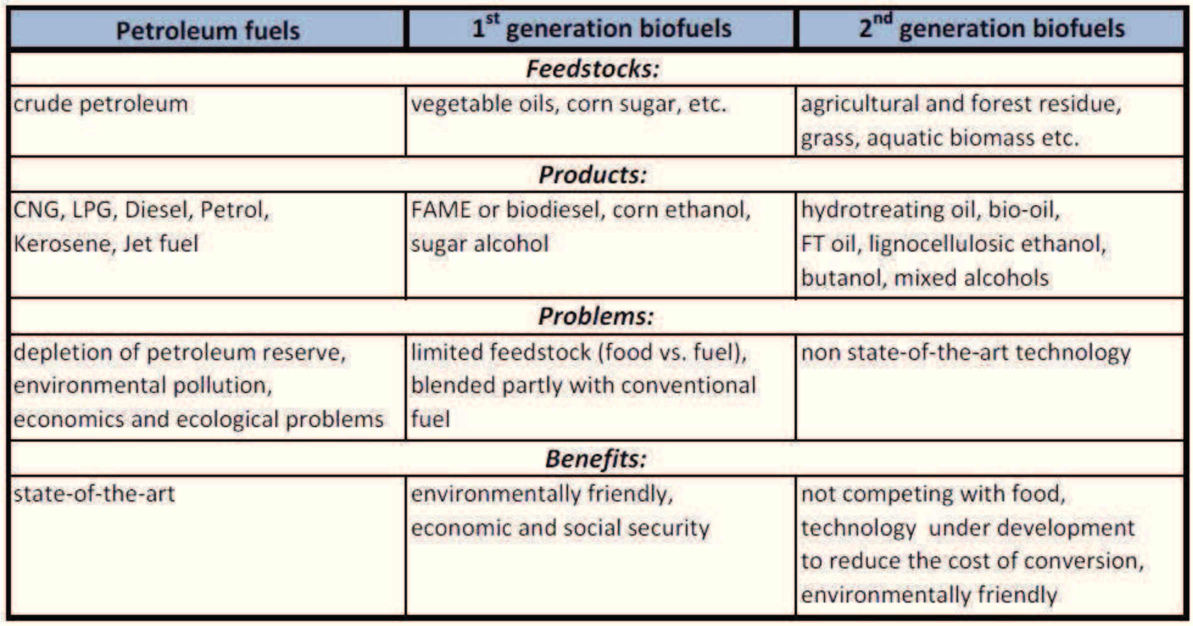
Considering that fuels play a major role within the energy mix, fuels from biomass have a great potential to replace fossil fuels by biofuels from sustainable resources. At present, the production of biofuels soars, due to a release of the European Union's policy and legislation on biofuels. This release of the European Biofuels Directive in 2003 has led to an increasing production of biofuels, particularly of biodiesel. With 81.5 % of the European biofuels production biodiesel is a leader, bioethanol adds up to 18.5 % of the biofuels production in the EU. However, the production of these biofuels amounts to less than 1 % of the European fuel consumption. [3], [4]

The three most important objectives to reach an increase in using biofuels in the EU are [3]:

- an enlarged security of supply for transportation fuels,
- the guarantee of the competitiveness of the EU as well the regional adding value, and
- the support of environmental safety.

Beyond that, biofuels are a new and promising possibility for agriculture and forestry and promote the regional development that way. [3]

Regarding fuels from biomass there is a differentiation between first and second generation biofuels. In Figure 2.1 the comparison of first and second generation biofuels as well as petroleum fuels is shown.



Petroleum fuels	1st generation biofuels	2nd generation biofuels
Feedstocks:		
crude petroleum	vegetable oils, corn sugar, etc.	agricultural and forest residue, grass, aquatic biomass etc.
Products:		
CNG, LPG, Diesel, Petrol, Kerosene, Jet fuel	FAME or biodiesel, corn ethanol, sugar alcohol	hydrotreating oil, bio-oil, FT oil, lignocellulosic ethanol, butanol, mixed alcohols
Problems:		
depletion of petroleum reserve, environmental pollution, economics and ecological problems	limited feedstock (food vs. fuel), blended partly with conventional fuel	non state-of-the-art technology
Benefits:		
state-of-the-art	environmentally friendly, economic and social security	not competing with food, technology under development to reduce the cost of conversion, environmentally friendly

Figure 2.1: First and second generation biofuels versus petroleum fuels (source: [5])

2.1.2 1st generation biofuels

The so-called 1st generation biofuels are primarily produced from food crops. The production takes place in commercial plants using conventional technologies with the following crops as raw material [6]:

- cereal crops (e.g. maize, wheat)
- oil crops (e.g. palm oil, rape)
- sugar crops (e.g. sugar beet, sugar cane)

Further feedstocks used for the production of 1st generation biofuels are starch, animal fats as well as vegetable oils.

The biofuels of the 1st generation covers basically biodiesel, biogas, bioalcohols and vegetable oils. These biofuels are produced over biochemical processes, e.g. the production of bioethanol shown in Figure 2.2.

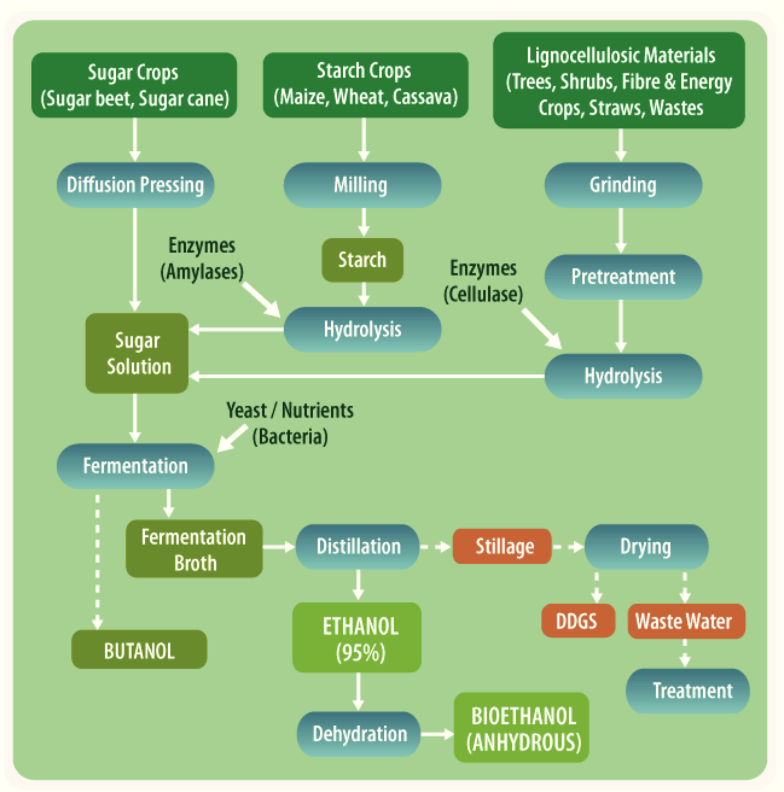


Figure 2.2: Biochemical pathways for biofuel production [6]

Biodiesel

Biodiesel or fatty acid methyl ester (FAME) is made from vegetable oils or animal fats over transesterification. Amongst others the used vegetable oils cover rape seed oil, sunflower seed oil, soybean oil as well as used frying oils (UFO). In the course of transesterification the triglyceride of the vegetable oil undergo a reaction with alcohol (methanol most suitable) to produce FAME and glycerine. The transesterification is an equilibrium reaction in which the chemical conversion is effected basically by mixing the reacting agents. The chemical properties of biodiesel produced via transesterification are very similar to those of fossil diesel and the conversion process is comparatively simple. [7], [8]

In Europe, various biodiesel plants on an industrial scale are in operation (mainly in Germany, Italy, Austria, France and Sweden). Biodiesel is used pure as well as blended with fossil diesel. Up to ratio of 20 % of biodiesel in such blended fuels no modification of the engine has to be carried out. For higher biofuel blends, several minor modifications are necessary because of the chemical corrosiveness of biodiesel against the materials used in automotive engines (metals, rubber seals, coatings and elastomers). Based on the wide field of application, biodiesel has a great potential in the area of biofuels. The most predominantly used biodiesel in Europe is Rapeseed Methyl Ester (RME). [7], [9]

Biogas

Biogas is produced by anaerobic digestion of wet organic material. These organic compounds result either from food crops or from organic wastes like manure, sewage or landfill. Biogas is composed of mainly biomethane (65-70 %) and carbon dioxide (30-35 %) as well as lower amounts of miscellaneous gases. [6]

The production of biogas over anaerobic digestion meets the state of the art. Anaerobic digestion is suitable both for small domestic scale (China, India) and larger community scale (Denmark, Germany). In most instances, the biogas is used for power generation via gas engines. In Europe, only a small percentage of the produced biogas is used as motor fuel due to accessory costs of the gas clean-up. In order to use biogas for fuel applications, hydrogen sulphide and carbon dioxide have to be removed. Failing this, H_2S would cause engine corrosion and CO_2 would take away the limited fuel tank space on-board. [10]

Bioalcohols

Bioalcohols of the first generation includes primarily bioethanol and biomethanol, as well as bio-ETBE (ethyl-tertio-butyl-ether).[11]

Bioethanol can be produced both by fermentation and by distillation. In most instances, bioethanol is produced by fermentation of corn, sugar cane and sugar beet using yeast to ferment sugars into ethanol. The use of e.g. corn as feedstock requires a pretreatment process at which carbohydrates are converted into sugars. This conversion is carried out by dry-milling or wet-milling processes. A disadvantage of the fermentation process is the low ethanol content of approx. 10 %. To gain pure ethanol which is applied in vehicles, a high-performance separation is therefore needed. [11]

Advantageous is the use of distillation due to the ability for extracting a 95 per cent ethanol (just under the azeotropic concentration). For higher ethanol concentrations, specific separation techniques have to be used like molecular sieves or azeotropic distillation. [12]

Bio-ETBE is produced from bioethanol and isobutylene. It is used as an additive in order to increase the octane number of petrol and to reduce emissions. Biomethanol is produced from biomass and biodegradable waste. Because of its highly corrosive and toxic behaviour, biomethanol does not have a great potential for using as a biofuel. [11]

Bioethanol is used mainly in vehicles, mixed with gasoline or diesel. Up to a defined quantity (5-22 % bioethanol with gasoline or up to 15 % bioethanol with diesel), the mixtures are counted among the low bioethanol blends. These fuel blends with low bioethanol content have the advantage, that no modifications of the engine are necessary. Amongst all biofuels, bioethanol is the most produced biofuel worldwide. In 2009, the US are the biggest producer of bioethanol (over 40 billion litres), followed by Brazil (nearly 25 bn litres) and the EU (approx. 3.7 bn litres). Currently, the most popular feedstocks for bioethanol production are maize (US), sugar-cane (Brazil) as well as sugar-beet and wheat in the EU. [11], [13]

Vegetable oils

Vegetable oils can be divided into two sections, pure vegetable oils (PVO) and waste vegetable oils (WVO). Pure vegetable oils, also known as straight vegetable oils (SVO), are extracted from oilseeds by either mechanical pressing or solvent extraction. Waste vegetable oils are recovered from cooking oil used in deep fat fryers, mainly applied in fast food restaurants or food production. [6]

Although vegetable oils have a relative high energy content (close to fossil diesel), their use in combustion engines causes several problems. By way of example, incomplete combustion as well as formation of deposits in the fuel injector of the diesel engine occur as a result of their high viscosity and low volatility. [8]

In a lot of European countries decentralised small-scale plants for producing PVOs are in operation (e.g. Germany, France, Netherlands and UK). The vegetable oils, both PVO and WVO, are used in vehicles in the agricultural and municipal sector as well as for private purposes. [6]

In respect of a worldwide consideration, the 1st generation biofuels are of global importance at this stage. The yearly production of ethanol and biodiesel has already reached a huge amount worldwide. In order to substitute fossil fuels more and more in the future, all countries around the world will be anxious to enhance the production of biofuels.[4].

2.1.3 2nd generation biofuels

The so-called 2nd generation biofuels are primarily produced from lignocellulosic materials. Relating to the used feedstock it can be distinguished between by-products, wastes and dedicated feedstocks. By-products are for example straw from cereals, sugar cane bagasse and forest residues. Amongst wastes mainly organic components of municipal solid wastes are appreciated. Feedstocks, which are grown especially for the purpose of producing biofuels, are for instance grasses, short rotation trees and miscellaneous energy crops. [14]

The biofuels of the 2nd generation covers basically biomass to liquid (BtL), bio-dimethyl ether (Bio-DME), biosynthetic natural gas (Bio-SNG) and biohydrogen. The BtL technology includes the production of biomethanol, bioethanol, higher bioalcohols as well as Fischer-Tropsch diesel. These 2nd generation biofuels are produced over thermochemical processes, e.g. the production of motor fuels like BtL or DME shown in Figure 2.3.

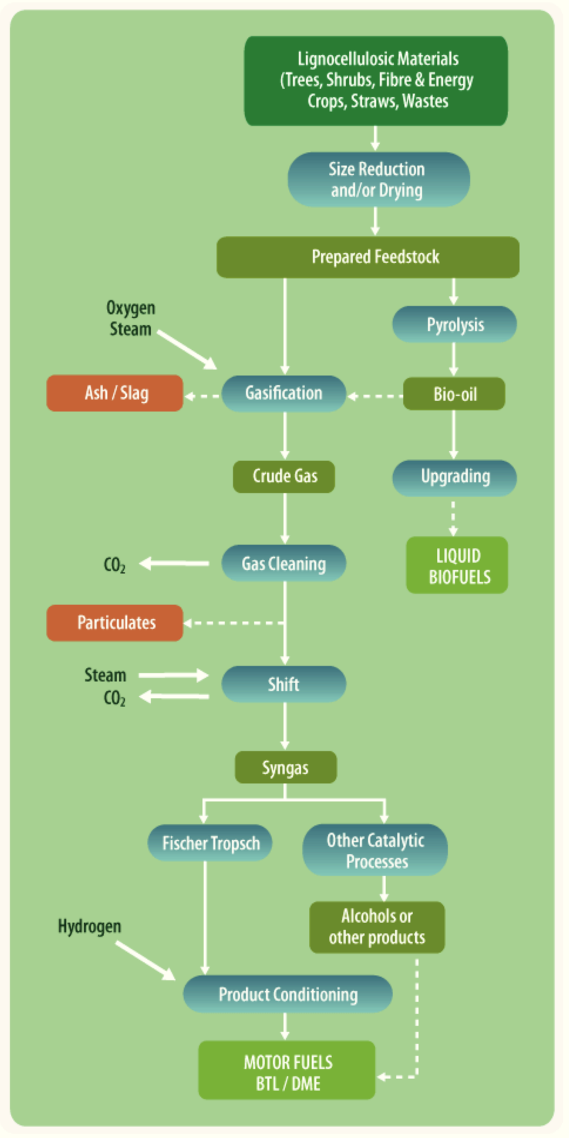


Figure 2.3: Thermochemical pathways for biofuel production [6]

Biomass to Liquid (BtL)

Biomass to Liquid fuels are synthetic fuels comparable with gas to liquid (GtL) and coal to liquid (CtL) fuels. These kinds of fuels have the advantage that they could be adapted to any requirements of the vehicle engines. By using these “customised” fuels an efficient and complete combustion is possible and only low amounts of exhaust emissions are emitted. The production of BtL fuels are not state of the art at the moment. Commercial plants are not available so far. However, research facilities as well as pilot plants are in operation to investigate the conversion of biomass to liquid fuels. [15], [16]

The conversion of biomass to the so-called biomass to liquid fuels is based on a two-step process. First, the biomass is converted into a synthesis gas over thermal processes like gasification or pyrolysis. [17] After this, different procedures are implemented to produce the following BtL products:

- biomethanol
- bioethanol
- higher bioalcohols
- bio-DME
- Fischer-Tropsch diesel

A more detailed description of the particular BtL fuels is effected in section 2.2 - Synthesis pathways.

Bio-SNG

Bio-SNG is a synthetic biofuel similar to natural gas (NG) from fossil source. Due to this similarity to natural gas, gaseous Bio-SNG could be fed in easily into the existing gas distribution system. The possibility to use the existing energy infrastructure (e.g. fuel station for vehicles and the natural gas grid) is very advantageous with respect to cost effectiveness. In order to use Bio-SNG as a motor fuel, it has to be converted into compressed natural gas (CNG) or into liquefied natural gas (LNG). Both CNG and LNG need large storage and fuel tanks due to their low volumetric energy content. Bio-SNG has a very high octane number. However, because of the very low cetane number, a modification of the gasoline engines has to be carried out so as to use it in vehicles. [6], [9]

The conversion of biomass to Bio-SNG takes place in a methanation plant, where syngas from biomass gasification is converted into a Bio-SNG fuel. The SNG process can be divided into three sub-steps. In the first step, the syngas from the biomass gasification is pre-treated in order to remove undesired sulphur compounds. After this, the methanation takes place in a fluidised bed reactor. With the aid of a nickel catalyst, a mixture of methane and carbon dioxide is produced. Finally, in the last step carbon dioxide is removed to achieve the quality of natural gas. [18]

A simplified illustration of the flow sheet of the 1 MW SNG demonstration plant in Güssing is shown in Figure 2.4.

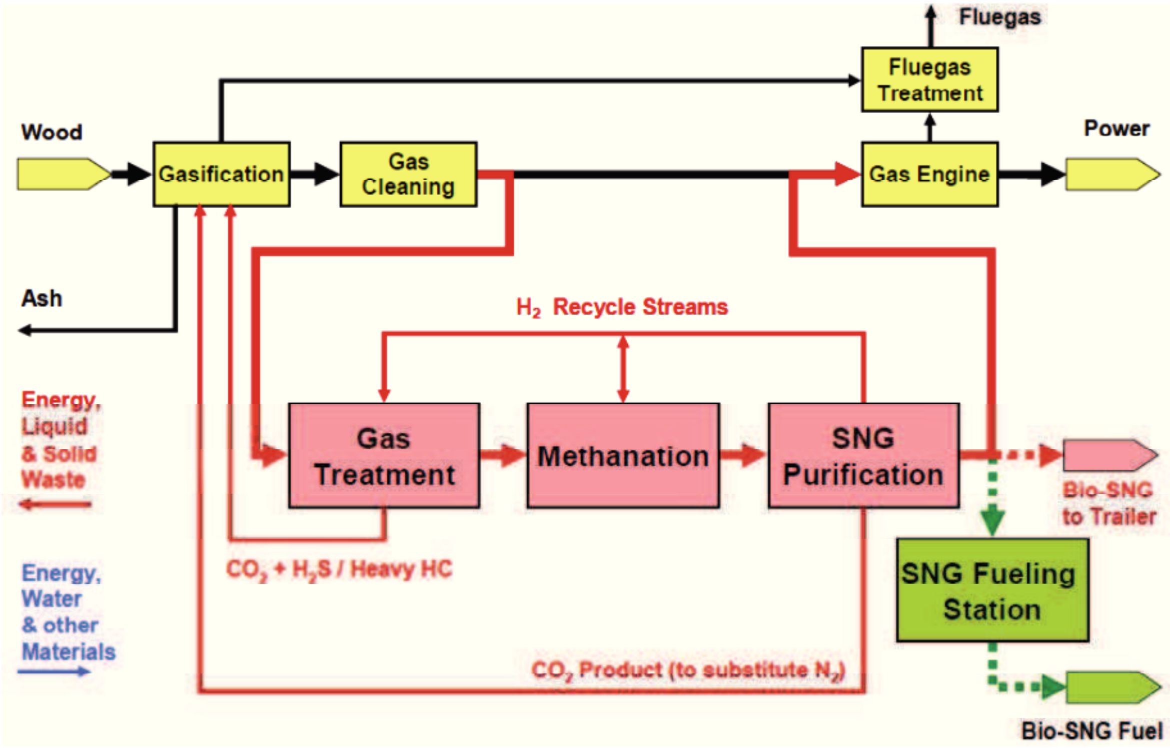


Figure 2.4: Simplified flow sheet of CHP (yellow) and SNG plant (red) in Güssing [19]

Biohydrogen

The term biohydrogen is used to denote hydrogen produced from renewable feedstocks like biomass, compared to hydrogen from fossil resources. Biohydrogen can be applied in many different fields of application. It can be used for power generation or as a fuel. Using biohydrogen as a fuel has the advantage that it produces no pollutant emissions. Moreover, water is produced which can be used for further production of hydrogen after recycling. Particularly with regard to the great efficiency of fuel cells contrary to gasoline-operated engines, biohydrogen will become very important in the future. Additional applications for biohydrogen are arranged in the chemical industry. In this sector, a multiplicity of utilisation is possible, e.g. production of chemical products (ammonia, methanol, syngas), removal of sulphur and nitrogen compounds or cracking of hydrocarbons. [20]

Regarding the production of hydrogen from biomass, there a several process pathways. Examples are thermochemical gasification connected with water gas shift (WGS), fast pyrolysis with subsequent reforming of carbohydrates of the produced bio-oil and biomass derived conversion of synthesis gas using sponge iron. The hydrogen production via gasification, WGS and pressure swing adsorption (PSA) is illustrated in Figure 2.5. [20]

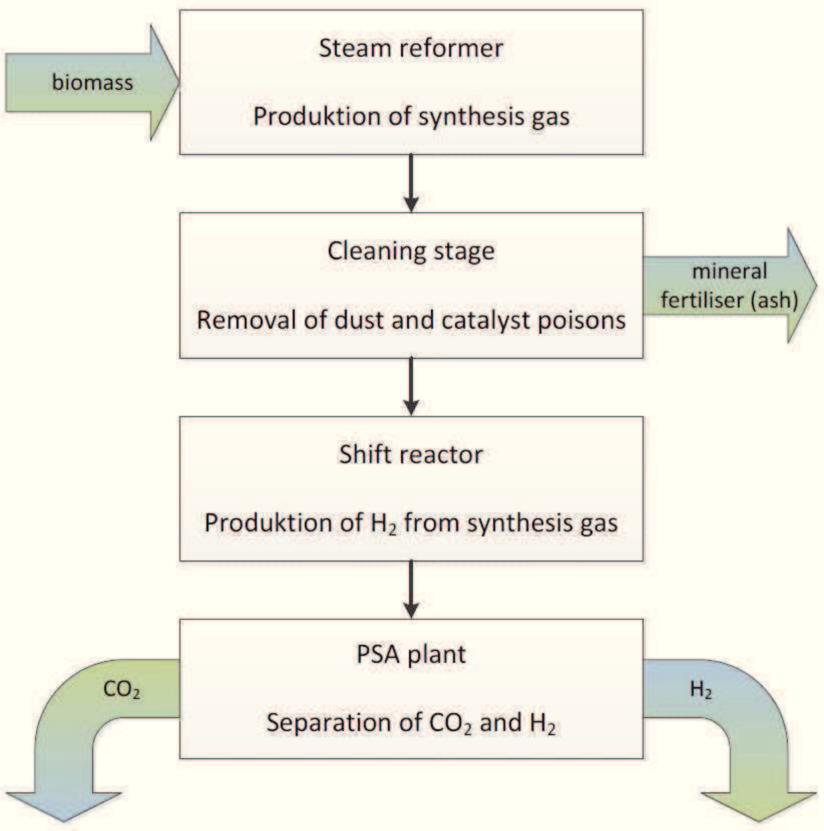


Figure 2.5: Production of hydrogen from biomass via gasification, WGS and PSA (own design according to [21])

2.2 Synthesis pathways

2.2.1 Overview of synthesis pathways

Since the invention of Fischer-Tropsch synthesis in the 1920s, research activities were launched to investigate the conversion of liquid hydrocarbons from syngas (Figure 2.7). By means of this synthesis, different main and by-products can be produced depending on catalysts, process parameters and composition of syngas feed. [22]

The different synthesis pathways including the respective products and by-products are summarised in Figure 2.6. A detailed description of the several syntheses is given in the following sections.

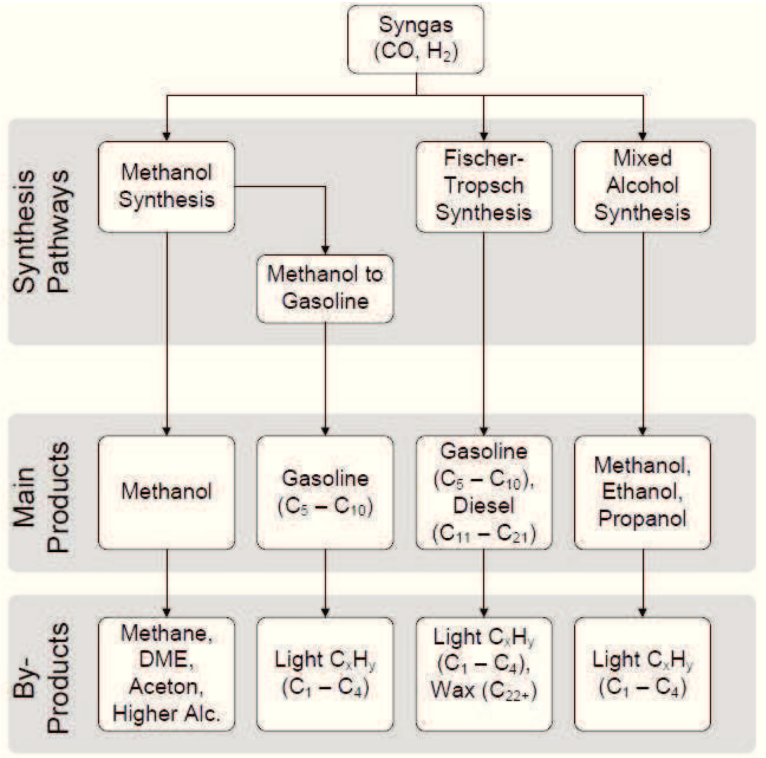


Figure 2.6: Scheme of different synthesis with its dedicated products and by-products [22]

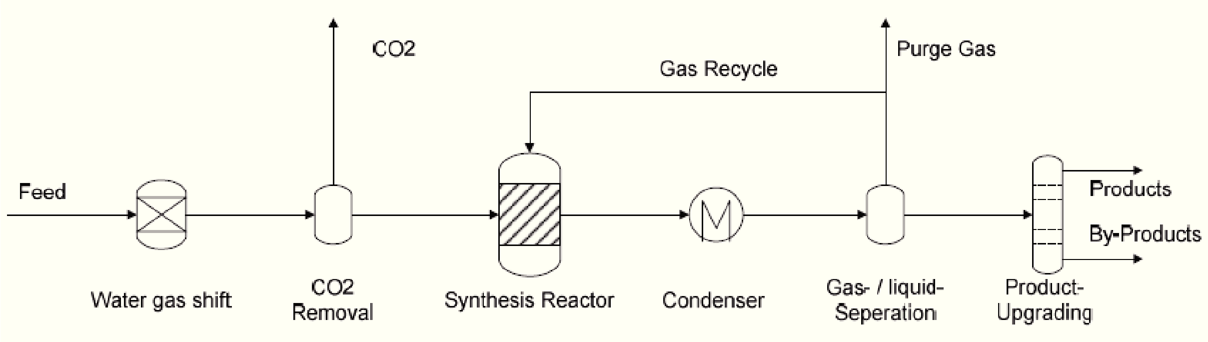


Figure 2.7: Simplified process for producing liquid products over syngas conversion [22]

2.2.2 Methanol synthesis

2.2.2.1 Process description

Technology

The main route for methanol synthesis is the production of methanol from synthesis gas. In the course of this process, the syngas is produced from natural gas using a steam reformer. The catalytic methanol synthesis takes place in a reactor where a mixture of methanol, water, ethanol, higher alcohols, ketones and ethers is produced. After the synthesis, the pure methanol is separated by distillation. The distillation plant consists of two units. In the first unit, the volatiles are removed and in the second unit the water and the higher alcohols are separated. A simplified flow diagram of a methanol synthesis process with natural gas as feedstock can be found in Figure 2.8. [23]

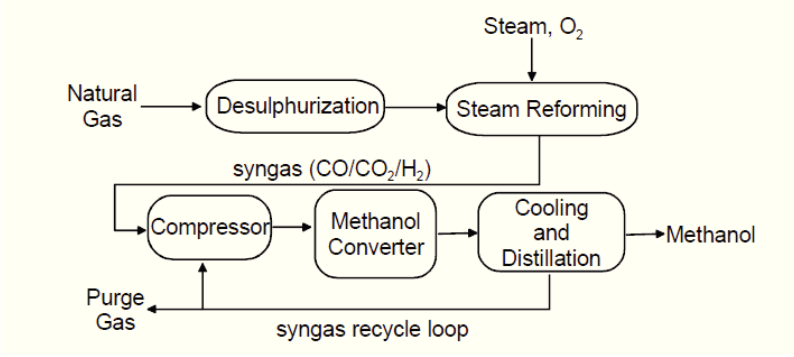


Figure 2.8: Flow diagram of a methanol synthesis process [23]

Chemistry

The synthesis of methanol from syngas consists of two exothermic reactions which take place by high temperatures and high pressures. First the water gas shift (WGS) reaction takes place, followed by the hydrogenation of carbon dioxide to methanol. The third equation describes the net reaction of WGS and hydrogenation reaction. [24]

The chemism of methanol synthesis follows the subsequent reactions [25]:

$CO + H_2O \rightarrow CO_2 + H_2$ $\Delta Hr = -41.47\ kJ/mole$ *WGS reaction*

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ $\Delta Hr = -49.67\ kJ/mole$ *hydrogenation*

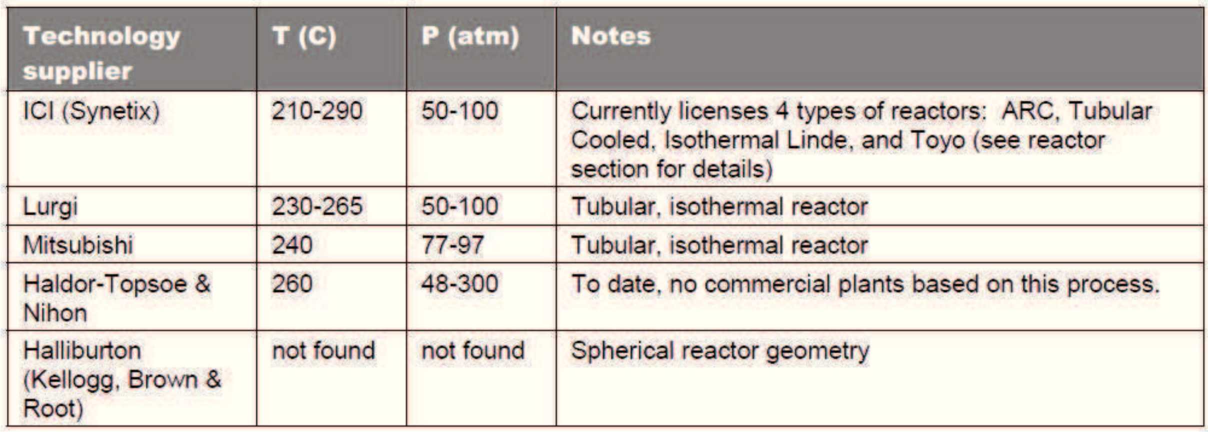
$CO + 2H_2 \rightarrow CH_3OH$ $\Delta Hr = -90.64\ kJ/mole$ *net reaction*

ΔHr ... enthalpy of formation at standard conditions (25 °C, 1 bar)

State of development

In the past, methanol was produced over high temperature (350 °C) and high pressure (250-350 bar) processes using ZnO/Cr_2O_3 catalysts. Today, methanol synthesis is operated at low temperatures (220-275 °C) and low pressures (50-100 bar). Therefore, $Cu/ZnO/Al_2O_3$ catalysts are used. Low pressure methanol synthesis is a well-established technique for producing methanol from syngas and is applied in all commercial methanol plants. Compared to high pressure processes, low pressure methanol synthesis has several advantages, e.g. lower investment and operational costs. [23]

Table 2.1 summarises the suppliers of methanol technologies.



Technology supplier	T (C)	P (atm)	Notes
ICI (Synetix)	210-290	50-100	Currently licenses 4 types of reactors: ARC, Tubular Cooled, Isothermal Linde, and Toyo (see reactor section for details)
Lurgi	230-265	50-100	Tubular, isothermal reactor
Mitsubishi	240	77-97	Tubular, isothermal reactor
Haldor-Topsoe & Nihon	260	48-300	To date, no commercial plants based on this process.
Halliburton (Kellogg, Brown & Root)	not found	not found	Spherical reactor geometry

Table 2.1: Suppliers of methanol technology [23]

Uses

Methanol is used as feed material in a lot of different processes for the production of chemicals. Most of the worldwide produced methanol in used in the production of formaldehyde (35 %). Methyl-tertiary butylether (MTBE) ranks in the second place of methanol consumer followed by acetic acid (9 %) in the third place. [26]

Further processes using methanol as feed material are listed as follows [23]:

- Methanol to Gasoline (MTG)
- Methanol to Olefins (MTO)
- Methanol to Gasoline and Diesel (MOGD)
- Topsoe Integrated Gasoline Synthesis (TIGAS)
- Dimethyl Ether (DME)
- M100 and M85

The conversion processes of methanol to gasoline (MTG), methanol to gasoline and diesel (MOGD) as well as the production of dimethyl ether (DME) are further discussed in the following sections.

2.2.2.2 Methanol to Gasoline (MTG)

The Methanol to Gasoline (MTG) synthesis is a two-stage process, in which methanol is converted to hydrocarbons using zeolite catalysts. In the first step, crude methanol is superheated and partly dehydrated using alumina as catalyst. In doing so, an equilibrium mixture is produced composed of methanol, dimethyl ether and water. In the second step, this mixture of methanol, DME and water as well as the recycled syngas is converted to hydrocarbons (44 %) and water (56 %) in a reactor filled with zeolite catalysts. The reactor is operated at temperatures of 350-366 ℃ and pressure s of approx. 19-23 bar. [23], [27]

Chemistry

In the MTG process developed by Mobil methanol is converted into dimethyl ether by dehydration. After this, the gained DME is converted to a C_2-C_5 olefins product by further dehydration. Finally, the olefins are converted to gasoline. The produced gasoline consists mainly of paraffins (53 vol%), aromatics (26 vol%), olefins (12 vol%) and cycloparaffins (9 vol%). [28]

The reactions for the Methanol to Gasoline synthesis are as follows [29]:

$$2\,CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \text{dehydration}$$

$$CH_3OCH_3 \rightarrow C_2 - C_5\,olefins \qquad \text{dehydration}$$

$$C_2 - C_5\,olefins \rightarrow paraffins, cycloparaffins, aromatics \qquad \text{conversion to gasoline}$$

The overall reaction of the MTG process is given in the following equation [30]:

$$n\,CH_3OH \rightarrow hydrocarbons + n\,H_2O$$

The stoichiometry of the MTG process can be seen in Figure 2.9.

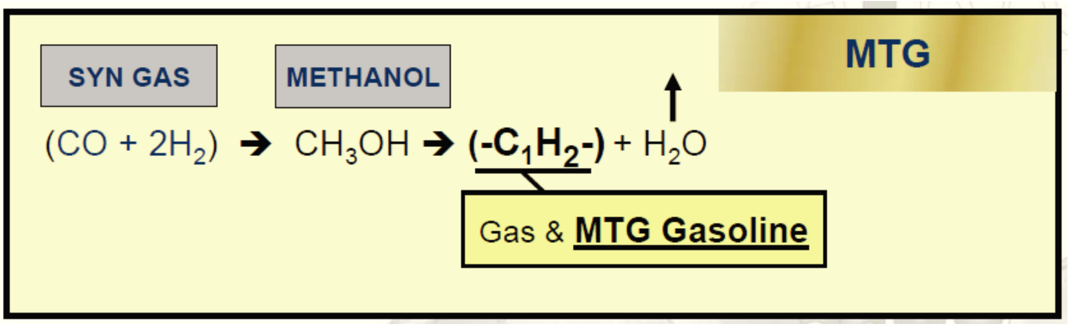


Figure 2.9: Stoichiometry of the MTG process [28]

2.2.2.3 Methanol to Olefins (MTO)

The Methanol to Olefins (MTO) process is another process developed by Mobil. In this synthesis methanol is converted into olefins over a ZSM-5 zeolite catalyst. In order to favour the production of light olefins, as opposed to MGT, higher reaction temperatures, lower pressures and lower acidity zeolites have to be achieved. [31]

A flow diagram of MTO to produce high purity ethylene and propylene is given in Figure 2.10.

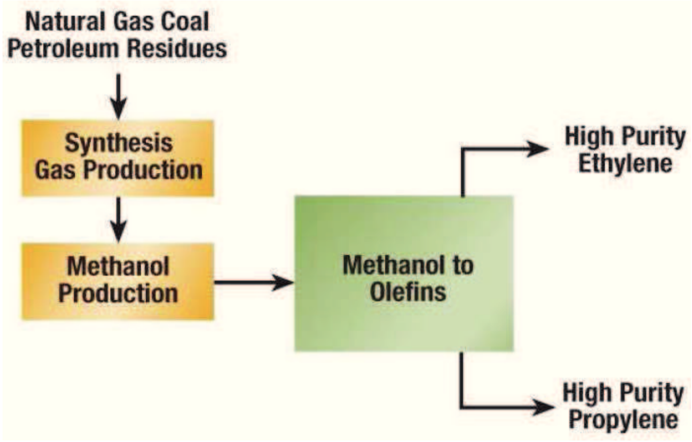


Figure 2.10: Flow diagram of the MTO process [32]

2.2.2.4 Methanol to Gasoline and Distillate (MOGD)

The so-called Mobil Olefins to Gasoline and Distillate (MOGD) process is characterised as a process for the production of gasoline and distillate from methanol. Using a ZSM-5 zeolite catalyst, light olefins from the MTO process were oligomerised to gasoline and distillate products. [33]

Moreover, there is the possibility to produce gasoline and diesel over a combined MTO/MOGD process (see Figure 2.11).

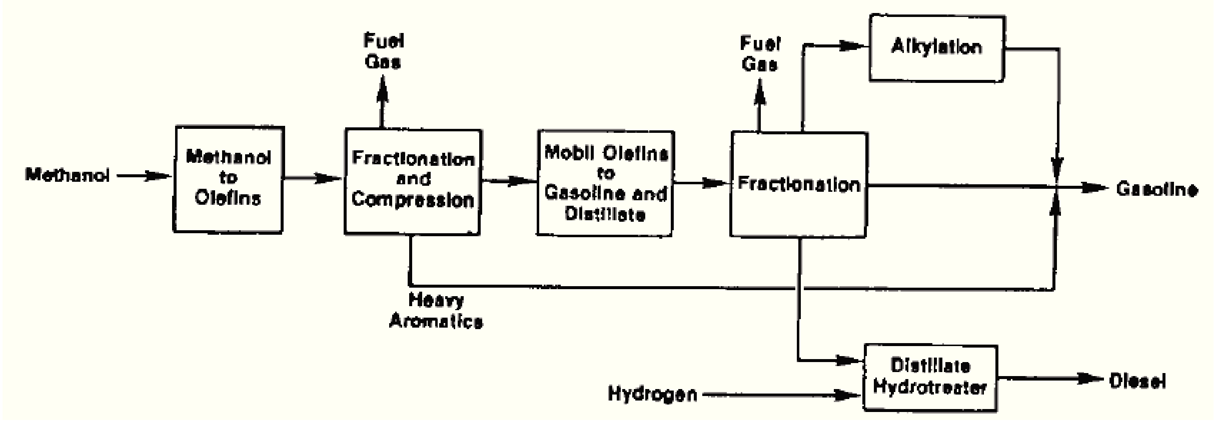


Figure 2.11: Flow diagram of MTO/MOGD process [34]

2.2.2.5 Dimethyl ether (DME)

Dimethyl ether (DME) is an important compound in the chemical industry. It is used as raw material for producing a series of chemicals, e.g. the production of dimethyl sulphate. Furthermore, DME is applied in the production of aerosol propellants like hair spray to substitute ozone-depleting chlorofluorocarbons (CFC). Another application area of DME is the use as vehicle fuel. DME becomes more and more important as alternative for diesel fuels. The advantages of DME versus fossil diesel are amongst other things higher thermal efficiency and lower NO_x emissions. [23], [35]

The synthesis of dimethyl ether (DME) from methanol takes place in a one-step process in which DME is directly converted from syngas. The DME synthesis is catalysed by two catalysts, a $Cu/ZnO/Al_2O_3$ catalyst as well as a gamma-alumina catalyst. [31]

<u>Chemistry</u>

The methanol to dimethyl ether (DME) process is carried out by three reactions which are simultaneous. In the methanol synthesis reaction, methanol is produced from syngas. The WGS reaction produces carbon dioxide, which increases the conversion rate of the methanol synthesis reaction. In the course of the methanol dehydration reaction, dimethyl ether is produced by methanol dehydration over acid catalysts. The overall reaction of the DME process is given in the last equation. Due to the synergy between the three reactions, higher productivity rates can be achieved in comparison to methanol synthesis from syngas. [36]

The reactions for the production of DME are as follows [37][36]:

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H = -90.4\ kJ/mole \qquad methanol\ synthesis$$

$$H_2O + CO \rightarrow H_2 + CO_2 \qquad \Delta H = -41.0\ kJ/mole \qquad WGS\ reaction$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H = -23.4\ kJ/mole \qquad methanol\ dehydration$$

$$3H_2 + 3CO \rightarrow CH_3OCH_3 + CO_2 \qquad \Delta H = -245.2\ kJ/mole \qquad overall\ reaction$$

2.2.3 Ethanol synthesis

Technology

The synthesis of ethanol from syngas can be performed either through biochemical or thermochemical routes (see Figure 2.12). Within the scope of this work, only the thermochemical process for the production of ethanol is considered.

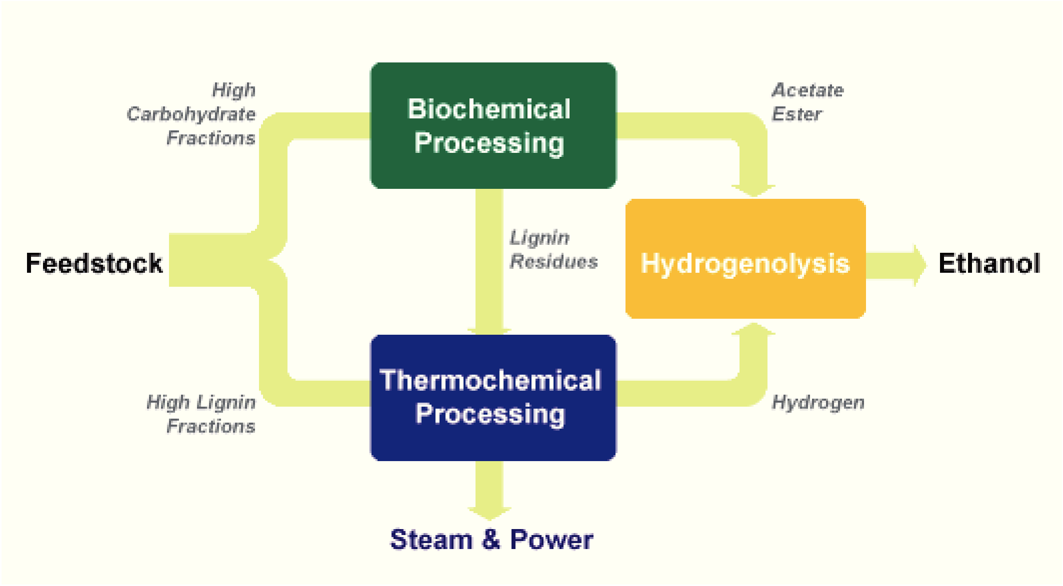


Figure 2.12: Biochemical and thermochemical routes for ethanol production [38]

Chemistry

Concerning the chemistry of ethanol synthesis from syngas, several reactions can occur. These reactions are mainly hydrogenation reactions to produce C_2^+ products. Additionally, side reactions like WGS and methanation reaction are incurred. [39]

The hydrogenation reactions of CO and CO_2 to ethanol are given below [39]:

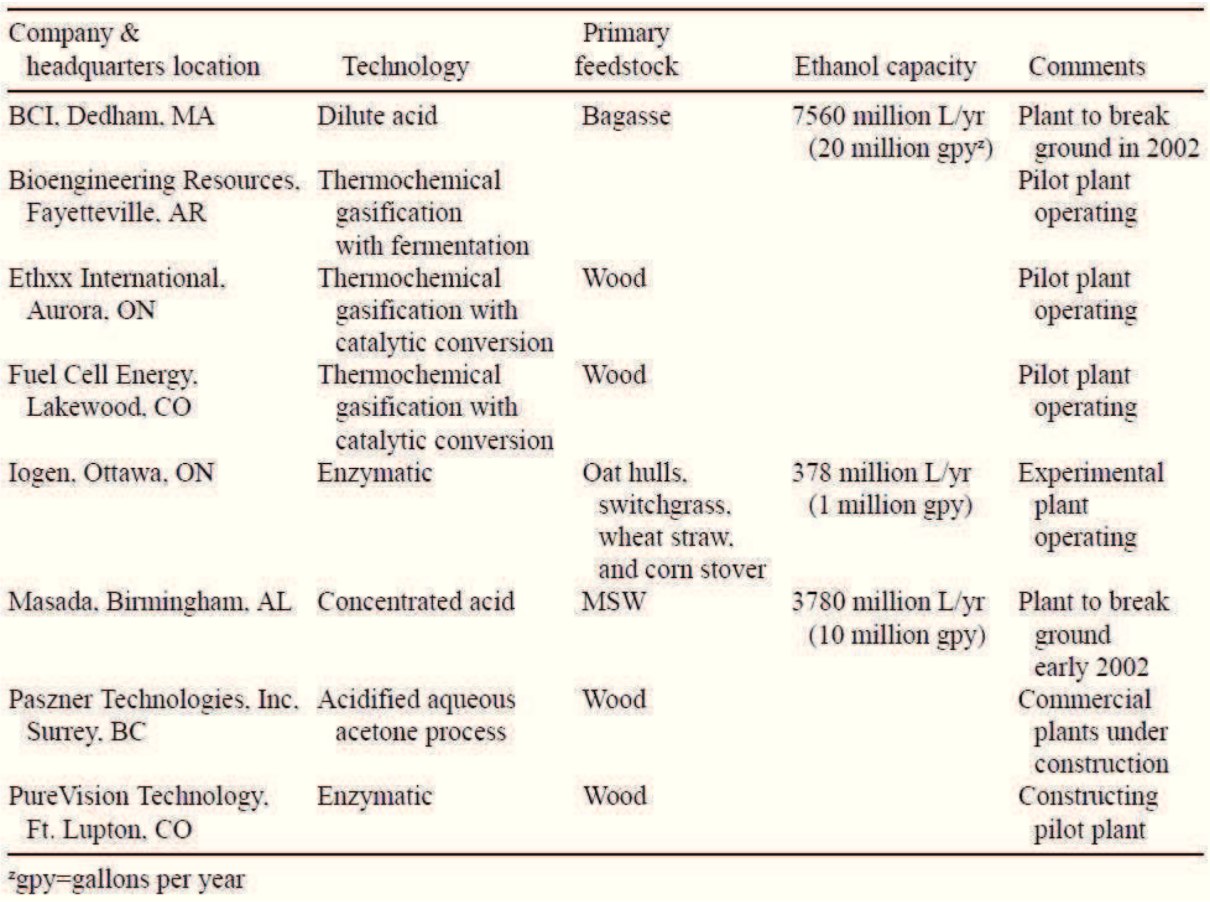
$$2CO + 4H_2 \rightarrow C_2H_5OH + H_2O \qquad \Delta G = -29.32\ kcal/mol$$

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \qquad \Delta G = -15.70\ kcal/mol$$

State of development

Today the production of ethanol from cellulosic biomass feedstock is not investigated sufficiently. In this regard, the major barrier is the conversion of cellulosic material. The restraints are arranged in the area of the ethanol-from-cellulose technologies like gasification of cellulosic feedstock due to the fact that they are currently not state of the art and therefore too expensive for commercial utilisation. [40]

Table 2.2 gives an overview of the suppliers of ethanol-from-cellulose technologies.



Company & headquarters location	Technology	Primary feedstock	Ethanol capacity	Comments
BCI, Dedham, MA	Dilute acid	Bagasse	7560 million L/yr (20 million gpy^{z})	Plant to break ground in 2002
Bioengineering Resources, Fayetteville, AR	Thermochemical gasification with fermentation			Pilot plant operating
Ethxx International, Aurora, ON	Thermochemical gasification with catalytic conversion	Wood		Pilot plant operating
Fuel Cell Energy, Lakewood, CO	Thermochemical gasification with catalytic conversion	Wood		Pilot plant operating
Iogen, Ottawa, ON	Enzymatic	Oat hulls, switchgrass, wheat straw, and corn stover	378 million L/yr (1 million gpy)	Experimental plant operating
Masada, Birmingham, AL	Concentrated acid	MSW	3780 million L/yr (10 million gpy)	Plant to break ground early 2002
Paszner Technologies, Inc. Surrey, BC	Acidified aqueous acetone process	Wood		Commercial plants under construction
PureVision Technology, Ft. Lupton, CO	Enzymatic	Wood		Constructing pilot plant

^{z}gpy=gallons per year

Table 2.2: Partial list of providers of ethanol-from-cellulose technologies [41]

Uses

Application areas for ethanol are both in the chemical and in the transportation sector. In the chemical sector it is mainly used as a solvent or it is converted to esters. In the transportation sector ethanol can be used as an additive or as a pure fuel. As an additive, it can be added to gasoline as an alternative to leaded fuels. Moreover, ethanol can be applied as a pure fuel or as a blend with gasoline. Such blends can be used in engines without any modifications up to 10 % bioethanol (E-10 fuels). For using blends with ethanol contents higher than 10 % the engine has to be modified. So-called flexible fuel vehicles (FFV) are available which can be operated with an ethanol/gasoline blend up to 85 % (E-85). For the use of pure bioethanol (E-100) special engines are needed. [42], [43]

2.2.4 Fischer-Tropsch synthesis

Technology

Concerning the Fischer-Tropsch synthesis, it can be distinguished between low-temperature (LTFT) and high-temperature process (HTFT). In the LTFT process diesel fuels and linear waxes are produced at temperatures of 200-240 ℃ over iron or cobalt catalysts. To produce gasoline and olefins the HTFT synthesis is used. In this process iron-based catalysts are used at temperature of 300-350 ℃. [44]

Figure 2.13 shows the flow diagram of the FT synthesis pilot plant operated at the pilot plant stations in Güssing.

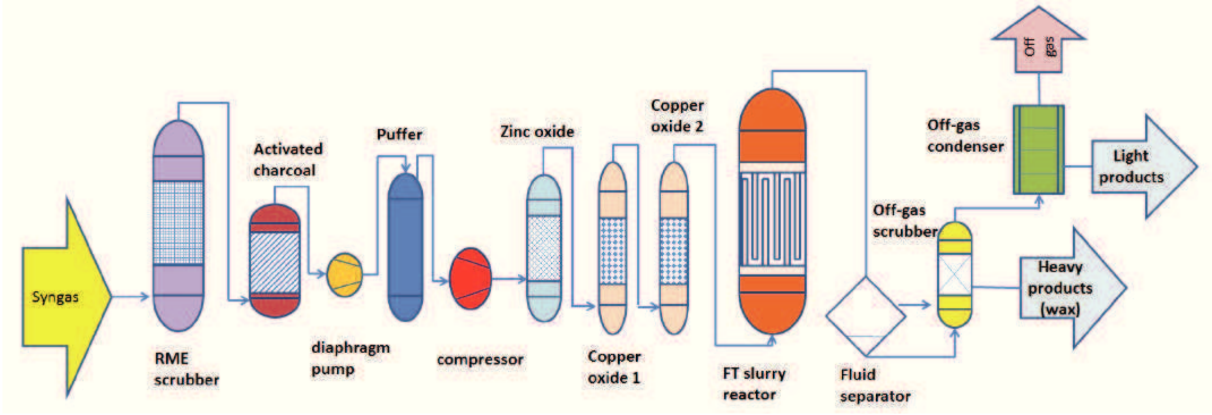


Figure 2.13: Flow diagram of FT synthesis pilot plant in Güssing [45]

Chemistry

The Fischer-Tropsch synthesis (FTS) is a so-called chain propagation reaction. In the presence of metallic catalysts carbon monoxide and hydrogen were converted to long-chain hydrocarbons. In the main FTS reaction, CH_2 components were built from carbon monoxide and hydrogen. With these components the long-chain reaction products were generated. [46]

The reactions of the FT synthesis are given below [23]:

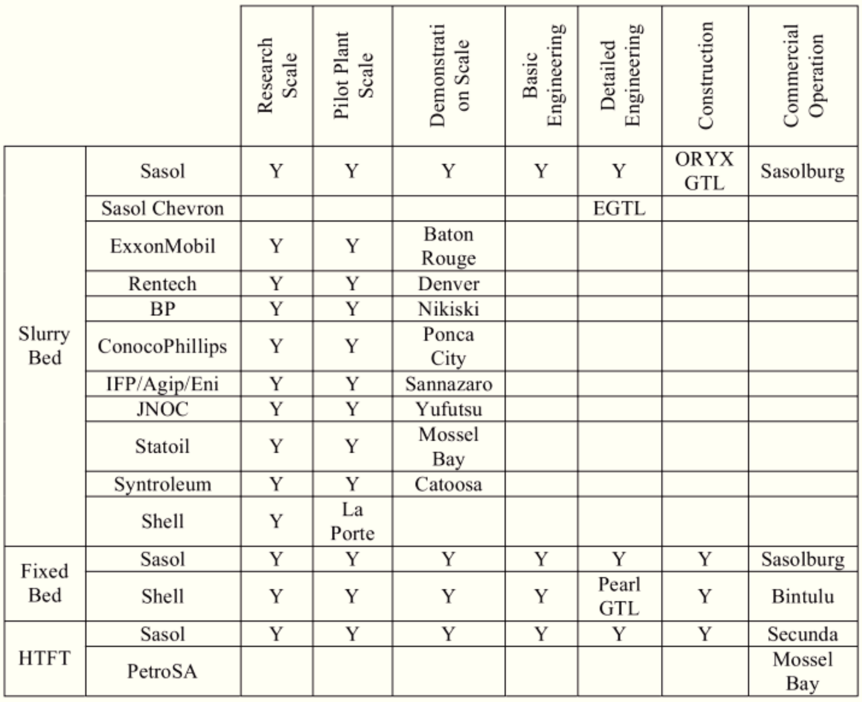
$$CO + 2H_2 \rightarrow CH_2 + H_2O \qquad \textit{FTS reaction}$$

$$H_2O + CO \rightarrow H_2 + CO_2 \qquad \textit{WGS reaction}$$

$$2CO + H_2 \rightarrow CH_2 + CO_2 \qquad \textit{overall FTS reaction}$$

State of development

The Fischer-Tropsch synthesis is a well established technology. At present, there a several companies investigating in FT synthesis. A summary of the major companies, active in GTL FT technology, as well as their development status is given in Table 2.3.



		Research Scale	Pilot Plant Scale	Demonstration Scale	Basic Engineering	Detailed Engineering	Construction	Commercial Operation
Slurry Bed	Sasol	Y	Y	Y	Y	Y	ORYX GTL	Sasolburg
	Sasol Chevron					EGTL		
	ExxonMobil	Y	Y	Baton Rouge				
	Rentech	Y	Y	Denver				
	BP	Y	Y	Nikiski				
	ConocoPhillips	Y	Y	Ponca City				
	IFP/Agip/Eni	Y	Y	Sannazaro				
	JNOC	Y	Y	Yufutsu				
	Statoil	Y	Y	Mossel Bay				
	Syntroleum	Y	Y	Catoosa				
	Shell	Y	La Porte					
Fixed Bed	Sasol	Y	Y	Y	Y	Y	Y	Sasolburg
	Shell	Y	Y	Y	Y	Pearl GTL	Y	Bintulu
HTFT	Sasol	Y	Y	Y	Y	Y	Y	Secunda
	PetroSA							Mossel Bay

Table 2.3: Current development status of major companies active in GTL FT technology [47]

Uses

Fuels from FTS can be used in several fields of application areas, especially in the transportation sector. There are several applications for using FT waxes as a feedstock for hydrotreating processes, for examples the production of naphtha, kerosene and diesel over co-hydrotreating of FT wax blended with fossil gasoils (see also Figure 2.14) [48].

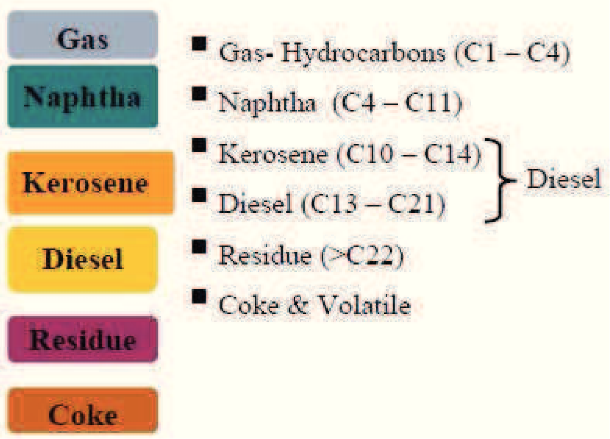


Figure 2.14: Product groups from the HPFT process [48]

2.2.5 Mixed Alcohol synthesis

The synthesis of mixed alcohols from synthesis gas is a highly exothermic catalytic reaction. For MAS, catalysts are used which are mainly alkali-doped oxides (zinc and chromium oxides) or alkali-doped sulfides (mainly MoS_2). The synthesis of mixed alcohols can be operated in fixed bed reactors as well as in slurry reactors. For MAS in fixed bed reactors the required pressures ranges between 30 and 200 bar and the required temperatures between 200 and 400 ℃. [49]

Using MoS_2 catalysts for MAS is greatly beneficial because they are extremely resistant to sulphur poisoning. Catalysts based on MoS_2 requires a H_2S-content in the synthesis of approx. 50-100 ppm gas to keep the sulphidation level constant which is essential for a steady activity. Hence, a removal of sulphur is not obligatory and this fact reduces both investment and operational costs dramatically. [49]

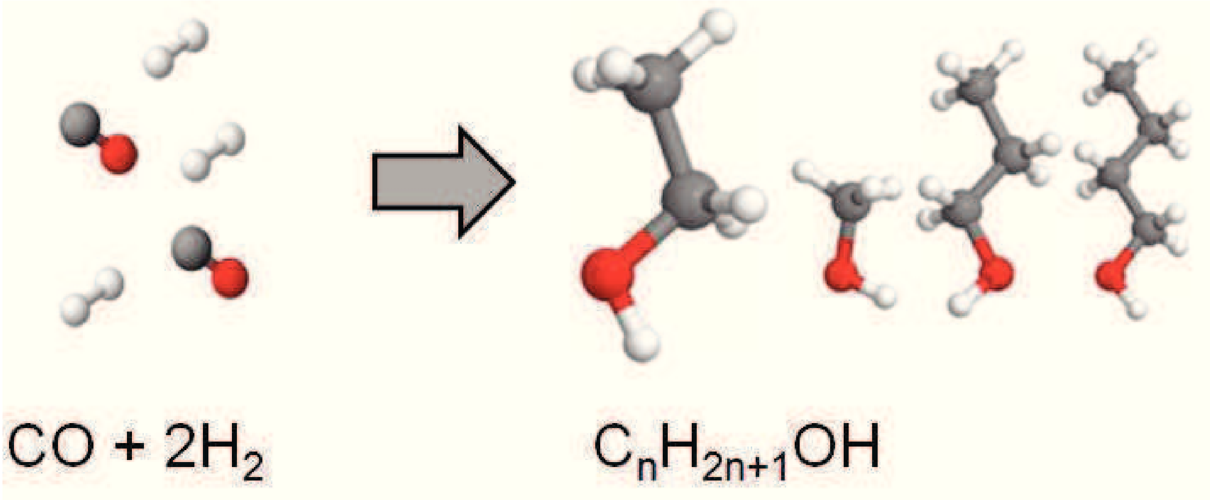


Figure 2.15: Chemistry of the MAS [49]

Up to now, few investigations have been made on MAS and hence no commercial process for producing a mixed alcohol fuel in the range of C_2-C_6 is available so far. [23]

The synthesis of mixed alcohols will be described in detail in the following sections.

2.3 Fundamentals of Mixed Alcohol synthesis

2.3.1 Technology Description

The Mixed Alcohols synthesis (MAS) is a thermochemical process for the conversion of biomass to a mixture of higher alcohols, composed of methanol, ethanol, propanol, butanol, pentanol and, in some cases, higher alcohols.

The MAS process is made up of the main plant components syngas production, gas cleaning and conditioning, MAS, alcohol separation and product purification (see Figure 2.16). The cleaning and accordingly conditioning of the syngas is implemented by steam reforming, water removal and compression. The gas is compressed via a flexible compressor which can achieve pressure between 90 and 350 bars. The MAS itself is done in a fixed bed reactor at reaction temperatures between 200-400℃. For the synthesis a catalyst is used based on MoS_2, so no removal of sulphur components is necessary. The separation of the alcohols from the not reacted tail gas takes place in a condenser.

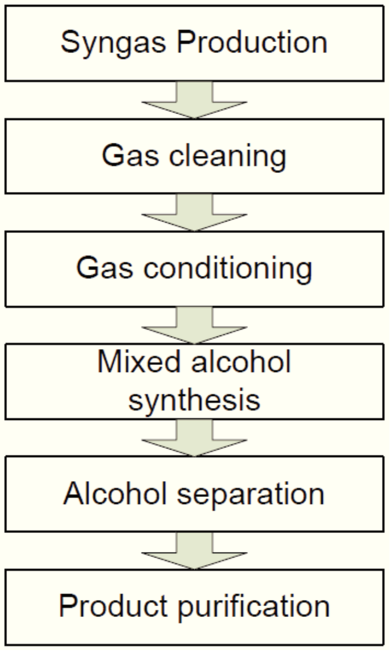


Figure 2.16: Process steps of MAS including syngas production

In the scope of this work, a pilot plant for MAS was built at the location of the CHP Güssing. The flow diagram of the MAS process after syngas production is shown in Figure 2.17.

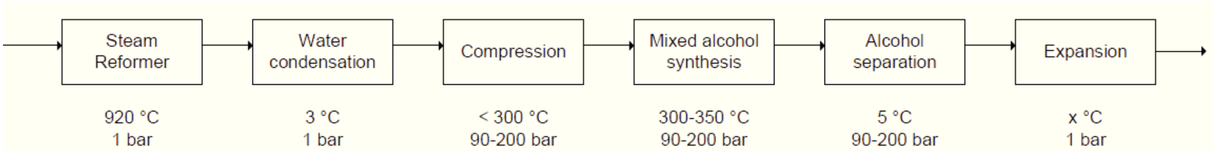


Figure 2.17: Flow diagram of MAS pilot plant in Güssing

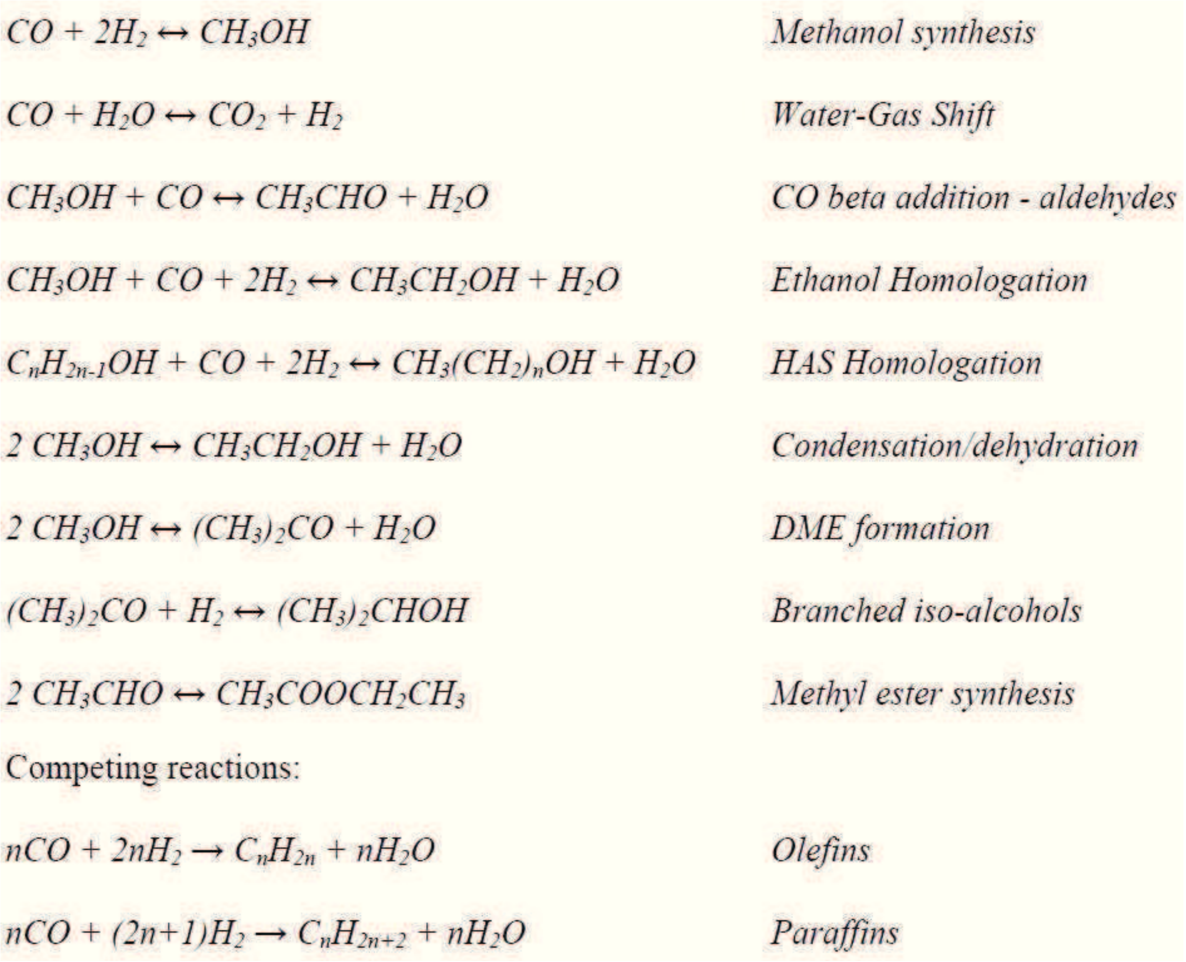
2.3.2 Chemistry

The MAS mechanism consists of a series of complex reactions which leads to a multiplicity of different products depending on kinetic and thermodynamic preconditions. In general, the major products are methanol and carbon dioxide according to process parameters and catalyst used. At first, the synthesis of methanol from syngas takes place. After this a C-C bond is generated by insertion of CO into CH_3OH (see Figure 2.19). Finally the production of linear alcohols is carried out step-by-step starting with methanol synthesis followed by homologation to higher alcohols [50]. Depending on what catalyst is used, branched or straight chain higher alcohols are produced. In the process, modified methanol and FT synthesis catalyst produce branched alcohols and MoS_2-based catalysts form straight chain alcohols. [23]

The overall stoichiometry of the general MAS reaction is as follows [51], [52]:

$$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O \qquad \Delta H_r = -61.2\ kcal/mol \qquad MAS\ reaction$$

The major reactions in conjunction with MAS are listed in Figure 2.18.



$CO + 2H_2 \leftrightarrow CH_3OH$	*Methanol synthesis*
$CO + H_2O \leftrightarrow CO_2 + H_2$	*Water-Gas Shift*
$CH_3OH + CO \leftrightarrow CH_3CHO + H_2O$	*CO beta addition - aldehydes*
$CH_3OH + CO + 2H_2 \leftrightarrow CH_3CH_2OH + H_2O$	*Ethanol Homologation*
$C_nH_{2n-1}OH + CO + 2H_2 \leftrightarrow CH_3(CH_2)_nOH + H_2O$	*HAS Homologation*
$2\ CH_3OH \leftrightarrow CH_3CH_2OH + H_2O$	*Condensation/dehydration*
$2\ CH_3OH \leftrightarrow (CH_3)_2CO + H_2O$	*DME formation*
$(CH_3)_2CO + H_2 \leftrightarrow (CH_3)_2CHOH$	*Branched iso-alcohols*
$2\ CH_3CHO \leftrightarrow CH_3COOCH_2CH_3$	*Methyl ester synthesis*
Competing reactions:	
$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$	*Olefins*
$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$	*Paraffins*

Figure 2.18: Fundamental reactions in conjunction with MAS [23]

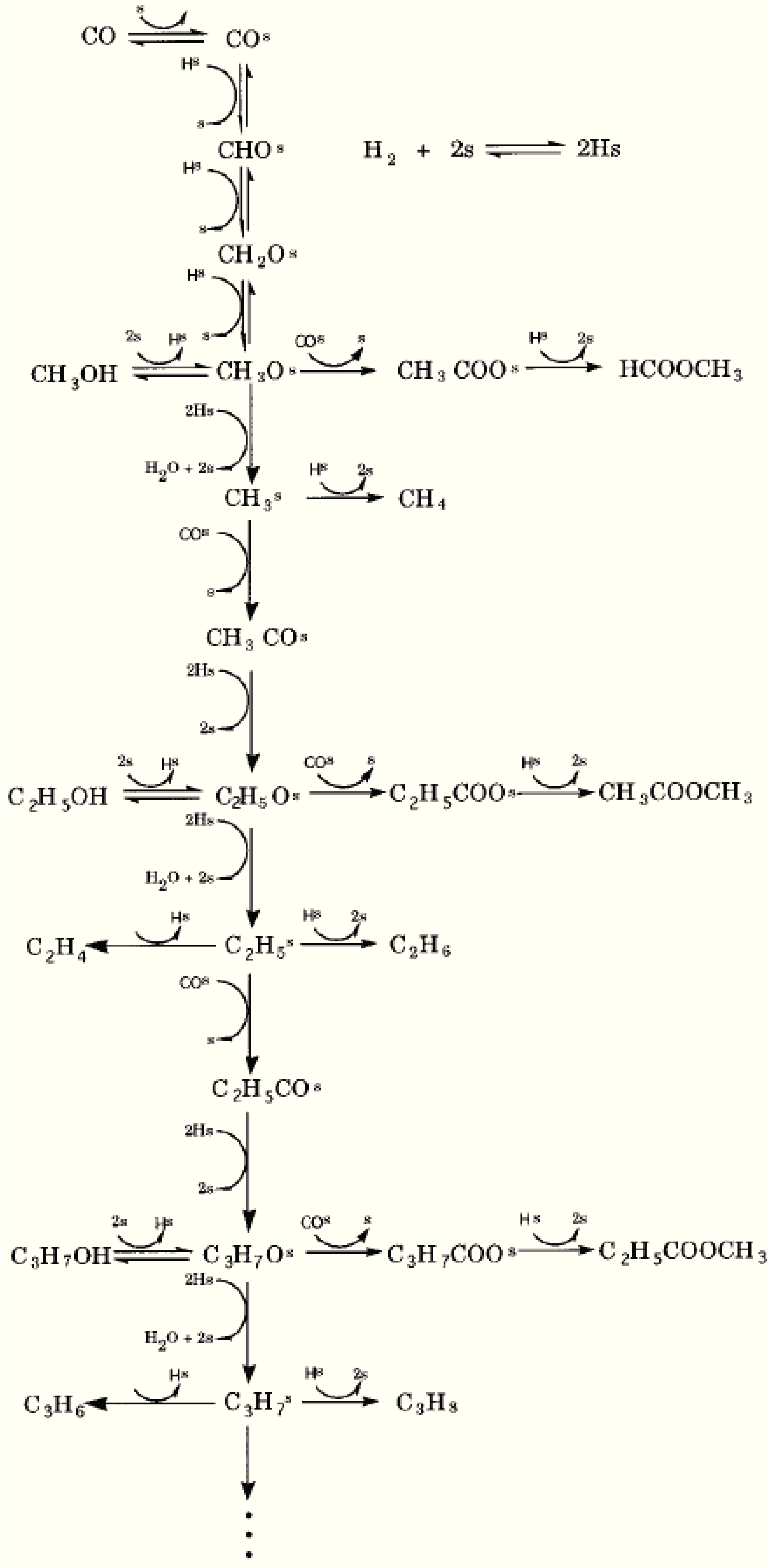


Figure 2.19: General diagram of CO insertion mechanism over K/MoS$_2$ catalyst [53]

2.3.3 Catalysts

In reference to productivity and selectivity of MAS, the choice of the most suitable catalyst is of great importance. As a result of the significance of alcohols for the chemical industry as well as for the transportation sector, processes for converting syngas to alcohols have been investigated for a long time. Routes for the production of chemical grade alcohols are relatively good developed and suitable catalysts are commercial available. Today, catalysts are developed to produce blends of fuel-grade alcohols from syngas due to the increasing interest in the use of alcohols as fuels. [54]

Catalysts applicable for MAS are based on bifunctional base-hydrogenation. Depending on their composition they can be categorised into several groups (see below). Customary for all MAS catalysts is the addition of alkali metals to the formulation because of their activating character as a result of their basicity. [23]

Catalysts for MAS can be divided into the following groups [54]:

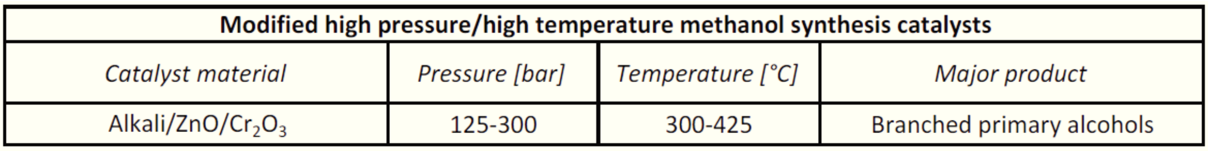
1. Modified high pressure/high temperature methanol synthesis catalysts - based on ZnO
2. Modified low pressure/low temperature methanol synthesis catalysts – based on Cu
3. Modified Fischer-Tropsch catalysts – based on Fe or Co
4. Modified methanation catalysts – based on MoS_2

In the scope of this work a MoS_2-based catalyst was used for the test runs on the MAS pilot plant. These types of catalysts have the advantage that they are resistant against sulphur poisoning. Hence, the syngas cleaning can be carried out in a very simple and cheap way. In the following sections the catalysts which can be used for MAS are specified.

2.3.3.1 Modified high pressure/high temperature methanol synthesis catalysts

Modified high pressure/high temperature (HP/HT) methanol synthesis catalysts are based on alkali-doped ZnO/Cr_2O_3. Using this kind of catalysts mainly branched primary alcohols were produced under high pressures and temperatures (see Table 2.4). [23]

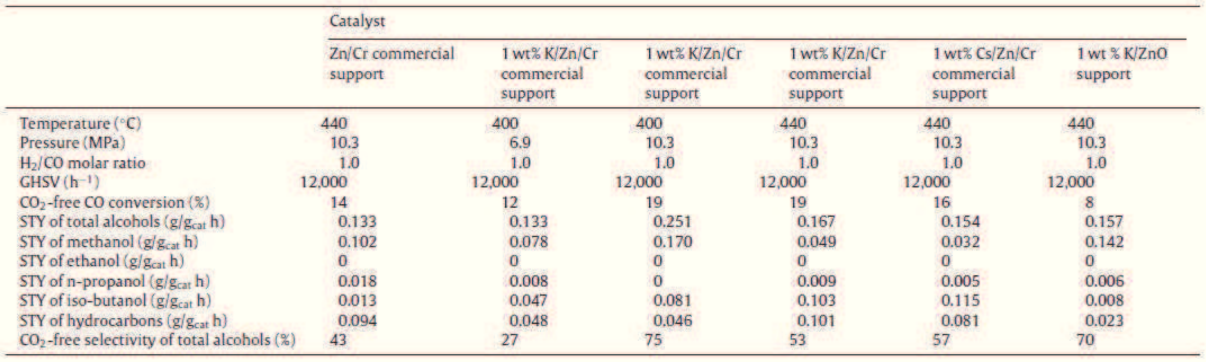
Table 2.4 gives some basis information of HP/HT methanol synthesis catalysts.



Modified high pressure/high temperature methanol synthesis catalysts			
Catalyst material	*Pressure [bar]*	*Temperature [°C]*	*Major product*
Alkali/ZnO/Cr_2O_3	125-300	300-425	Branched primary alcohols

Table 2.4: Basic data of modified HP/HT methanol synthesis catalysts (source: [54])

Depending on what formulation is used by the manufacturing of the catalyst, miscellaneous results concerning CO-conversion, alcohol yields and selectivity can be achieved. A summary of the several HP/HT methanol synthesis catalysts is presented in Table 2.5.



	Catalyst					
	Zn/Cr commercial support	1 wt% K/Zn/Cr commercial support	1 wt% K/Zn/Cr commercial support	1 wt% K/Zn/Cr commercial support	1 wt% Cs/Zn/Cr commercial support	1 wt % K/ZnO support
Temperature (°C)	440	400	400	440	440	440
Pressure (MPa)	10.3	6.9	10.3	10.3	10.3	10.3
H_2/CO molar ratio	1.0	1.0	1.0	1.0	1.0	1.0
GHSV (h^{-1})	12,000	12,000	12,000	12,000	12,000	12,000
CO_2-free CO conversion (%)	14	12	19	19	16	8
STY of total alcohols (g/g_{cat} h)	0.133	0.133	0.251	0.167	0.154	0.157
STY of methanol (g/g_{cat} h)	0.102	0.078	0.170	0.049	0.032	0.142
STY of ethanol (g/g_{cat} h)	0	0	0	0	0	0
STY of n-propanol (g/g_{cat} h)	0.018	0.008	0	0.009	0.005	0.006
STY of iso-butanol (g/g_{cat} h)	0.013	0.047	0.081	0.103	0.115	0.008
STY of hydrocarbons (g/g_{cat} h)	0.094	0.048	0.046	0.101	0.081	0.023
CO_2-free selectivity of total alcohols (%)	43	27	75	53	57	70

Table 2.5: Specifications of modified HP/HT methanol synthesis catalysts [55]

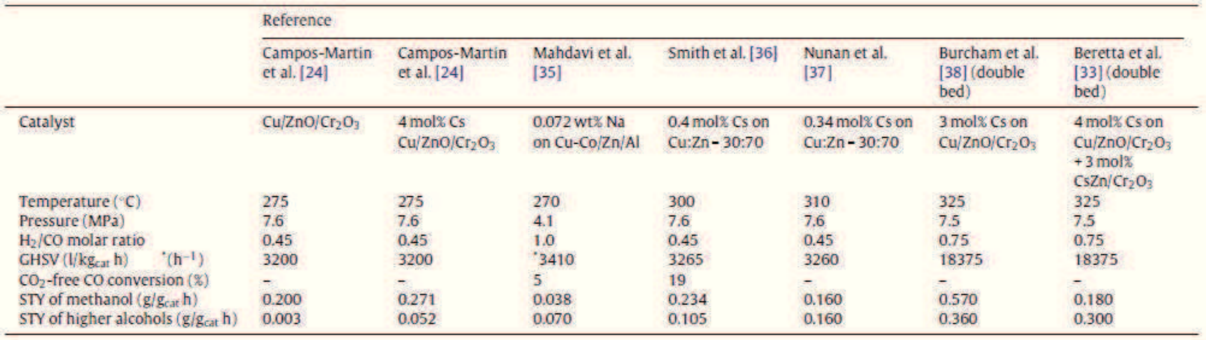
2.3.3.2 Modified low pressure/low temperature methanol synthesis catalysts

Regarding modified low pressure/low temperature (LP/LT) methanol synthesis catalysts mainly alkali-doped Cu/ZnO and Cu/ZnO/Al_2O_3 catalysts are used. These catalysts were applied to produce mainly primary alcohols under LP/LT process parameters (see Table 2.6). [23]

Modified low pressure/low temperature methanol synthesis catalysts			
Catalyst material	*Pressure [bar]*	*Temperature [°C]*	*Major product*
Alkali/Cu/ZnO(Al_2O_3)	50-100	275-310	Primary alcohols

Table 2.6: Basic data of modified LP/LT methanol synthesis catalysts (source: [54])

CO-conversion and alcohol yields of the several LP/LT methanol synthesis catalysts as well as the corresponding process parameters are summarised in Table 2.5.

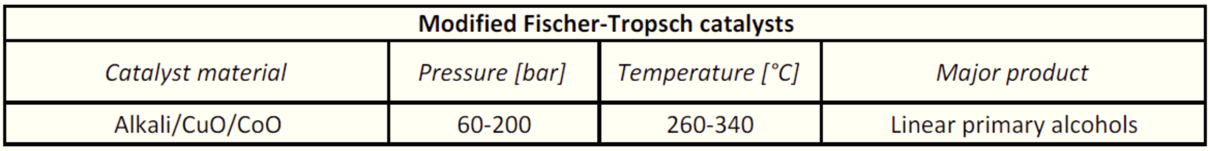


	Reference						
	Campos-Martin et al. [24]	Campos-Martin et al. [24]	Mahdavi et al. [35]	Smith et al. [36]	Nunan et al. [37]	Burcham et al. [38] (double bed)	Beretta et al. [33] (double bed)
Catalyst	Cu/ZnO/Cr_2O_3	4 mol% Cs Cu/ZnO/Cr_2O_3	0.072 wt% Na on Cu-Co/Zn/Al	0.4 mol% Cs on Cu:Zn - 30:70	0.34 mol% Cs on Cu:Zn - 30:70	3 mol% Cs on Cu/ZnO/Cr_2O_3	4 mol% Cs on Cu/ZnO/Cr_2O_3 + 3 mol% CsZn/Cr_2O_3
Temperature (°C)	275	275	270	300	310	325	325
Pressure (MPa)	7.6	7.6	4.1	7.6	7.6	7.5	7.5
H_2/CO molar ratio	0.45	0.45	1.0	0.45	0.45	0.75	0.75
GHSV (l/kg_{cat} h) *(h^{-1})	3200	3200	*3410	3265	3260	18375	18375
CO_2-free CO conversion (%)	–	–	5	19	–	–	–
STY of methanol (g/g_{cat} h)	0.200	0.271	0.038	0.234	0.160	0.570	0.180
STY of higher alcohols (g/g_{cat} h)	0.003	0.052	0.070	0.105	0.160	0.360	0.300

Table 2.7: Specifications of modified LP/LT methanol synthesis catalysts [56]

2.3.3.3 Modified Fischer-Tropsch catalysts

Modified Fischer-Tropsch (FT) synthesis catalysts can be made from alkali-doped CuO/CoO. The major products of these FT catalysts are linear primary alcohols. The used pressures and temperatures can be seen from Table 2.8.



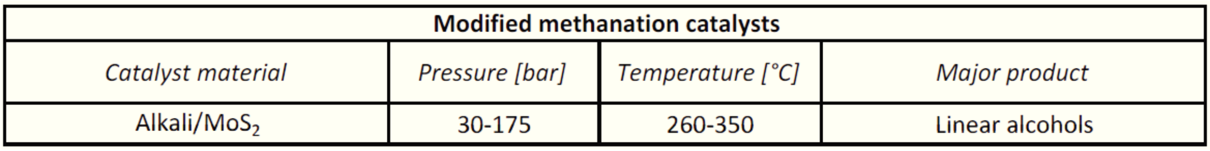
Modified Fischer-Tropsch catalysts			
Catalyst material	*Pressure [bar]*	*Temperature [°C]*	*Major product*
Alkali/CuO/CoO	60-200	260-340	Linear primary alcohols

Table 2.8: Basic data of modified FT catalysts (source: [54])

In general, iron (Fe), cobalt (Co), nickel (Ni) and ruthenium (Ru) can be used for FTS. However, only Fe and Co were applied in commercial FTS plants due to the drawbacks of Ni and Ru. Ni produces too much methane because of its hydrogenating character. Moreover Ni forms volatile carbonyls under higher pressures so that the catalyst volatilises continuously out of the reactor. Ru is indeed the most active catalyst for FTS but it is very expensive as a result of its rareness. [57]

2.3.3.4 Modified methanation catalysts

Modified methanation catalysts are a further alternative to be used for MAS. They are based on alkali-doped sulphides, mainly MoS_2. By the use of MoS_2 catalysts, linear alcohols are produced under high pressures and temperatures (see Table 2.9).



Modified methanation catalysts			
Catalyst material	*Pressure [bar]*	*Temperature [°C]*	*Major product*
Alkali/MoS_2	30-175	260-350	Linear alcohols

Table 2.9: Basic data of modified methanation catalysts (source: [54])

The main advantage of MoS_2-based catalysts is their extremely resistance against sulphur poisoning. To keep the sulphidity status of the catalyst up, 50-100 ppm of sulphur is needed in the gas feed [58]. Thus, complex gas treatment facilities are not necessary which decreases both the installation and operational costs dramatically.

Effects of hydrogen sulphide (H_2S) on MAS have been investigated by [59]. It has been observed that the duration of the period to reach a stabilized behaviour depends on the H_2S content in the syngas feed. With a H_2S content of more than 103 ppmv the MAS process reaches the steady state of the product distribution quite fast. Besides, higher alcohols were produced primarily. By operations with H_2S contents less than 57 ppmv in the gas feed the stabilisation period lasts much longer and the major product is methanol. [59]

The impact of the different H_2S levels on the higher alcohols to methanol ratio depending on time on stream is demonstrated in Figure 2.20.

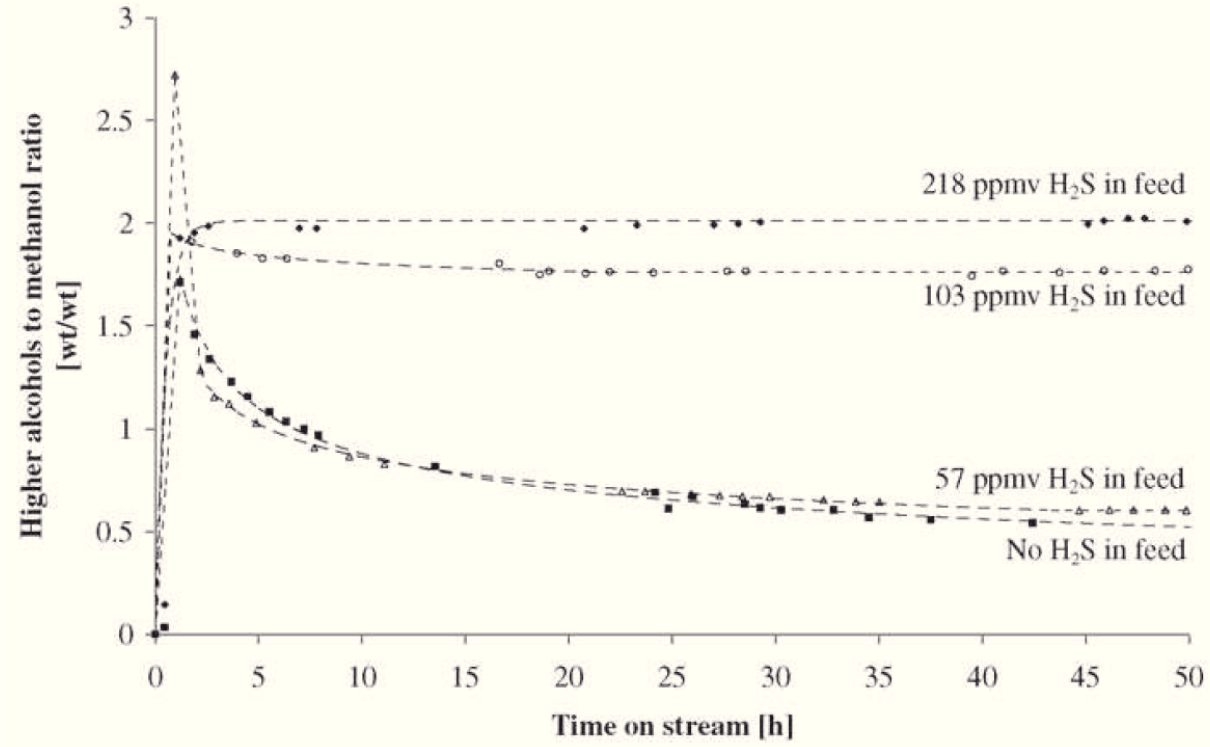


Figure 2.20: Impact of different H_2S levels on higher alcohols/methanol ratio with respect to time on stream; KCoMo-1 catalyst; approx. process parameters: T=360 ℃, p=100 bar, GHSV=5300 h^{-1}; Feed:50 vol%H_2, 50 vol%CO. [59]

Another advantage of MoS_2-based catalysts is the slight sensitiveness of sulphide catalysts to carbon dioxide. However with larger amounts of CO_2 the activity of the catalyst decreases. Furthermore, the presence of even low amounts of CO_2 reduces the selectivity to higher alcohols compared to methanol. For this reason, CO_2 should be removed from the syngas in order to achieve a high selectivity to higher alcohols. [54]

2.3.4 Reactors

In view of the design of MAS reactors, the removal of the excess heat of the highly exothermic MAS reaction is an aspect of particular importance. To keep the process temperatures at a constant level guarantees maximum yields as well as minimum deactivation of the catalyst due to sintering reactions. [23]

To achieve the objective of an optimal removal of the excess heat, MAS reactors can be designed as fixed-bed, multiple or as slurry reactor. While fixed-bed reactors (Figure 2.21) are already commercially available, multiple and slurry reactors (Figure 2.22) represent novel technologies. [60]

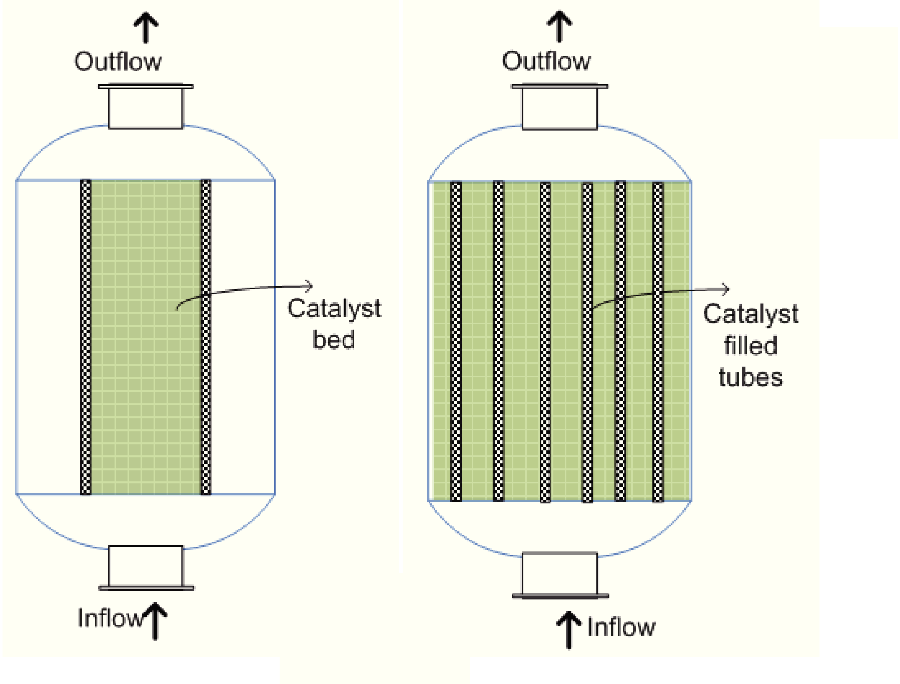


Figure 2.21: Single fixed-bed reactor (left) and multi tubular reactor (right) [61]

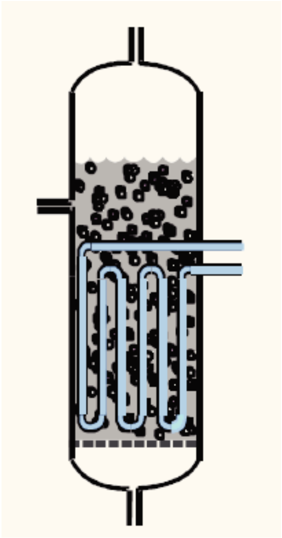


Figure 2.22: Slurry phase reactor (tree-phase bubble column) [62]

A kinetic study of MAS from syngas over K/MoS_2 catalyst was investigated by [53]. In this kinetic analysis, MAS takes place in a tubular fixed-bed integral reactor. The reactor was designed as a tube with 0.9 cm inside diameter made of stainless steel. The amount of catalyst filled in the reactor amounts to 1.0 g. The following process parameters were determined: T = 250-350 ℃, p = approx. 15-90 bar, τ = 4-22 g-cat*h/mol, H_2/CO molar feed ration θ_{H2} = 0.5-4. [53]

An investigation of MAS from syngas originated from biomass gasification was done by [63]. Here, the synthesis was carried out in a fixed-bed continuous-flow reactor. The amount of catalyst filled in the reactor was 1.0 g too. The following process parameters were determined: T = 300-340 ℃, p = 60 bar, GHSV = 7.5- 15 L/(g*h). [63]

Further investigations on MAS operated in fixed-bed reactors were performed by [64].

MAS carried out in a slurry reactor was explored by [65]. The synthesis takes place in a slurry-phase continuously stirred tank reactor with a filling volume of 500 ml. The process parameters were as follows: T = 250 ℃, p = 30 bar, H_2/CO = 2, SV = 360 ml/(g*h). [65]

2.3.5 Gas cleaning

As already mentioned above, using MoS_2 catalysts for MAS only low demands on gas cleaning are required. For modified methanol synthesis and FTS catalysts the same gas treatment standards are necessary as for the respective synthesis. By way of example, for FTS the gas cleaning of the syngas includes the removal of NH_3, H_2S, tars and CO_2 using a methanol scrubber (Rectisol process). [23]

In the MAS pilot plant investigated in this work, the gas cleaning section is composed of only a wet scrubber operated with glycol. Purpose of this scrubber is the removal of the water content of the syngas.

2.3.6 State of development

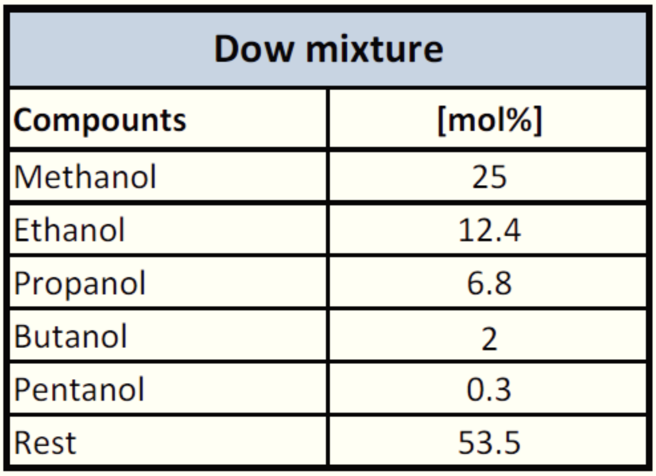
Today there are no commercial MAS plants in operation which produces a MAS fuel in the range of C_2-C_6. Though, a couple of companies are working on MAS, as noted below.

Snamprogetti

The MAS plant developed by Snamprogetti (also referred to as SEHT - Snamprogetti, Enichem, Haldor Topsoe) was first operated in 1982. This process is comparable with methanol synthesis, but with a different catalyst as well as higher reaction temperatures. The MAS takes place in adiabatic fixed-bed reactors. The MAS product is obtained by distillation of the crude alcohol via three distillation columns.[23]

Dow

Dow proclaimed its process for the production of mixed alcohols first in 1984. Their synthesis was carried out in both a fixed-bed and a fluid-bed reactor using K/Mo catalysts. In this process, mainly straight chain alcohols in the range of C_2-C_6 were produced. In Table 2.10 the detailed composition of the product from the Dow process can be seen.[23]



Dow mixture

Compounts	**[mol%]**
Methanol	25
Ethanol	12.4
Propanol	6.8
Butanol	2
Pentanol	0.3
Rest	53.5

Table 2.10: Product composition of Dow's MAS process (comment: "rest" includes aldehydes, ketones and water amongst others) [66]

Lurgi

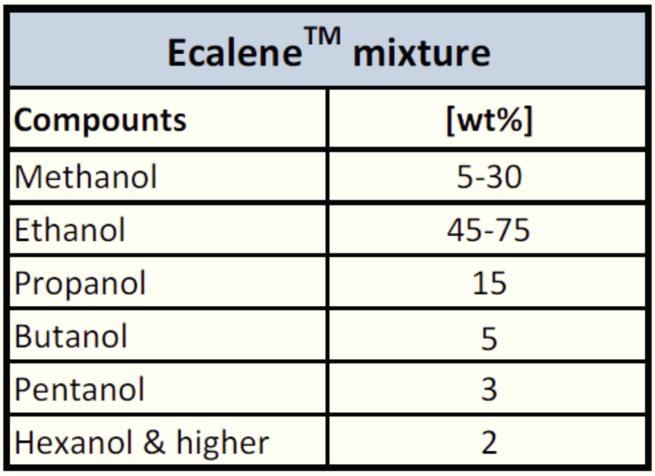
Lurgis's process is a modification of methanol synthesis. The MAS process differs from methanol synthesis only in two points – installation of CO_2 removal and product purification. The product of this process is also referred to as Octamix. [23]

IFP (Institut français du pétrole)

The French Institute of Petroleum (IFP) developed a process in which mixed alcohols are produced over steam reforming, multibed quench synthesis reactors and distillation. The product is also referred to as Substifuel. [23]

Ecalene^{TM}

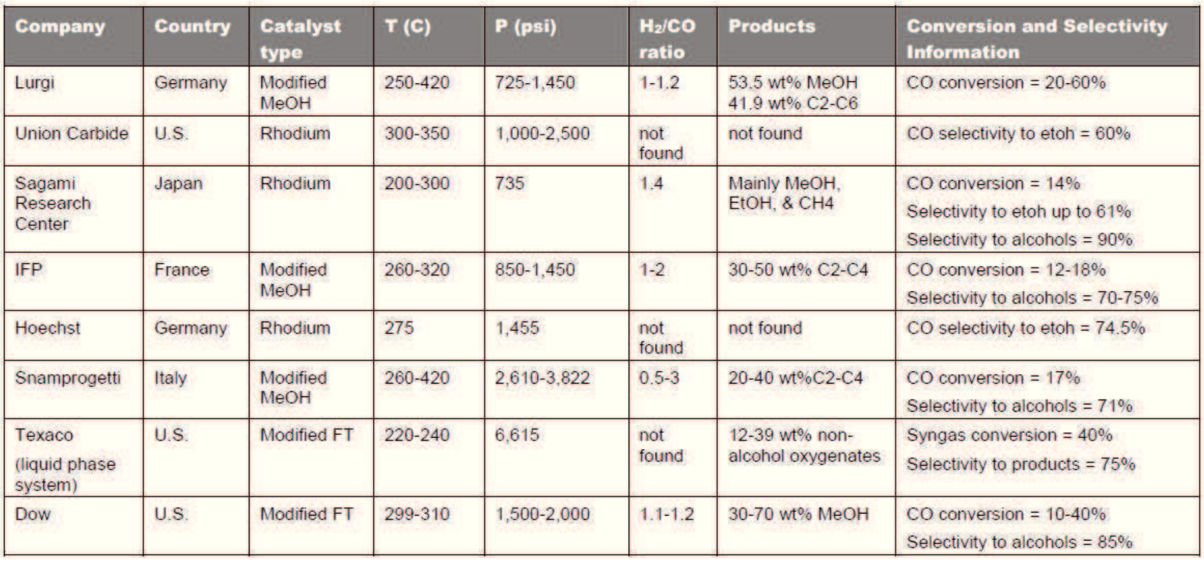
Ecalene^{TM} is the name of a MAS process, developed by Western Research Institute (WRI) and Power Energy Fuels, Inc. (PEFI). The main product of this process is ethanol, the detailed composition of Ecalene^{TM} fuels can be seen from Table 2.11.[23]



Ecalene^{TM} mixture	
Compounts	**[wt%]**
Methanol	5-30
Ethanol	45-75
Propanol	15
Butanol	5
Pentanol	3
Hexanol & higher	2

Table 2.11: Product composition of Ecalene^{TM} process [67]

A comparison of companies working on MAS as well as information and process conditions is given in Table 2.12.



Company	Country	Catalyst type	T (C)	P (psi)	H_2/CO ratio	Products	Conversion and Selectivity Information
Lurgi	Germany	Modified MeOH	250-420	725-1,450	1-1.2	53.5 wt% MeOH 41.9 wt% C2-C6	CO conversion = 20-60%
Union Carbide	U.S.	Rhodium	300-350	1,000-2,500	not found	not found	CO selectivity to etoh = 60%
Sagami Research Center	Japan	Rhodium	200-300	735	1.4	Mainly MeOH, EtOH, & CH4	CO conversion = 14% Selectivity to etoh up to 61% Selectivity to alcohols = 90%
IFP	France	Modified MeOH	260-320	850-1,450	1-2	30-50 wt% C2-C4	CO conversion = 12-18% Selectivity to alcohols = 70-75%
Hoechst	Germany	Rhodium	275	1,455	not found	not found	CO selectivity to etoh = 74.5%
Snamprogetti	Italy	Modified MeOH	260-420	2,610-3,822	0.5-3	20-40 wt%C2-C4	CO conversion = 17% Selectivity to alcohols = 71%
Texaco (liquid phase system)	U.S.	Modified FT	220-240	6,615	not found	12-39 wt% non-alcohol oxygenates	Syngas conversion = 40% Selectivity to products = 75%
Dow	U.S.	Modified FT	299-310	1,500-2,000	1.1-1.2	30-70 wt% MeOH	CO conversion = 10-40% Selectivity to alcohols = 85%

Table 2.12: Comparison of companies and information concerning MAS [23]

3 Plant design

3.1 Test set-up

The synthesis of mixed alcohols from biomass is build up of the following main components (see Figure 3.1):

- The gasification unit,
- the gas cleaning unit, and
- the MAS unit.

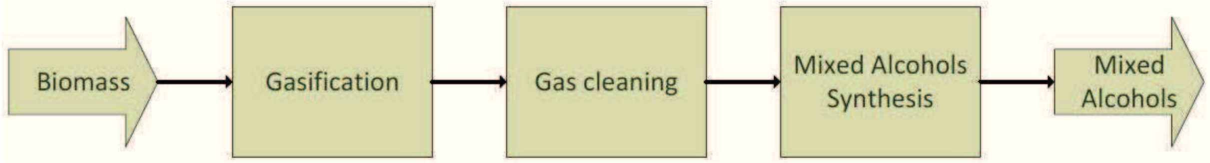
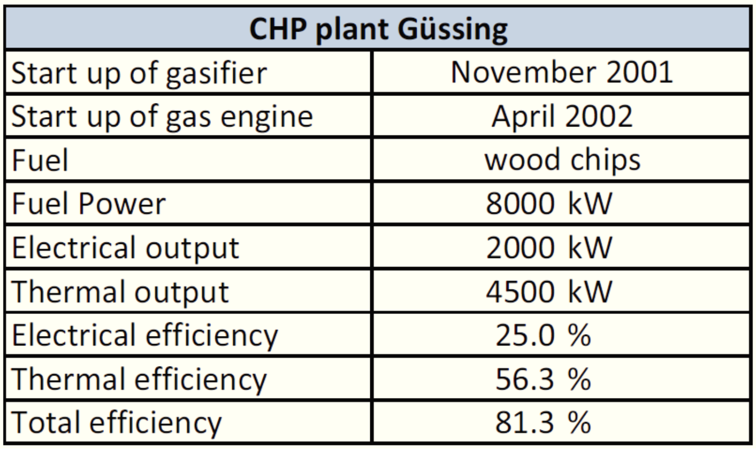


Figure 3.1: Simplified flow chart of MAS from biomass

The synthesis gas used in the MAS pilot plant is taken from the biomass combined heat and power plant (CHP) Güssing. The gasification as well as the gas cleaning is carried out by the CHP Güssing. An additional gas treatment (reforming of hydrocarbons, drying, and compression) and the synthesis of the mixed alcohols take place at the MAS pilot plant.

3.2 The CHP Güssing

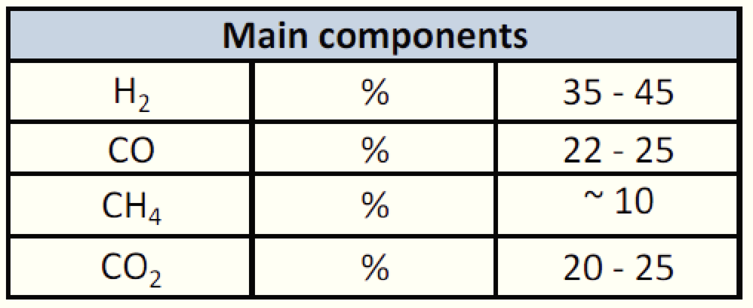
The CHP plant in Güssing was built in 2000 to produce heat and power from biomass. As biomass feedstock for the demonstration plant wood chips are used. The produced heat from the plant (from the synthesis gas and flue gas heat exchangers and the gas engine) is fed into the district heating grid of Güssing. The produced electricity from the gas engine is fed into the national grid. The design data of the CHP plant Güssing can be seen in Table 3.1



CHP plant Güssing	
Start up of gasifier	November 2001
Start up of gas engine	April 2002
Fuel	wood chips
Fuel Power	8000 kW
Electrical output	2000 kW
Thermal output	4500 kW
Electrical efficiency	25.0 %
Thermal efficiency	56.3 %
Total efficiency	81.3 %

Table 3.1: Design data of the CHP plant in Güssing [68]

By means of the Fast Internal Circulating Fluidized Bed (FICFB) gasification system in the biomass CHP Güssing a high quality synthesis gas is produced. This FICFB gasification system was developed by the Institute of Chemical Engineering (Technical University of Vienna) in cooperation with AE Energietechnik. The principal components of this synthesis gas are hydrogen (H_2) and carbon monoxide (CO), as listed in Table 3.2.



Main components		
H_2	%	35 - 45
CO	%	22 - 25
CH_4	%	~ 10
CO_2	%	20 - 25

Table 3.2: Main components in the dry synthesis gas from the CHP [69]

The mechanism of the FICFB gasification process is predicated on allothermal gasification with external heat input. For this reason a dual fluidized bed (DFB) concept is applied (see Figure 3.2).

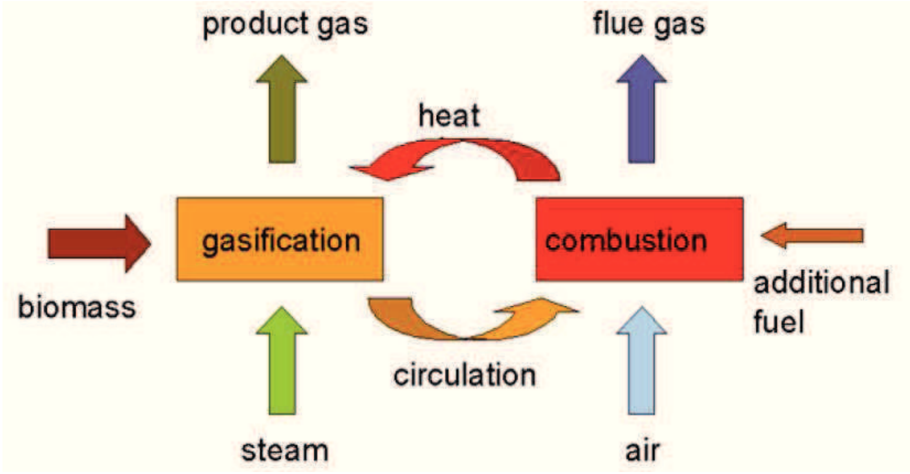


Figure 3.2: Principle of the FICFB gasification process [70]

For the purpose of gaining a widely nitrogen-free synthesis gas the FICFB gasification process based on two physically separated chambers, which are connected with a chute (see Figure 3.3). The gasification takes place in a stationary fluidized bed reactor, which is fluidized with steam (produced from process heat). The combustion takes place in a fast fluidized bed reactor, which is fluidized with preheated air. Bed material and the non-gasified carbon are transported into the combustion zone over the chute. The heat required for the strongly endothermic gasification is carried into the gasification zone by the hot bed material from the combustion.

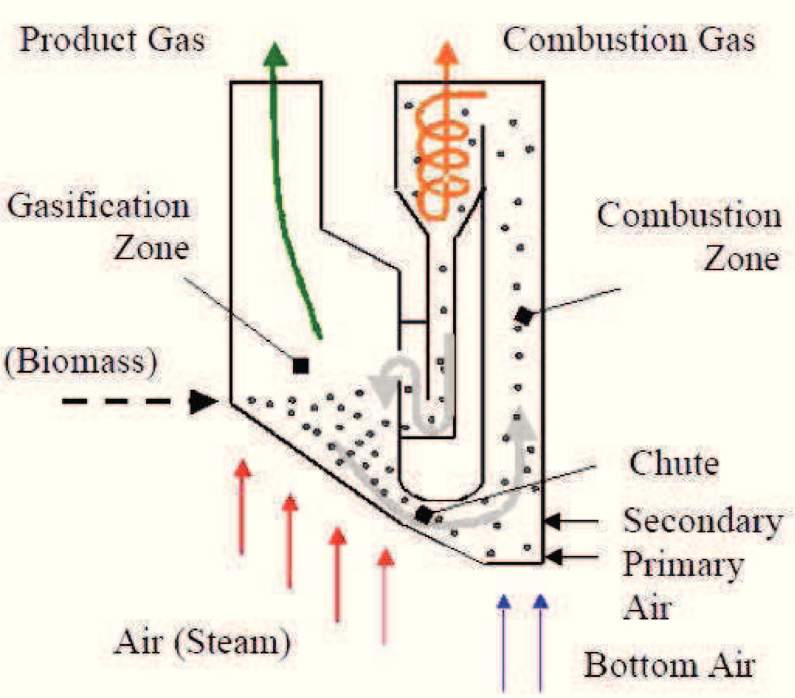


Figure 3.3: Cold flow model of the FICFB gasification system [71]

In the gasification chamber wood chips are converted during heating up, drying, devolatilisation and gasification mainly into H_2, CO, CO_2, CH_4, H_2O (gas) and C (char). By-products (mainly C_2H_4 and C_2H_6) and undesirable components (mainly tars and H_2S) are also produced, as listed in Table 3.3.

Minor components		
C_2H_4	%	2 - 3
C_2H_6	%	~ 0.5
C_2H_2	%	~ 0.4
O_2	%	< 0.1
N_2	%	1 - 3
C_6H_6	g/m³	~ 8
C_7H_8	g/m³	~ 0.5
$C_{10}H_8$	g/m³	~ 2
Tars	mg/m³	20 - 30

Possible poisons		
H_2S	mgS/Nm³	~ 200
Mercaptans	mgS/Nm³	~ 30
Thiophens	mgS/Nm³	~ 7
HCl	ppm	~ 3
NH_3	ppm	500 - 1000
Dust	mgS/Nm³	< 20

Table 3.3: Minor components (left) and possible poisons (right) in the syngas [69]

The temperature in the gasification zone is approx. 850 °C and about 930 °C in the combustion zone. For additional applications the synthesis gas is cooled down to approximately 150 °C in the heat exchanger. Particles are removed by using a fabric filter. A RME (Rapeseed Methyl Ester) scrubber is used to remove the undesired tar and to cool down the synthesis gas to approximately 40 °C. [70] , [72] A flow chart of the biomass CHP plant in Güssing is given in Figure 3.4. For the MAS pilot plant a slip stream of synthesis gas from the CHP is taken after the gas cleaning system.

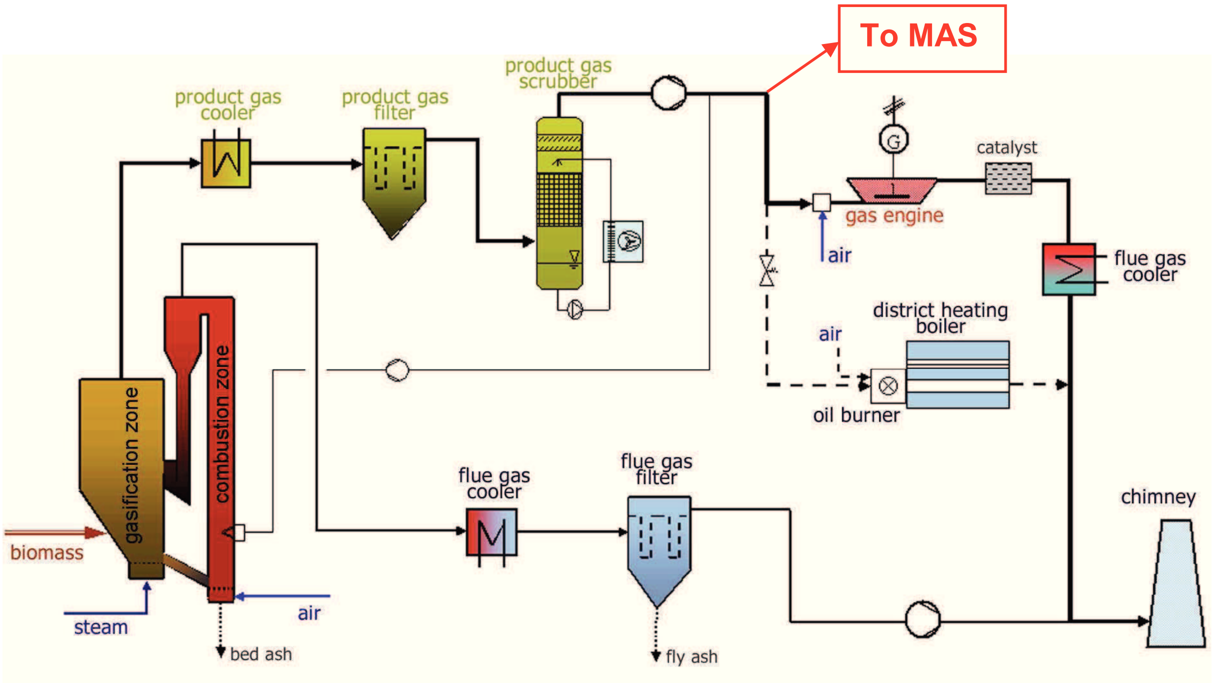


Figure 3.4: Flow Chart of the biomass CHP Güssing[70]

3.3 The MAS pilot plant

3.3.1 Plant description

The MAS pilot plant was designed as a high pressure and high temperature plant with a fixed bed reactor. The principal parts of the MAS pilot plant are composed of steam reformer, glycol scrubber, compressor, MAS reactor, condenser and expansion valve (see Figure 3.5).

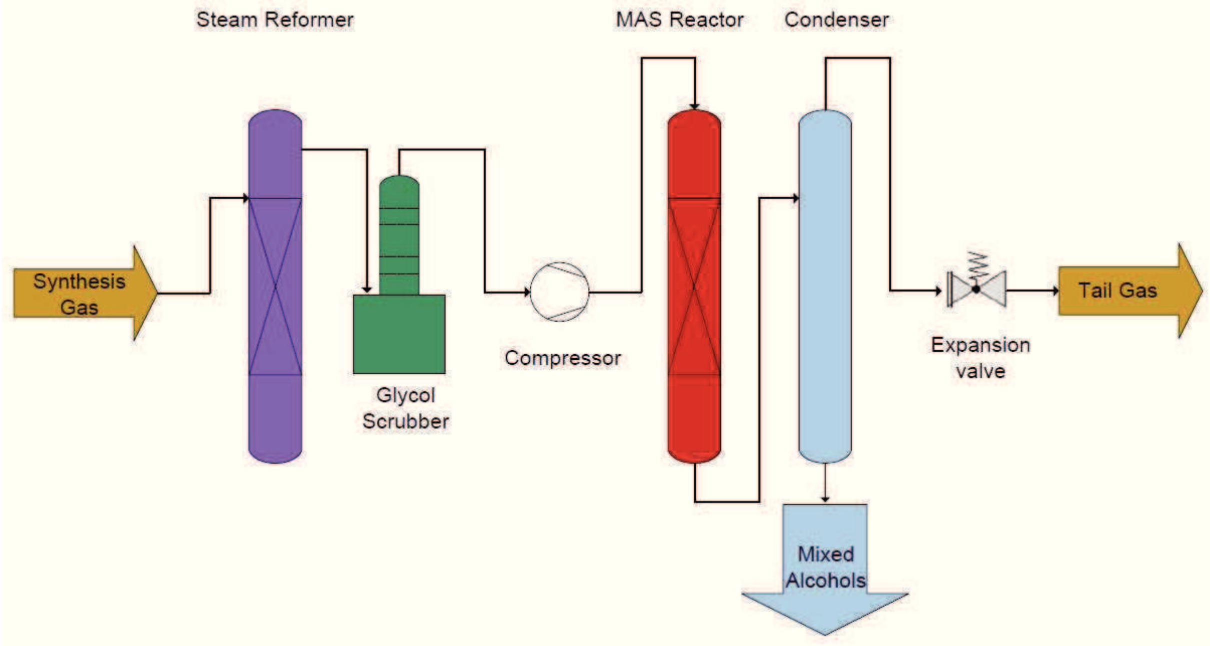


Figure 3.5: Flow chart of the MAS pilot plant [49]

The design data for the MAS pilot plant are given in Table 3.4. In the following sections, the pressure specifications are designated as gauge pressures.

Design data MAS pilot plant		
Pressure	bar	90-300
Temperature	°C	260-350
catalyst	kg	2.5
Volume flow	Nm^3/h	5
Space velocity	$Nm^3*kg^{-1}_{cat}*s^{-1}$	5.556E-04
CO-conversion	%	22
produced liquids (CH_3OH)	kg/h	0.31

Table 3.4: Design data of the MAS pilot plant

3.3.2 Plant components

3.3.2.1 Steam Reformer

The steam reformer consists of two seamless stainless steel pipes, the preheating pipe and the reaction pipe. In the preheating pipe the synthesis gas from the CHP Güssing is heated up and the steam is added using a peristaltic pump. The steam is preheated up to approx. 350 ℃ via a heating rod. In the reaction pipe the steam reforming reaction takes place. The synthesis gas is flowing through the steam reforming catalyst, which is lying on a gas distribution plate. A nickel based catalyst is used. To reduce the pressure loss over the steam reformer the form of the catalyst is ring-shaped. Against the odds, the Ni-content of the construction material of the steam reformer has not shown an indication of a catalytic activity during the empty tube experiments.

The design of the steam reformer is pictured in Figure 3.6.

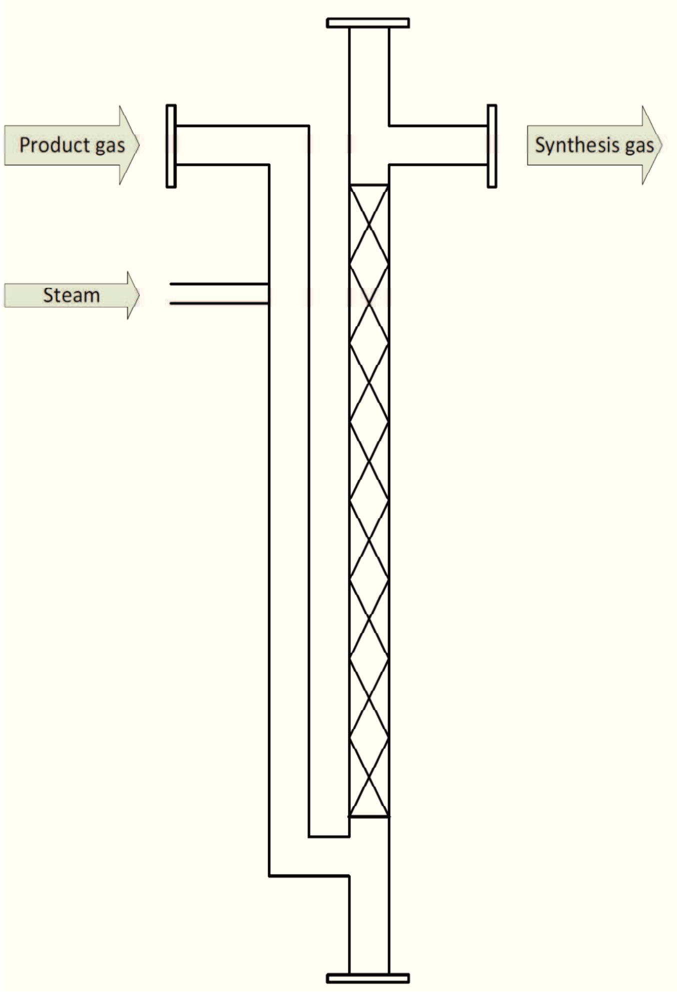
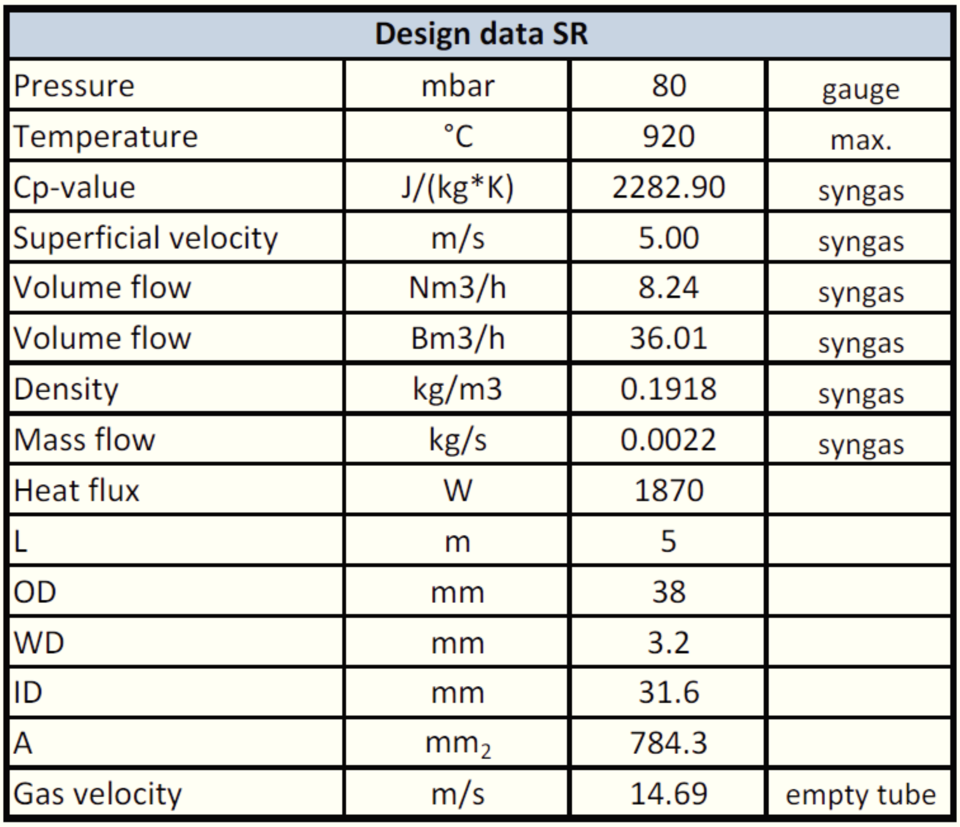


Figure 3.6: Steam reformer scheme

The design data for the steam reformer can be seen from Table 3.5.



Design data SR			
Pressure	mbar	80	gauge
Temperature	°C	920	max.
Cp-value	J/(kg*K)	2282.90	syngas
Superficial velocity	m/s	5.00	syngas
Volume flow	Nm3/h	8.24	syngas
Volume flow	Bm3/h	36.01	syngas
Density	kg/m3	0.1918	syngas
Mass flow	kg/s	0.0022	syngas
Heat flux	W	1870	
L	m	5	
OD	mm	38	
WD	mm	3.2	
ID	mm	31.6	
A	mm_2	784.3	
Gas velocity	m/s	14.69	empty tube

Table 3.5: Design data of the steam reformer

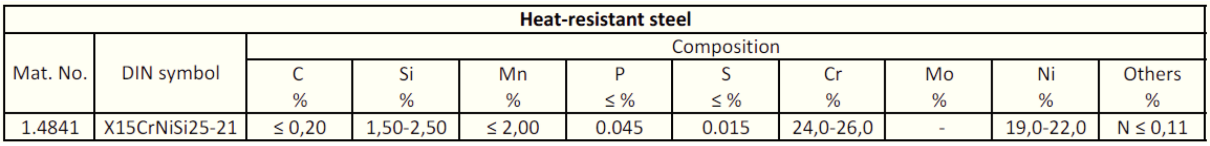
In the steam reformer, the synthesis gas from the CHP Güssing is heated up electrically. The heating modules are carried out as half cylinders with embedded heating elements, which can reach a maximum temperature of 1150 ℃. The heating modules were installed alternating with insulating parts of the same dimension as the heating modules. So every second half cylinder act as heating element and the rest of the modules act as insulating modules.

These kind of ceramic fibre modules were used for the steam reformer because of the following advantages:

- Lightweight construction,
- fast and easy installation,
- low thermal conductivity,
- high electrical power.

Materials selection

Because of the high temperature of approx. 920 ℃ appearing in the steam reformer the whole steam reformer is made of heat-resistant steel (see Table 3.6).



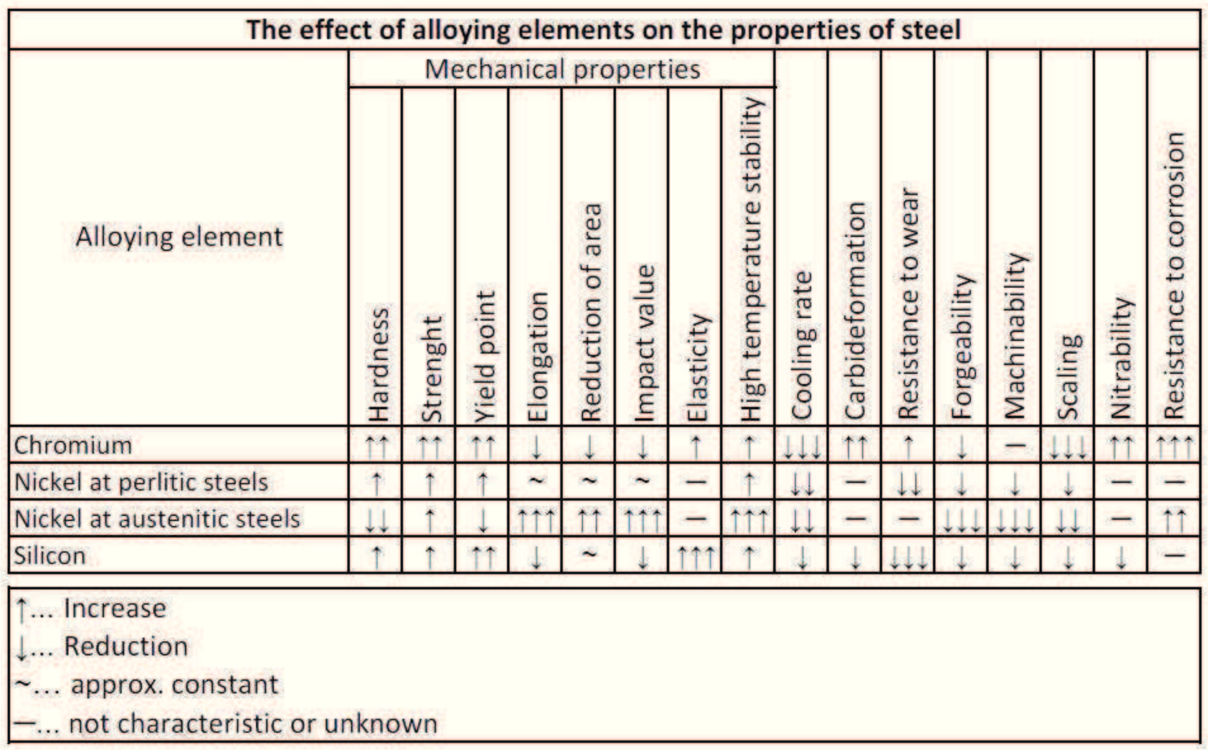
Heat-resistant steel										
Mat. No.	DIN symbol	Composition								
		C %	Si %	Mn %	P ≤ %	S ≤ %	Cr %	Mo %	Ni %	Others %
1.4841	X15CrNiSi25-21	≤ 0,20	1,50-2,50	≤ 2,00	0.045	0.015	24,0-26,0	-	19,0-22,0	N ≤ 0,11

Table 3.6: Material data of heat-resistant steel [73]

The steel no. 1.4841 is heat-proofed under atmospheric air to a temperature of 1150 ℃. The density is 7,9 kg/dm³ and the hardness amounts to ≤ 223 HB (Brinell hardness). The main field of application of heat-resistant steels are industrial furnaces, waste incineration plants, thermal treatment plants as well as the petrochemical industry. [74]

The primary-alloying elements of steel no. 1.4841 are chromium (Cr), nickel (Ni) and silicon (Si). According to the percentage of the alloying element different specific properties can be achieved. As an alloying element chromium (melting point 1903 ℃) reduces both the thermal conductivity and the electric conductivity. The thermal expansion is reduced as well. Nickel (melting point 1455 ℃) as an alloying element strongly increases thermal and electric conductivity. High contents of Ni with a specific alloy composition result in a lower thermal expansion (Invar steel). Silicon (melting point 1410 ℃) is contained in every kind of steel as a result of the composition of the iron ore. To characterise steels as silicon steels the Si-content has to been higher than 0,40 %. Silicon is used as an alloying element for heat-resistant steels due to its ability to increase the scaling resistance. [73]

An overview of the effect of alloying elements on the properties of steel is given in Table 3.7.



The effect of alloying elements on the properties of steel

Alloying element	Mechanical properties																
	Hardness	Strenght	Yield point	Elongation	Reduction of area	Impact value	Elasticity	High temperature stability	Cooling rate	Carbideformation	Resistance to wear	Forgeability	Machinability	Scaling	Nitrability	Resistance to corrosion
Chromium	↑↑	↑↑	↑↑	↓	↓	↓	↑	↑	↓↓↓	↑↑	↑	↓	—	↓↓↓	↑↑	↑↑↑
Nickel at perlitic steels	↑	↑	↑	~	~	~	—	↑	↓↓	—	↓↓	↓	↓	↓	—	—
Nickel at austenitic steels	↓↓	↑	↓	↑↑↑	↑↑	↑↑↑	—	↑↑↑	↓↓	—	—	↓↓↓	↓↓↓	↓↓	—	↑↑
Silicon	↑	↑	↑↑	↓	~	↓	↑↑↑	↑	↓	↓	↓↓↓	↓	↓	↓	↓	—

↑... Increase
↓... Reduction
~... approx. constant
—... not characteristic or unknown

Table 3.7: Effect of alloying elements on steel properties [73]

3.3.2.2 Glycol Scrubber

The glycol scrubber consists of a column (borosilicate glass) with structured packings (stainless steel). The glass column is built up of three planar flange pipes, a reducing T-fitting, an angled discharge pipe and a hose connector. The different glass parts are connected with couplings which includes two flanges and two inserts. Among the planar flange pipes O-ring gaskets are installed for sealing.

The design of the glycol scrubber is pictured in Figure 3.7.

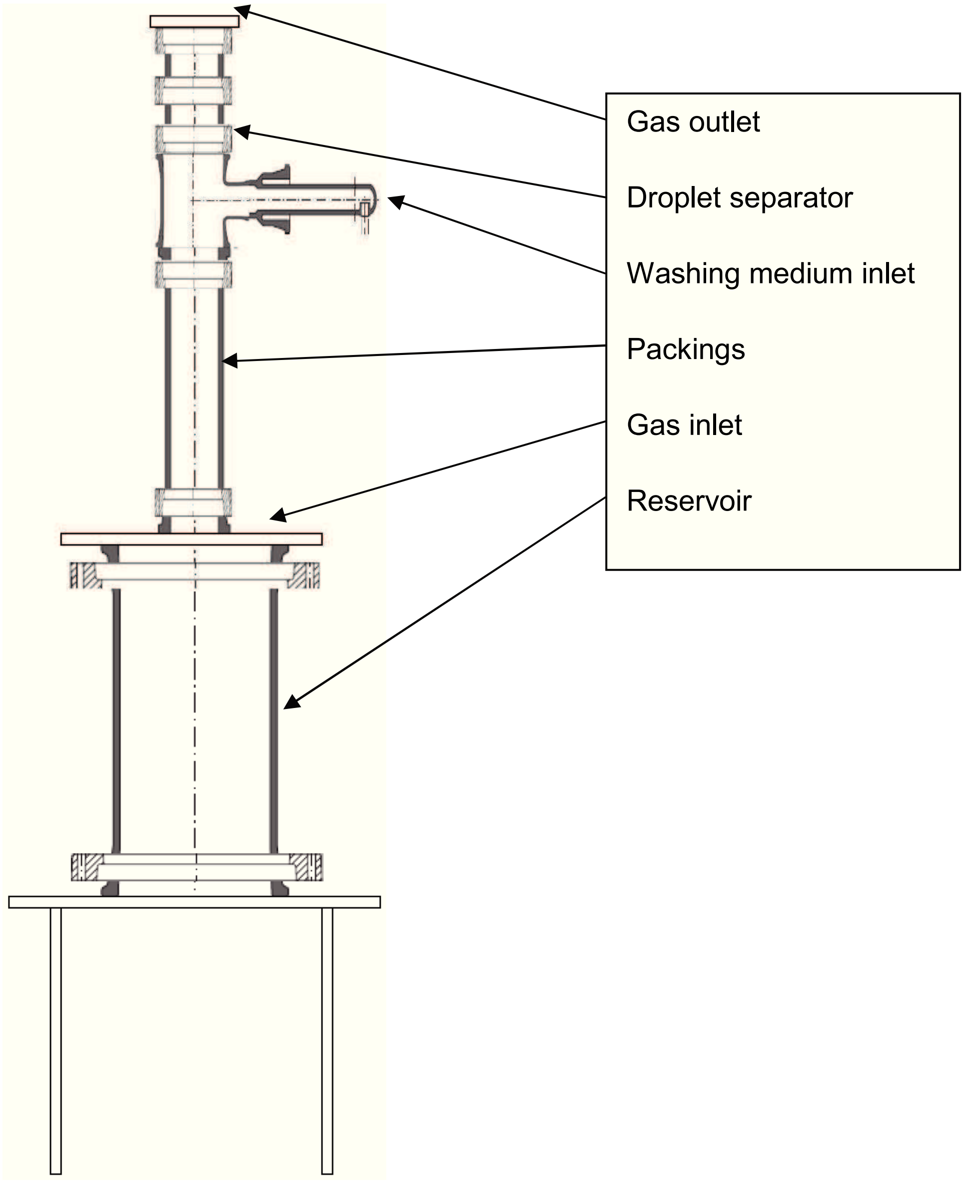


Figure 3.7: Glycol scrubber scheme

After steam reforming, the synthesis gas goes to the glycol scrubber, where the water content of the gas is removed. The scrubber is filled with a glycol-water mixture of approx. 80 % distilled water and 20 % triethylene glycol. The washing liquid is recirculated using a standard heating pump.

In large scale the glycol water mixture would be regenerated by stripping. As in this small scale regeneration is too costly, the used washing liquid is drained and disposed. The fresh glycol is added by means of a peristaltic pump.

The glycol scrubber is operated at a temperature of about 3 ℃. To achieve this temperature, a plate heat exchanger is installed. The therefore needed cold water is provided by a chiller, which supplies all plants, operated in the Technikum Güssing, with cold water.

The whole scrubber is insulated with a flexible insulating material to avoid loss of cooling energy.

Materials selection

Glass parts

As material for the glycol scrubber borosilicate glass was used due to its high chemical resistance. The allowable operating temperature of borosilicate glass is between – 80 ℃ and 200 ℃. The allowable operating pressure depends on the nominal size (DN) of the glass pipes and ranges from full vacuum to e.g. 2 bar at DN 100. [75]

The special properties of this glass material are as follows [75]:

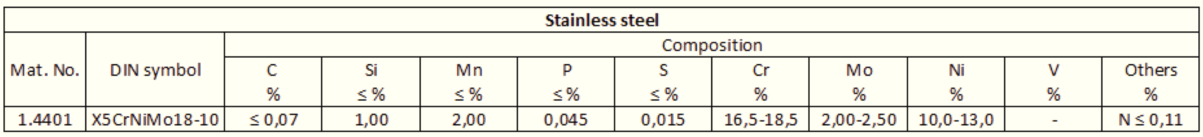
- transparency
- plane surface (non-porous)
- excellent resistance to corrosion
- no catalytic activity
- non-flammability
- environmental acceptable

Couplings

The backing flanges are made of plastic which is advantageous due to the low weight and the relatively good corrosion resistance. The inserts are made of plastic too which simplifies the installation. The O-ring gaskets are composed of polytetrafluoroethylene (PTFE). It is advantageous that PTFE is extremely resistant to alcohols and chemically inert. The gaskets are self-centring on the periphery of the pipe end.

Packings

As packings inserted in the glycol scrubber Sulzer Mellapak M250.Y are used. The packings are made from stainless steel (see Table 3.8). This type of packing is universal suitable for a large application range. They can be used in columns with diameters up to 15 m. The pressure range goes from vacuum to moderate pressures. Another advantage is the low pressure drop, which is only 2 mbar/m at 80 % flooding. [76]



Stainless steel											
		Composition									
Mat. No.	DIN symbol	C %	Si ≤ %	Mn ≤ %	P ≤ %	S ≤ %	Cr %	Mo %	Ni %	V %	Others %
1.4401	X5CrNiMo18-10	≤ 0,07	1,00	2,00	0,045	0,015	16,5-18,5	2,00-2,50	10,0-13,0	-	N ≤ 0,11

Table 3.8: Material data of stainless steel no. 1.4401 [73]

Insulation

The insulating material of the scrubber, named ARMAFLEX, is made of foamed nitrile rubber. Due to its flexibility and lightweight, the material is very quick and easy to assemble. Another benefit is its excellent resistance to oils and chemicals. This kind of insulating material provides a safe protection against energy loss and condensation. The surface temperature of ARMAFLEX is between – 50 ℃ and + 105 ℃, which enables a large field of application. [77]

3.3.2.3 Compressor

For the compression of the synthesis gas an industrial high-pressure compressor is used. The operating pressure of the compressor is in the range of 90 - 350 bar. With the compressor, volume flows (FAD as VDMA 4362) between 5.4 and 7.1 m³/h can be achieved. The intake temperature of the compressor is 5 – 45 ℃. The compressor is featured with an automatic control system with an electric monitoring device.

The compressor unit consists of the following primary components [78]:

- Compressor block,
- driving motor,
- framework and super silent enclosure,
- filter set,
- automatic condensate drain, and
- electrical control with electronic monitoring system.

In Figure 3.8 a picture of the compressor unit is shown.

Figure 3.8: Compressor unit (Bauer Poseidon high pressure compressor, Verticus 5, Type HTA 120-4-5: operating pressure = 90-350 bar, F.A.D. = 5.4-7.1 m³/h)

3.3.2.4 Reactor

The MAS reactor was designed as a fixed-bed reactor, realised as a long, seamless stainless steel pipe. The reactor is filled with a molybdenum based catalyst applicable for high pressure MAS. The compressed syngas passes through the reactor top down. To achieve the requested reaction temperature (between 280 and 320 C) three pairs of heating rods are installed. Every pair of heating rod can be set separately, so there is the possibility to achieve three different temperature zones over the reactor. Furthermore an air cooling is installed to control the highly exothermal reaction of the MAS.

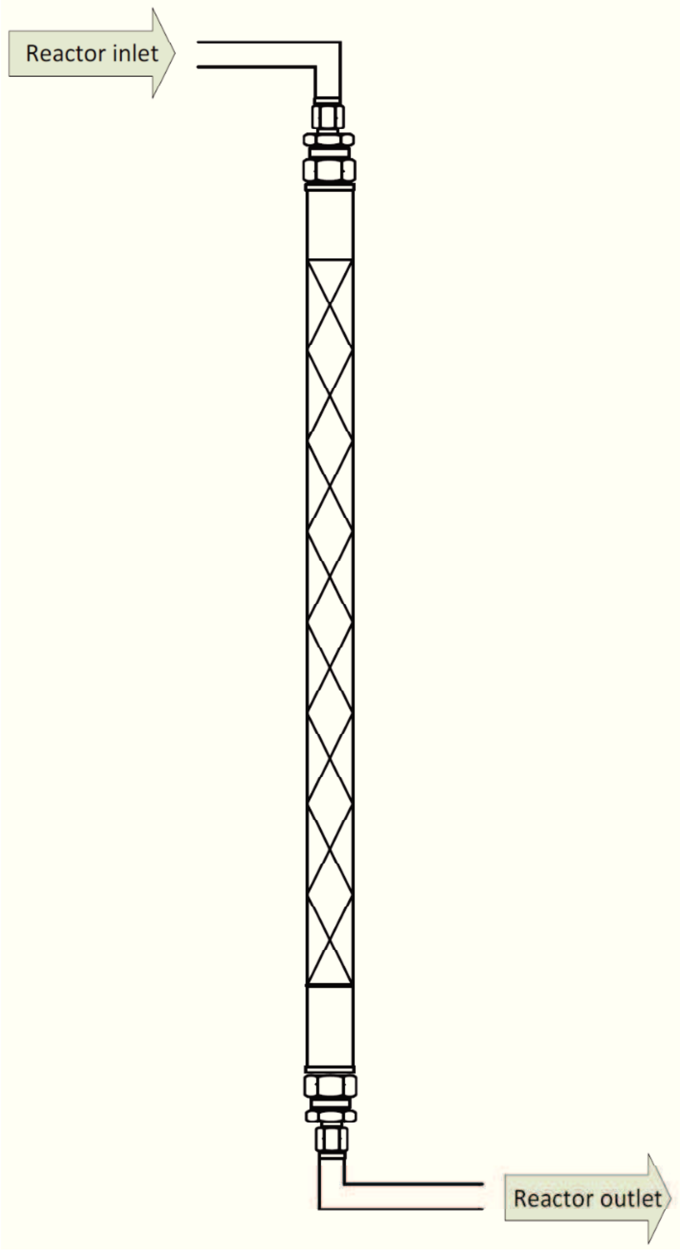
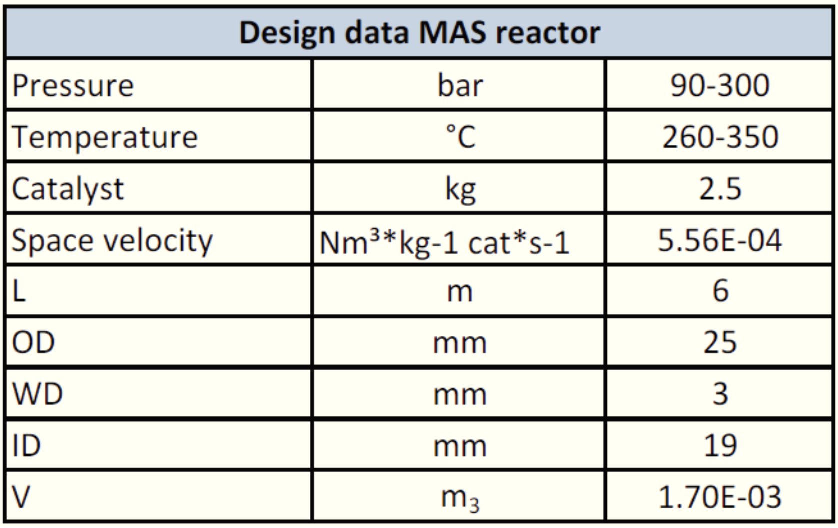


Figure 3.9: Reactor scheme

In Table 3.9 the design data of the MAS reactor are shown.



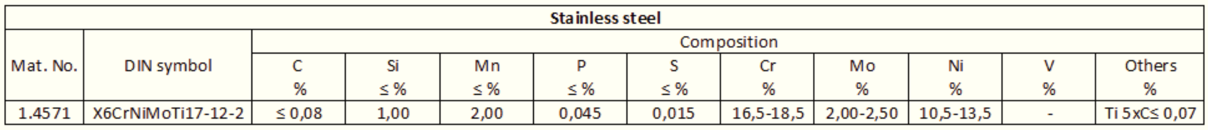
Design data MAS reactor		
Pressure	bar	90-300
Temperature	°C	260-350
Catalyst	kg	2.5
Space velocity	Nm^3*kg-1 cat*s-1	5.56E-04
L	m	6
OD	mm	25
WD	mm	3
ID	mm	19
V	m_3	1.70E-03

Table 3.9: Design data of the MAS reactor

Materials selection

For the MAS reactor, stainless steel no. 1.4571 was chosen as material because of its high resistance to corrosion. As a result of using Mo as an alloy addition, the material has a better acid-resistant. Furthermore, steel no. 1.4571 has good high temperature strength behaviour.

The material data of stainless steel no. 1.4571 is given in Table 3.10.



Stainless steel											
		Composition									
Mat. No.	DIN symbol	C %	Si ≤ %	Mn ≤ %	P ≤ %	S ≤ %	Cr %	Mo %	Ni %	V %	Others %
1.4571	X6CrNiMoTi17-12-2	≤ 0,08	1,00	2,00	0,045	0,015	16,5-18,5	2,00-2,50	10,5-13,5	-	Ti 5xC≤ 0,07

Table 3.10: Material data of stainless steel no. 1.4571 [73]

3.3.2.5 Condenser

The condenser was, just as well as the reactor, designed as a long, seamless stainless steel pipe. Using a water cooling system the condenser is cooled down to approx. 10 °C and the condensation of the mixed alcohols takes place at the operating pressure of the synthesis. At the bottom of the condenser, the condensed alcohols are withdrawn using a high pressure needle valve. The tail gas leaves the condenser at the top and goes back to the CHP.

The whole condenser is insulated with the same insulating material as the glycol scrubber to assure low temperatures, where the mixed alcohols can condense.

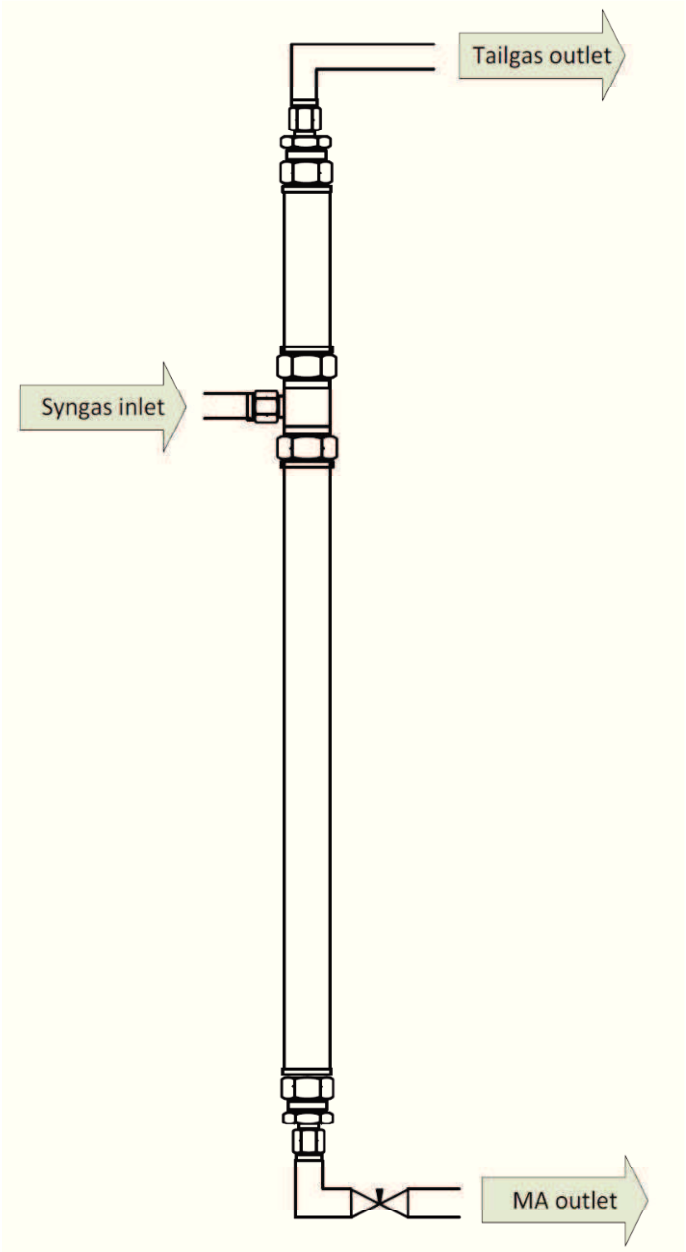


Figure 3.10: Condenser scheme

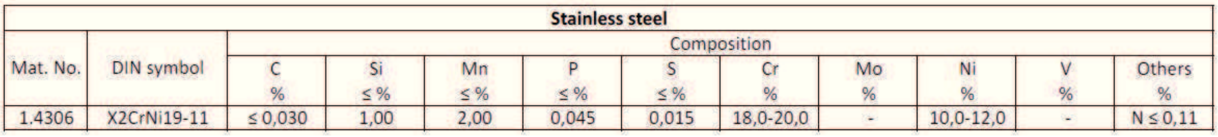
3.3.2.6 Expansion valve

For the expansion of the synthesis gas an overload relief valve is installed (see Figure 3.11). This high pressure expansion valve is continuously adjustable in the range of 50-300 bar. It is suitable for gases with a temperature between – 10 °C and + 80 °C.

Figure 3.11: Overload relief valve

Materials selection

The housing of the expansion valve is made of steel 1.4306 (see Table 3.11). Austenitic Cr-Ni steels are resistant to the influence of reducing (based on the Ni-content) and oxidising chemicals (based on the Cr-content) and, hence, very common for chemical processes [73].



Stainless steel											
Mat. No.	DIN symbol	Composition									
		C %	Si ≤ %	Mn ≤ %	P ≤ %	S ≤ %	Cr %	Mo %	Ni %	V %	Others %
1.4306	X2CrNi19-11	≤ 0,030	1,00	2,00	0,045	0,015	18,0-20,0	-	10,0-12,0	-	N ≤ 0,11

Table 3.11: Material data of stainless steel no. 1.4306 [73]

The membrane is made out of NBR (nitrile butadiene rubber) and the sealings are made of Perbunan®, which is the registered trade name of NBR. In this connection it is a copolymer of two different components, acrylonitrile and butadiene. The production of NBR is carried out via emulsion polymerisation in the temperature range of 5-30 °C. The acrylonitrile percentage (generally 28-38 %) has an important impact on certain properties, e.g. low-temperature performance or swelling behaviour. [79]

Especially for the expansion of high pressures to atmospheric conditions the low-temperature performance of sealings is of particular importance because of the Joule-Thomson effect.

3.3.3 Process measuring and control technology

3.3.3.1 P&I diagram

The P&I diagram for the MAS pilot plant is divided into two parts – the low-pressure and the high-pressure part - as you can see from Figure 3.12 and Figure 3.13. The important regulator control elements are listed in the appendix.

The whole plant is controlled by an automation system. The temperatures are measured via thermocouples in order to control the heating elements in the different parts of the pilot plant.

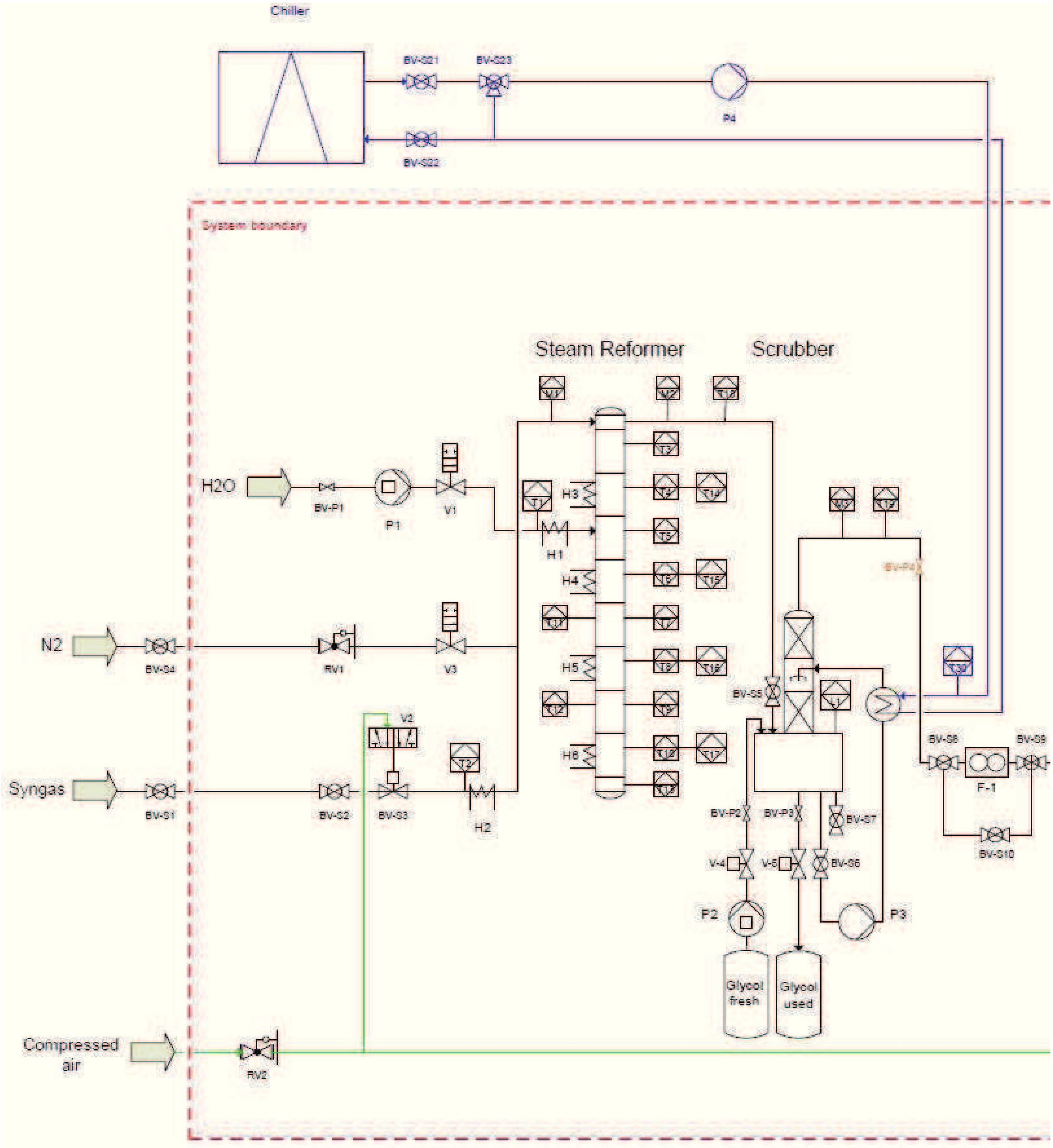


Figure 3.12: P&I diagram – low-pressure part

The volumetric flow of the pilot plant is controlled by the bypass of the compressor. The pressure of the MAS reaction is controlled by the overflow valve after the condensation of the mixed alcohols.

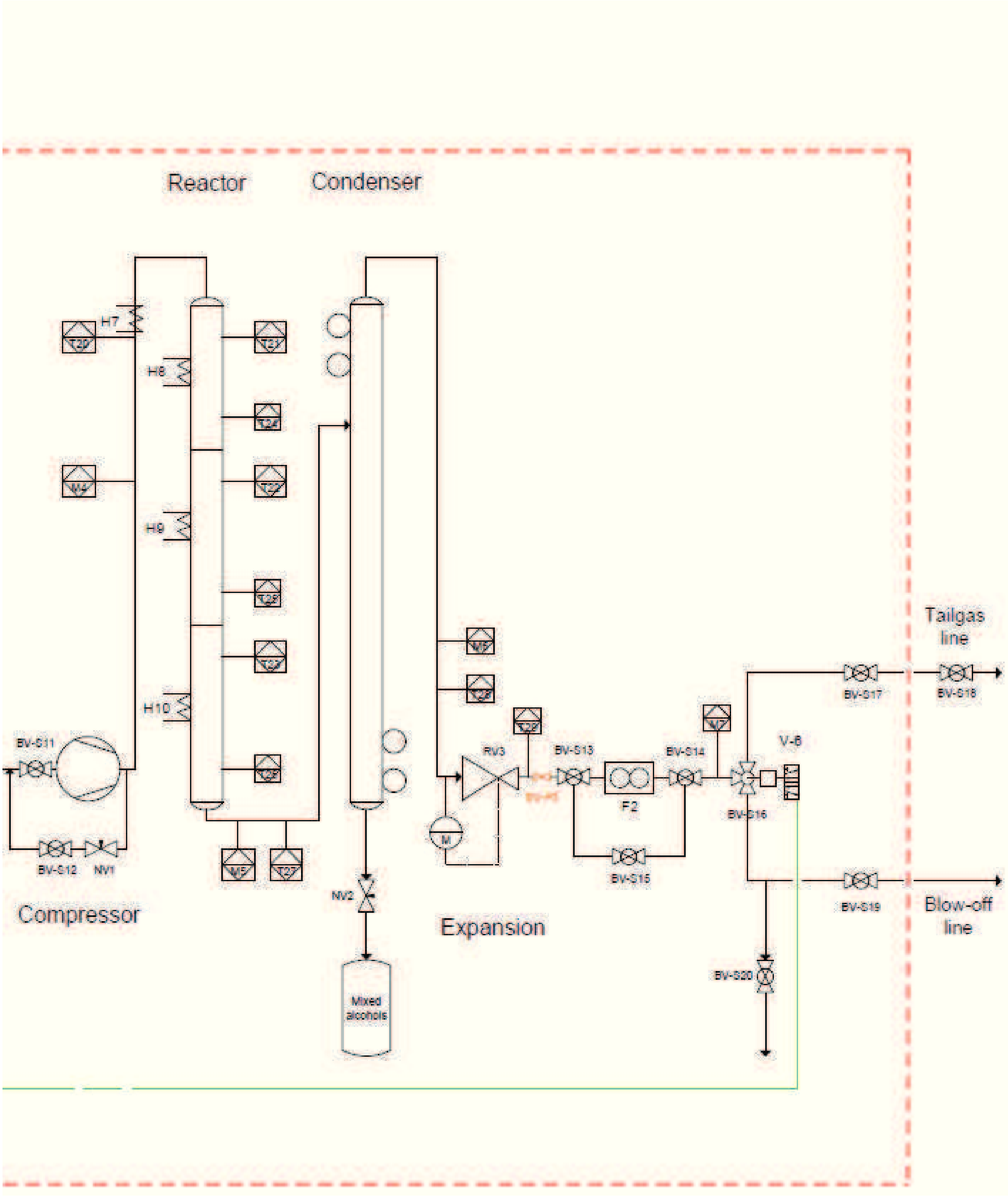


Figure 3.13: P&I diagram – high-pressure part

3.3.3.2 Temperature measuring

In the total MAS pilot plant temperature measurement is carried out by type K thermocouples. These NiCr-Ni thermocouples are optimally applicable for measuring high temperatures up to 1200 ℃. They can be used in gaseous mediums as well as in liquid mediums. As a result of the specific mounting systems this kind of mineral-insulated thermocouple is capable for applications with high pressures and vibrations. Further advantages are the flexibility of the thermocouples and their very fast response time. [80]

The test points of the pilot plant are made of stainless steel pipes which have a clamping threaded connection to the test point junction. In these pipes the thermocouples are assembled in such a way as the point of the thermocouple is situated at the end of the pipe. This practice reduces the insulating effects of the hose connection tube and ensures that the point is located in the centre of the gas stream. Due to the lower pressure tightness of the thermocouple connections, this type of temperature measurement takes place only in the low-pressure (LP) parts of the pilot plant. In case of temperature measuring in the high-pressure (HP) part of the plant as well as temperature measuring for controlling the heating elements, the thermocouples were installed on the surface of the pipe respectively between heating rod and pipe surface.

All installed thermocouples are connected to the programmable logic controller (PLC), thus, all temperatures are logged and recorded. Some of the measured temperatures are used for controlling the heating elements of the pilot station.

Measurement principle

Temperature measurement via thermocouples relies on the Seebeck effect. This effect reveals that heat will flow from the warm to the cold part of a conductor, and this heat flow rate is proportional to the thermal conductivity of the conductor. Besides, the thermal gradient generates an electric field within the conductor, which results in a measurable voltage.

In Figure 3.14, the measurement setup of a thermocouple is illustrated. At the measuring point, metal A and metal B are electrically conjunct. The measurable voltage is the difference of the thermoelectrical potential of the two metals. [81]

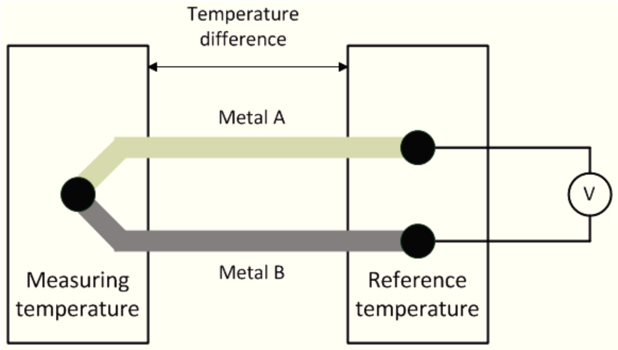


Figure 3.14: Measuring principle of a thermocouple

The design of mineral insulated thermocouples can be seen in Figure 3.16.

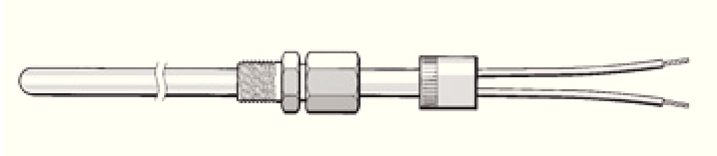
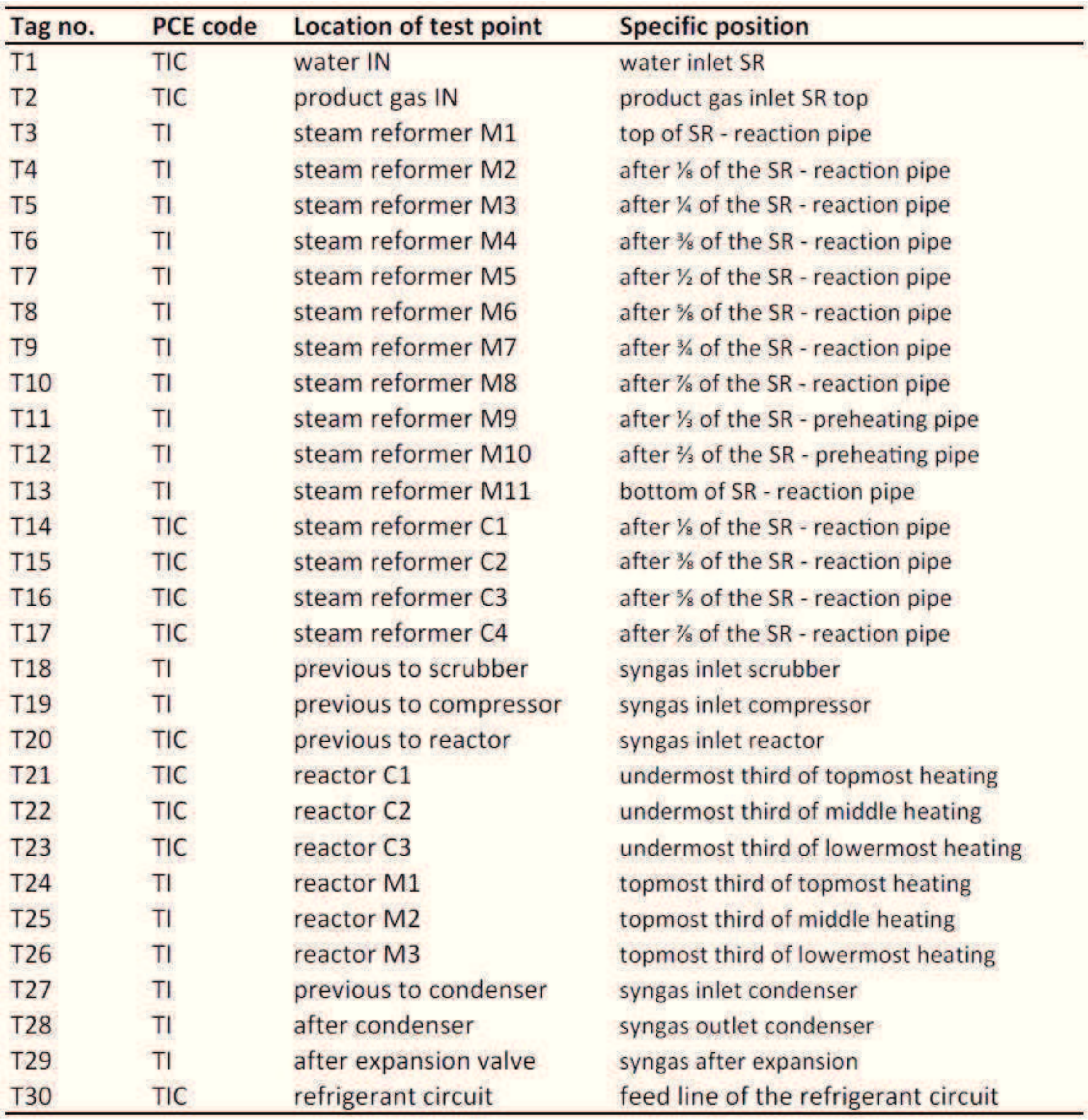


Figure 3.15: Design of mineral insulated thermocouples[82]

An overview of all temperature measurement points is given in Table 3.12.



Tag no.	PCE code	Location of test point	Specific position
T1	TIC	water IN	water inlet SR
T2	TIC	product gas IN	product gas inlet SR top
T3	TI	steam reformer M1	top of SR - reaction pipe
T4	TI	steam reformer M2	after ⅛ of the SR - reaction pipe
T5	TI	steam reformer M3	after ¼ of the SR - reaction pipe
T6	TI	steam reformer M4	after ⅜ of the SR - reaction pipe
T7	TI	steam reformer M5	after ½ of the SR - reaction pipe
T8	TI	steam reformer M6	after ⅝ of the SR - reaction pipe
T9	TI	steam reformer M7	after ¾ of the SR - reaction pipe
T10	TI	steam reformer M8	after ⅞ of the SR - reaction pipe
T11	TI	steam reformer M9	after ⅓ of the SR - preheating pipe
T12	TI	steam reformer M10	after ⅔ of the SR - preheating pipe
T13	TI	steam reformer M11	bottom of SR - reaction pipe
T14	TIC	steam reformer C1	after ⅛ of the SR - reaction pipe
T15	TIC	steam reformer C2	after ⅜ of the SR - reaction pipe
T16	TIC	steam reformer C3	after ⅝ of the SR - reaction pipe
T17	TIC	steam reformer C4	after ⅞ of the SR - reaction pipe
T18	TI	previous to scrubber	syngas inlet scrubber
T19	TI	previous to compressor	syngas inlet compressor
T20	TIC	previous to reactor	syngas inlet reactor
T21	TIC	reactor C1	undermost third of topmost heating
T22	TIC	reactor C2	undermost third of middle heating
T23	TIC	reactor C3	undermost third of lowermost heating
T24	TI	reactor M1	topmost third of topmost heating
T25	TI	reactor M2	topmost third of middle heating
T26	TI	reactor M3	topmost third of lowermost heating
T27	TI	previous to condenser	syngas inlet condenser
T28	TI	after condenser	syngas outlet condenser
T29	TI	after expansion valve	syngas after expansion
T30	TIC	refrigerant circuit	feed line of the refrigerant circuit

Table 3.12: Overview of temperature test points

3.3.3.3 Pressure measuring

The pressure measurement is carried out using piezo-resistive pressure sensors. The benefits of these sensors are besides accuracy, reliability and mechanical strength, a good repeatability and an easy assembling. Due to its stainless steel design the pressure sensors have an excellent resistance to corrosion. [83]

In Table 3.13 an overview of all pressure measurement points is given.

Tag no.	PCE code	Location of test point	Specific position
M1	PI	previous to steam reformer	product gas inlet SR top
M2	PI	previous to scrubber	syngas inlet scrubber
M3	PI	previous to compressor	syngas inlet compressor
M4	PIC	after compressor	syngas outlet compressor
M5	PI	after reactor	syngas outlet reactor
M6	PI	previous to expansion valve	syngas outlet condenser
M7	PI	after expansion valve	syngas after expansion

Table 3.13: Overview of pressure test points

The metering range of the low pressure sensors is +1 to +600 mbar. The metering range of the high pressure sensors is +1 to +600 bar. The permissible medium and ambience temperatures are in the range of 0 – 80 ℃. The sen sors are based on 2-wire system with an output signal range of 4 – 20 mA. [84]

Measurement principle

The measurement principle of the pressure sensor is based on a sensor element, which is fed with auxiliary energy. The applied pressure is converted into an amplified, standardised electrical signal through the deformation of the diaphragm. This electrical signal changes proportionally to the pressure and can be exploited accordingly. [84]

An image of the pressure sensor can be seen in Figure 3.16.

Figure 3.16: Image of pressure sensor (tecsis pressure sensor compact with internal diaphragm) [83]

3.3.3.4 Level measuring

For level measuring in the glycol scrubber, a level limit switch is installed at the top of the scrubber (see Table 3.14). The advantages of this level limit switch are low costs, a flexible instrumentation and the possibility to detect several limits with only one device [85].

Tag no.	PCE code	Location of test point	Specific position
L1	LIC	glycol srubber	top of glycol scrubber

Table 3.14: Level test point

The function of this level limit switch is to protect the scrubber from an overspill. The level measuring device consists of a Liquipoint® sensor and a nivotester®. The Liquipoint® sensor is mounted directly at the top of the scrubber. It is suitable for conductive liquids with a conductivity to a minimum value of 10 µS/cm. The operating pressure of the sensor is in the range of -1 to +10 bar. The medium temperature ranges between -40 ℃ and +100 ℃. The nivotester® is mounted in the automation switchboard, where it is controlled from the PLC system. [85]

Measurement principle

In the empty scrubber an alternating voltage is impressed between the two rod probes. As soon as the conductive liquid in the scrubber makes contact between the ground probe rod and the maximum probe rod, a current is flowing. This current is measured and the Liquipoint® sends a signal to the nivotester®, that the maximum level is achieved. As soon as the liquid level is below the maximum probe, the sensor switched back. [85]

In Figure 3.17 the level measuring system with Liquipoint® sensor, nivotester® as well as the PLC system is shown.

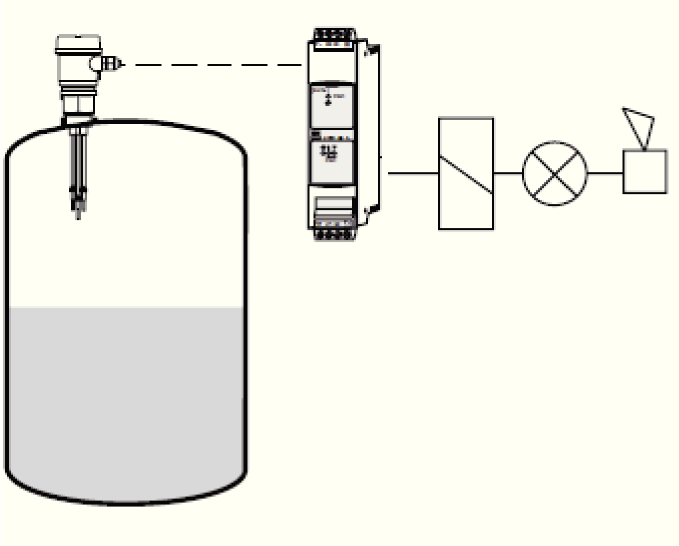


Figure 3.17: Level measuring system [85]

3.3.4 Automation

As the aim of the MAS synthesis are long term experiments for more than 200 hours, the MAS pilot plant is designed for fully automatic operation, without any personal.

The automation of the MAS pilot plant was performed with the control system X20 System® from the company B&R (Bernecker + Rainer Industrie-Elektronik GmbH). This system is a peripheral I/O system which can be enlarged to a complete control solution. The X20 System® consists of three basic elements, namely a terminal block, an electronic module and a bus module (see Figure 3.18). The CPU is designed as mounting rail offering the possibility to mount up to 250 I/O modules. A benefit of this control system is the large field of application from standard to high performance applications. Further benefits are the great variety of interfaces (RS232, Ethernet and USB) as well as the easy maintenance due to the module design. [86]

Figure 3.18: Design of the X20 System® [86]

The electronic modules, used in the MAS pilot plant, are specified as follows:

- analog input modules
- digital input modules
- analog output modules
- digital output modules
- temperature modules

3.3.5 Visualisation

The visualisation of the MAS pilot plant was carried out with the software LabView® from National Instruments. LabView® is a graphical programming environment which provides tools for measurement and control applications. By means of graphical icons and wires, measurement and control systems can be created resembling a flowchart. The use of this software has many advantages, e.g. the faster programming. The program uses the drag-and-drop function as well as graphical function blocks, which makes the programming much clearer in place of writing text lines. The possibility of integration with a multiplicity of instruments or sensors with built-in libraries is an additional benefit of LabView®. [87]

The visualisation software is connected with the automation software over an OPC-Server. For industrial bus systems, the OPC server provides the opportunity to communicate among each other.

Concerning the structuring of the visualisation, seven main tabs and five detail tabs were established. Figure 3.19 illustrates the main tab "Mixed Alcohols", where the flowchart of the whole MAS plant can be seen. The CO values and the alarm lamps are indicated too. In this main tab, the operator can define the PLC mode (automatic/manual) as well as the status of the CHP Güssing (automatic/offline). In addition, the emergency stop switch can be enabled. In case of an alarm, the emergency code is displayed and the alarm can be quitted. Ancillary, there is the possibility to switch between the different detail tabs.

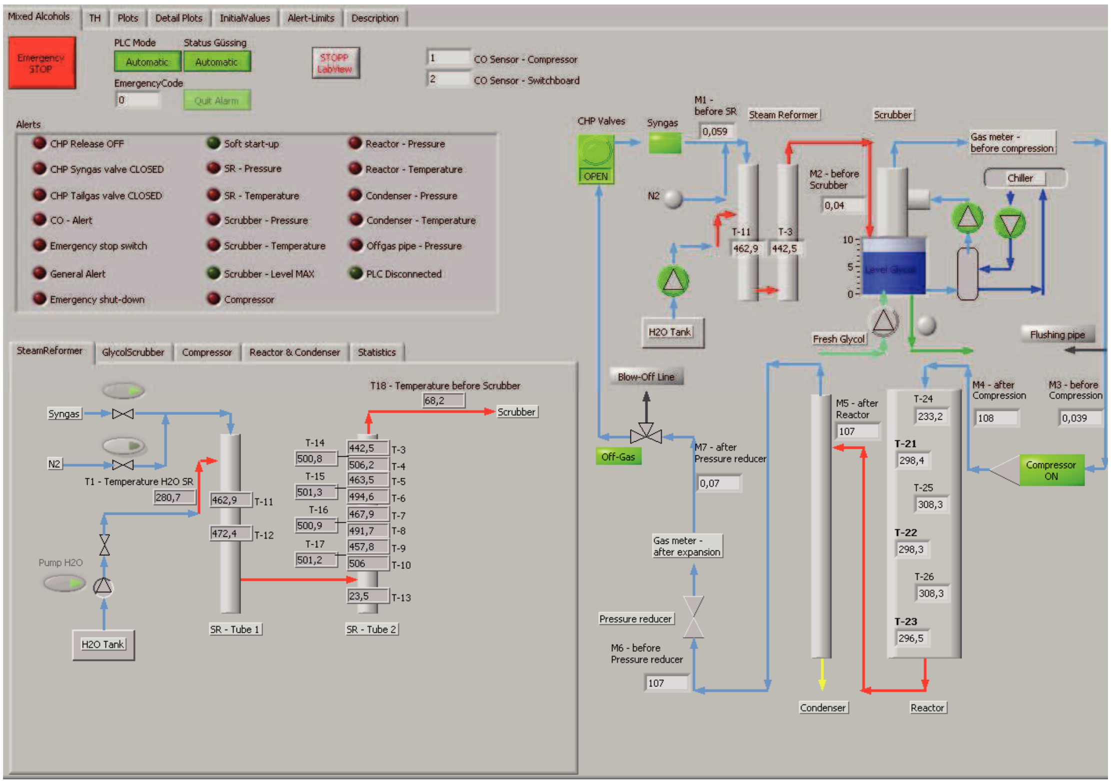
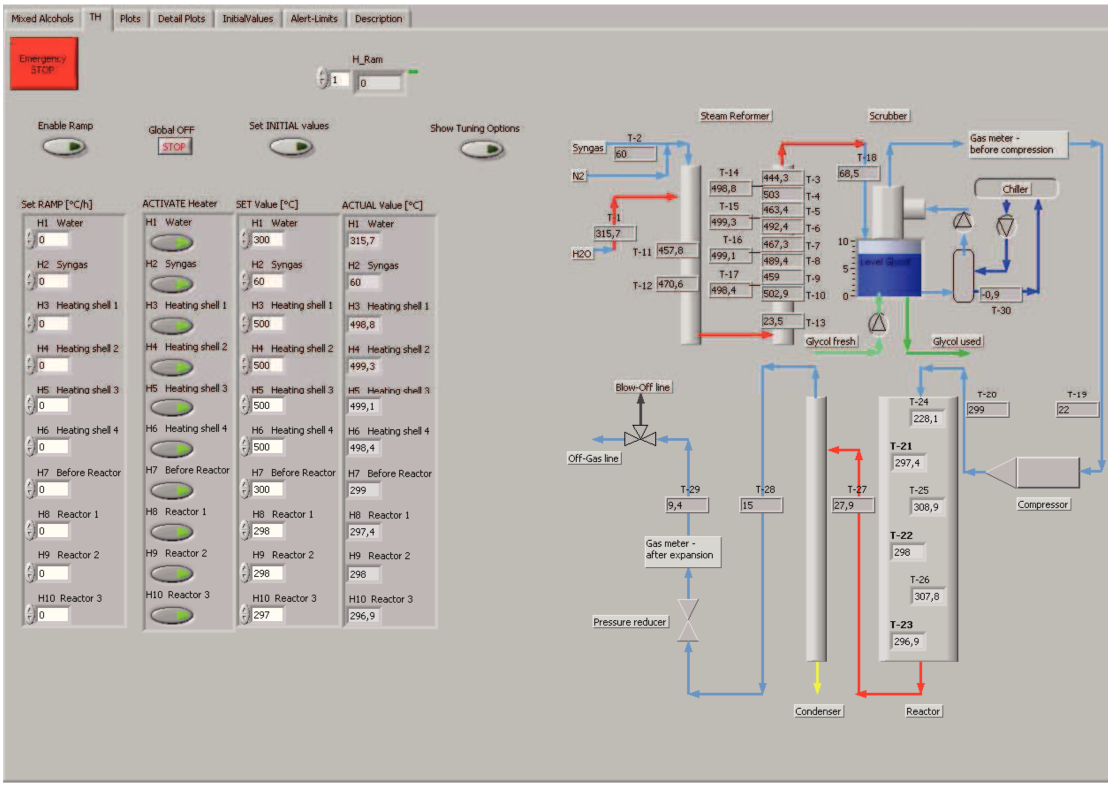

PLC Mode: Automatic
Status Güssing: Automatic
EmergencyCode: 0
1 CO Sensor - Compressor
2 CO Sensor - Switchboard
CHP Valves: OPEN
T18 - Temperature before Scrubber: 68,2
T1 - Temperature H2O SR: 280,7
T-11: 462,9
T-12: 472,4
T-14: 500,8
T-15: 501,3
T-16: 500,9
T-17: 501,2
T-3: 442,5
T-4: 506,2
T-5: 463,5
T-6: 494,6
T-7: 467,9
T-8: 491,7
T-9: 457,8
T-10: 506
T-13: 23,5
M1 - before SR: 0,059
M2 - before Scrubber: 0,04
M3 - before Compression: 0,039
M4 - after Compression: 108
M5 - after Reactor: 107
M6 - before Pressure reducer: 107
M7 - after Pressure reducer: 0,07
T-24: 233,2
T-21: 298,4
T-25: 308,3
T-22: 298,3
T-26: 308,3
T-23: 296,5
Compressor ON

Figure 3.19: Screenshot of main tab „Mixed Alcohols"

Plottings of the main tabs „TH“ and „Detail Plots“ are shown in Figure 3.20 and Figure 3.21.



H_Ram: 1, 0

Set RAMP [°C/h]	ACTIVATE Heater	SET Value [°C]	ACTUAL Value [°C]
H1 Water 0	H1 Water	H1 Water 300	H1 Water 315,7
H2 Syngas 0	H2 Syngas	H2 Syngas 60	H2 Syngas 60
H3 Heating shell 1 0	H3 Heating shell 1	H3 Heating shell 1 500	H3 Heating shell 1 498,8
H4 Heating shell 2 0	H4 Heating shell 2	H4 Heating shell 2 500	H4 Heating shell 2 499,3
H5 Heating shell 3 0	H5 Heating shell 3	H5 Heating shell 3 500	H5 Heating shell 3 499,1
H6 Heating shell 4 0	H6 Heating shell 4	H6 Heating shell 4 500	H6 Heating shell 4 498,4
H7 Before Reactor 0	H7 Before Reactor	H7 Before Reactor 300	H7 Before Reactor 299
H8 Reactor 1 0	H8 Reactor 1	H8 Reactor 1 298	H8 Reactor 1 297,4
H9 Reactor 2 0	H9 Reactor 2	H9 Reactor 2 298	H9 Reactor 2 298
H10 Reactor 3 0	H10 Reactor 3	H10 Reactor 3 297	H10 Reactor 3 296,9

T-2 60
T-1 315,7
T-11 457,8
T-12 470,6
T-14 498,8
T-15 499,3
T-16 499,1
T-17 498,4
T-3 444,3
T-4 503
T-5 463,4
T-6 492,4
T-7 467,3
T-8 489,4
T-9 459
T-10 502,9
T-13 23,5
T-18 68,5
T-30 -0,9
T-20 299
T-19 22
T-24 228,1
T-21 297,4
T-25 308,9
T-22 298
T-26 307,8
T-23 296,9
T-29 9,4
T-28 15
T-27 27,9

Figure 3.20: Screenshot of main tab „TH” (trace heating)

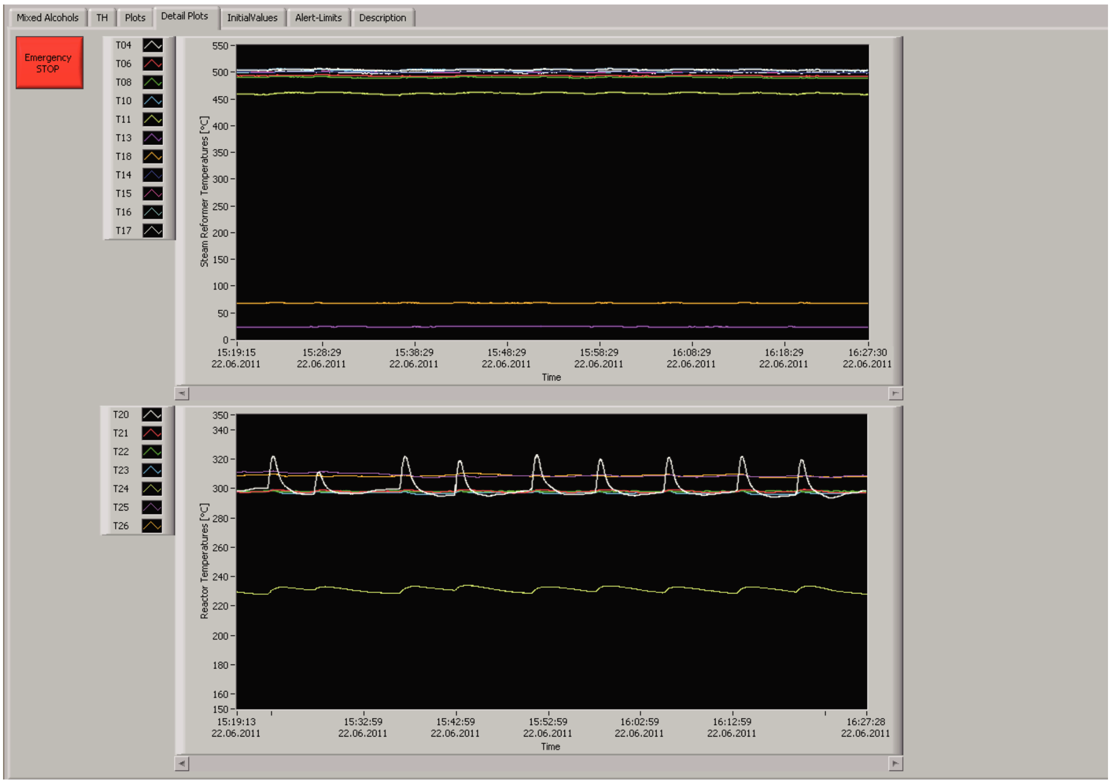


Figure 3.21: Screenshot of main tab „Detail Plots”

In Figure 3.22, Figure 3.23, Figure 3.24, Figure 3.25 and Figure 3.26, screenshots of the detail tabs “SteamReformer” “GycolScrubber”, “Compressor”, “Reactor and Condenser” and “Statistics” are shown.

In the figures below, the pressures and temperatures for every subunit of the pilot plant are displayed. In the manual mode, the valves can be opened/closed respectivly the pumps can be switched on/off via the buttons in the detail tabs. In the automatic mode, the buttons are disabled and the different devices are controled by the PLC.

Addionally, there are input fields for the cycle time of the gycol circuit as well as for the temperature of the cooling circuit.

In the “Statistics” tab, the data logging can be enabled. Moreover, the operating hours of the CHP Güssing and of the equipment of the pilot plant as well as the total flows of the gas meters are counted.

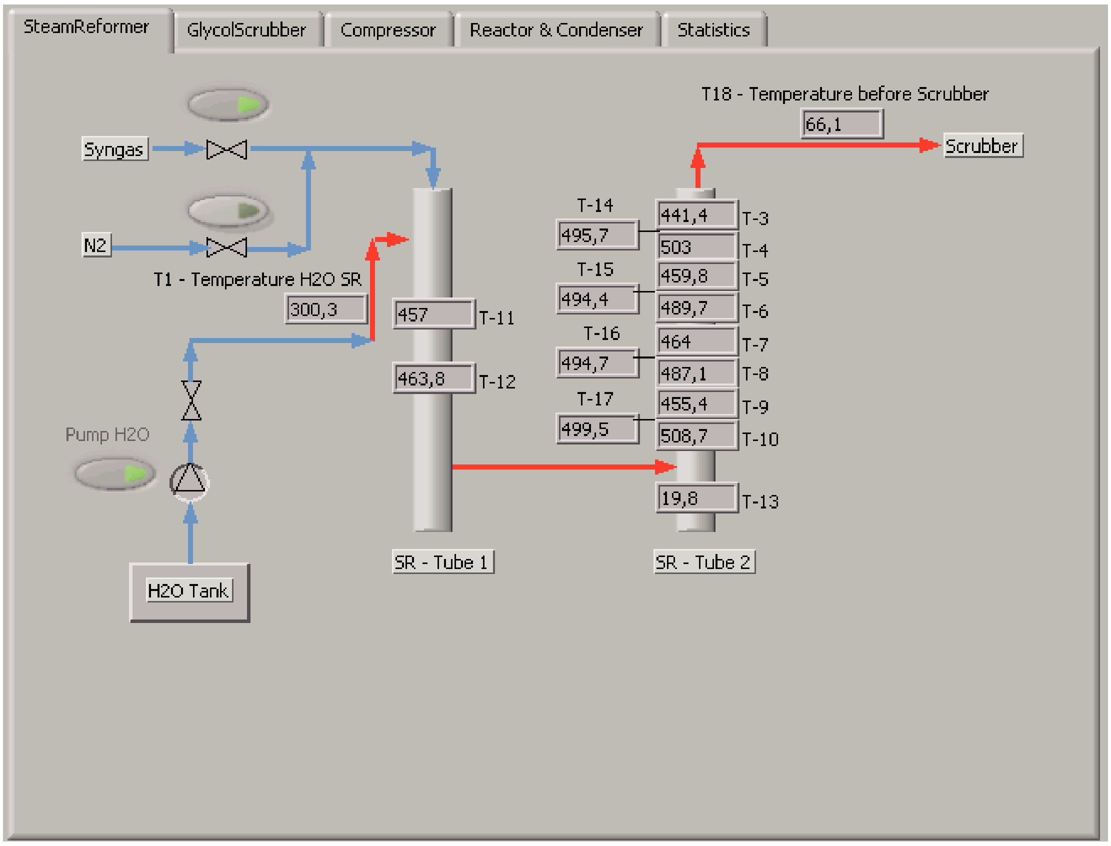
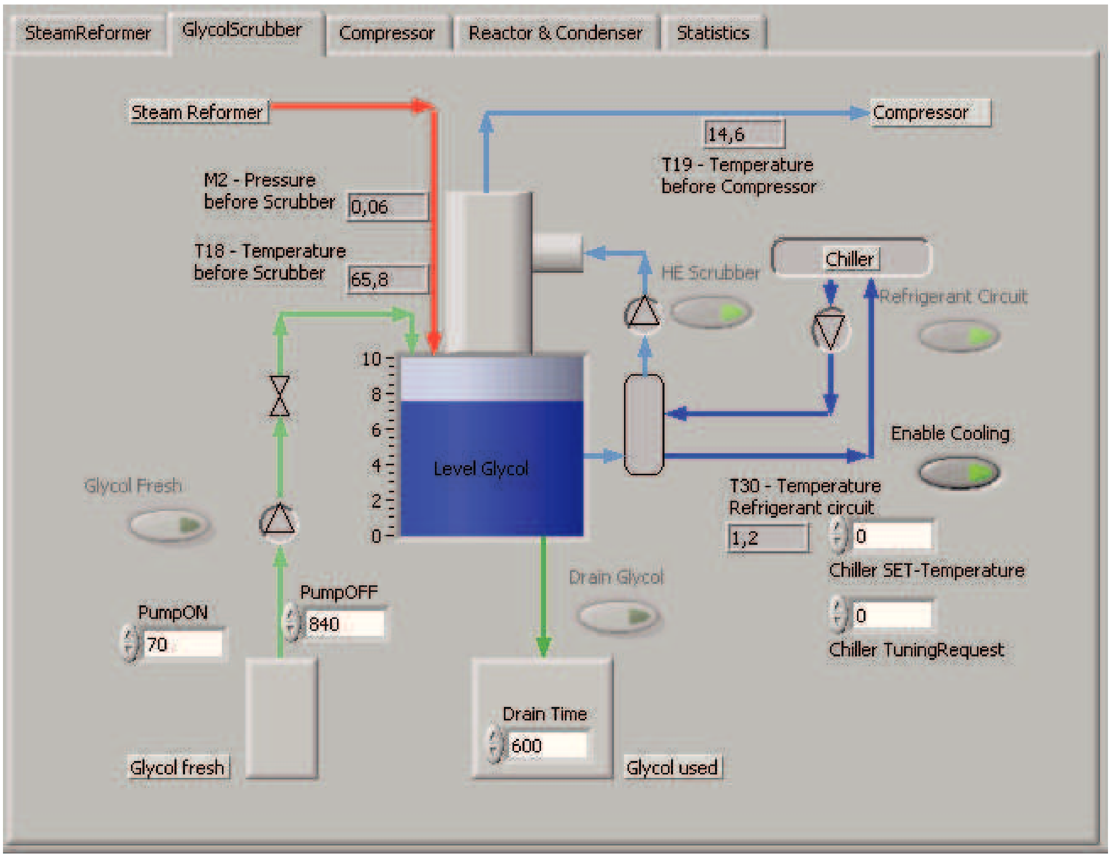


Figure 3.22: Screenshot of detail tab „SteamReformer”



M2 - Pressure before Scrubber 0,06

T18 - Temperature before Scrubber 65,8

T19 - Temperature before Compressor 14,6

T30 - Temperature Refrigerant circuit 1,2

Chiller SET-Temperature 0

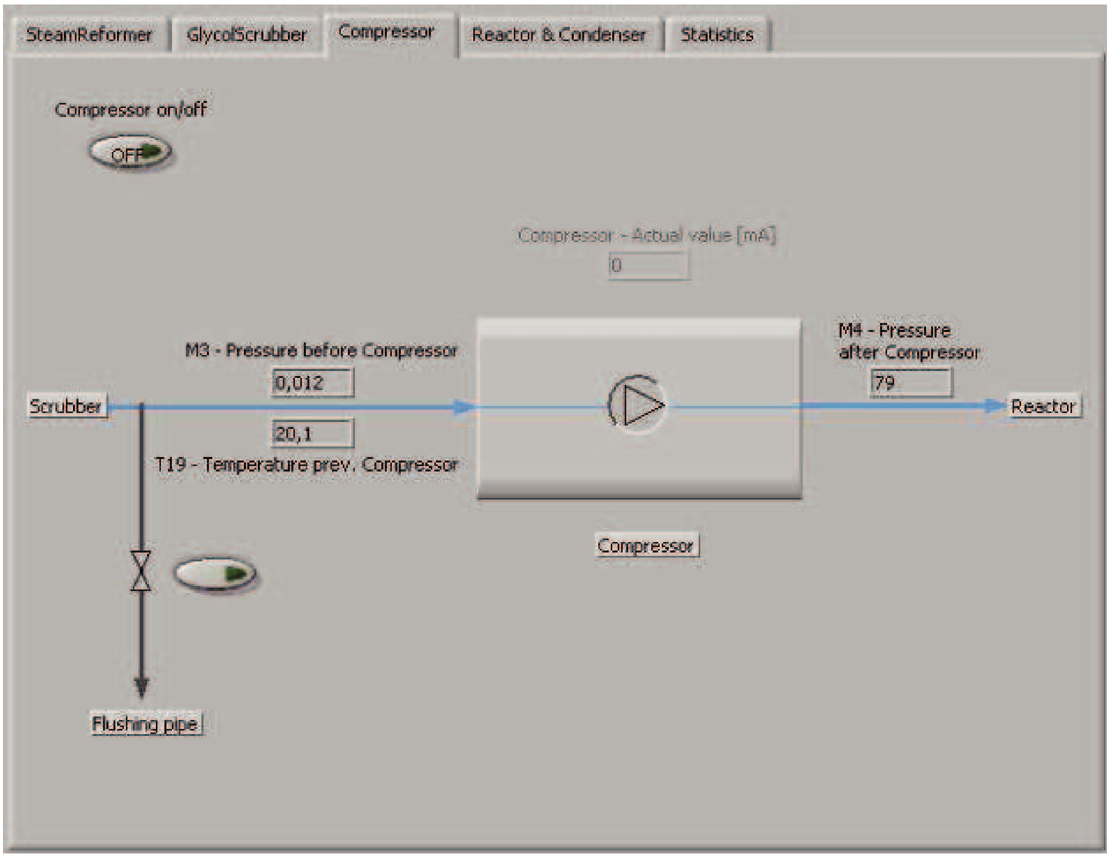
Chiller TuningRequest 0

PumpON 70

PumpOFF 840

Drain Time 600

Figure 3.23: Screenshot of detail tab „GlycolScrubber"



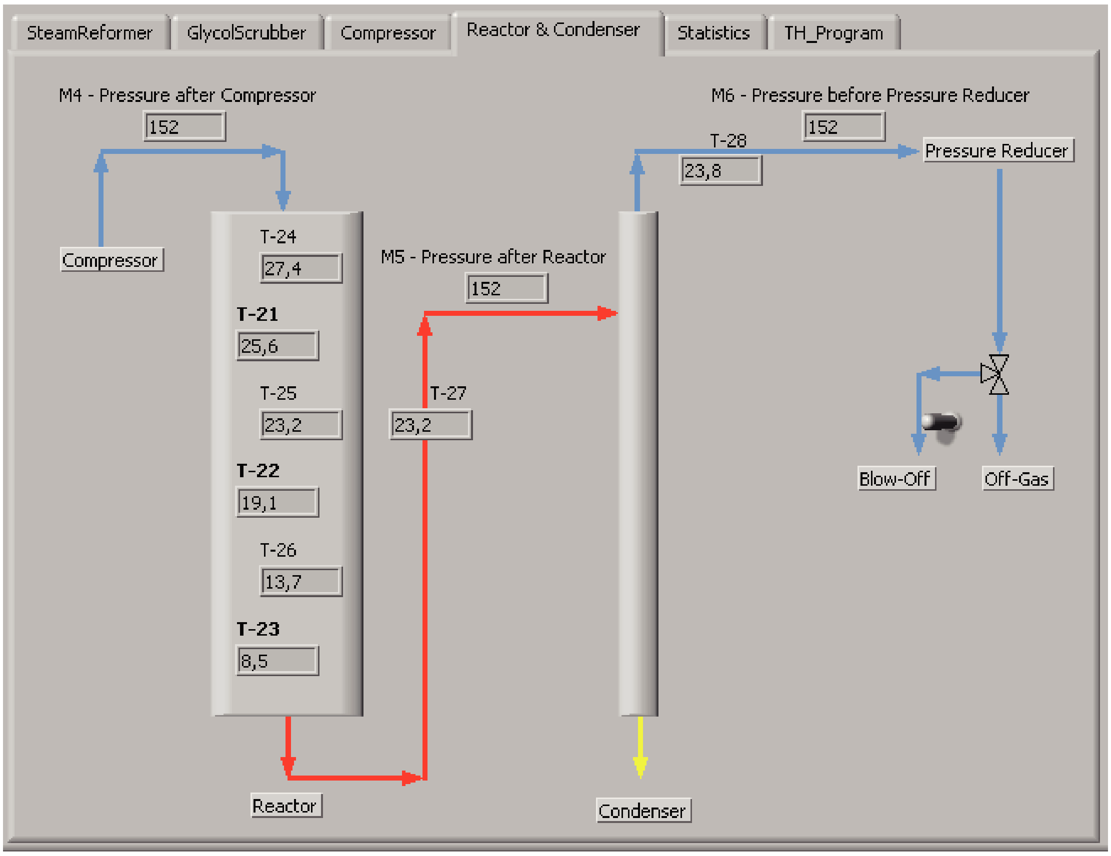
Compressor - Actual value [mA] 0

M3 - Pressure before Compressor 0,012

T19 - Temperature prev. Compressor 20,1

M4 - Pressure after Compressor 79

Figure 3.24: Screenshot of detail tab „Compressor"



M4 - Pressure after Compressor
152

M6 - Pressure before Pressure Reducer
152

T-28
23,8

T-24
27,4

T-21
25,6

M5 - Pressure after Reactor
152

T-25
23,2

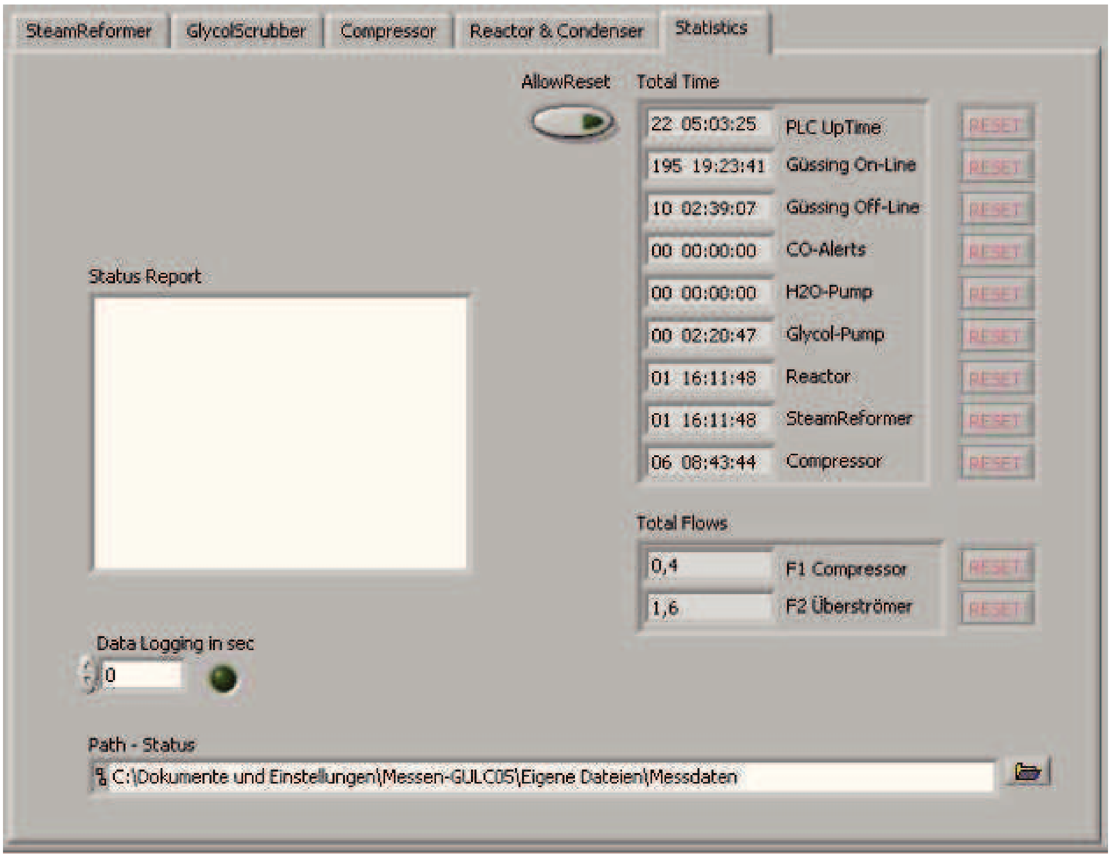
T-27
23,2

T-22
19,1

T-26
13,7

T-23
8,5

Figure 3.25: Screenshot of detail tab „Reactor & Condenser”



Total Time

22 05:03:25	PLC UpTime	RESET
195 19:23:41	Güssing On-Line	RESET
10 02:39:07	Güssing Off-Line	RESET
00 00:00:00	CO-Alerts	RESET
00 00:00:00	H2O-Pump	RESET
00 02:20:47	Glycol-Pump	RESET
01 16:11:48	Reactor	RESET
01 16:11:48	SteamReformer	RESET
06 08:43:44	Compressor	RESET

Total Flows

0,4	F1 Compressor	RESET
1,6	F2 Überströmer	RESET

Status Report

Data Logging in sec
0

Path - Status
C:\Dokumente und Einstellungen\Messen-GULC05\Eigene Dateien\Messdaten

Figure 3.26: Screenshot of detail tab „Statistics”

4 Pilot plant operation

4.1 Basic information

In the process description following on the next pages, the status of the different measurement and control equipment is explained with the following definitions:

- active: the equipment is in on position
- inactive: the equipment is in standby/switch-off position
- automatically: the equipment is controlled by the PLC
- manually: the equipment is controlled by the operator
- opened: the equipment is in the open position
- closed: the equipment is in the closed position

The definition of the alarm set points for pressure, temperature and CO control can be found in Table 4.1. A deviation from normal conditions, which results in values close to the MAS limits, causes a yellow alert. A deviation from normal conditions, which results in values close to the design limits of the pilot plant, causes a red alert. A yellow alert leads to a shut-down of the pilot plant; a red alert leads to an emergency shut-down of the plant. The values for the yellow alert can be modified in LabView in contrast to the values for the red alert, which are hard-coded.

Alarm type	Description	Deviation from normal conditions	Alarm level
HH	high high alarm	SP + deviation close to design limits	red alert
H	high alarm	SP + deviation close to MAS limits	yellow alert
-	process value	SP	set point
L	low alarm	SP - deviation close to MAS limits	yellow alert
LL	low low alarm	SP - deviation close to design limits	red alert

Table 4.1: Definition of the alarm set points

4.2 Process description

For the MAS a slip stream of the synthesis gas from the CHP Güssing is taken downstream from the gas cleaning system. The synthesis gas is piped to the MAS pilot plant over a heated pipe, which supplies all plants operated in the pilot plant station. Alternative for starting or shut downs all pilot plants can be operated with nitrogen, also supplied by the biomass CHP.

At first, the synthesis gas (respectively N_2) passes through a 2-way ball valve with a pneumatic actuator at the entrance of the pilot plant. This actuator is run by compressed-air over a 5/2-way solenoid valve. After entering the plant, the synthesis gas flows into the steam reformer. There steam is added using a peristaltic pump as well as a 2/2-way solenoid valve. In the steam reformer the gas is heated up to approx. 900 ℃. The function of the steam reformer is to convert hydrocarbons into H_2 and CO and so to increase the H_2- and CO -content of the gas to reach a H_2/CO-ratio of approx. 2.

After steam reforming the synthesis gas flows through a cooling pipe to the glycol scrubber. The purpose of the scrubber is to remove the water content from the syngas. To keep the glycol-water ratio constant, fresh glycol has to be added and the used glycol has to be discharged. For these purposes a peristaltic pump and two 2/2-way solenoid valves were installed. In addition, a heat exchanger is mounted to reach the requested temperature of about 3 ℃.

Next the dry synthesis gas flows to the high-pressure compressor, where it is compressed to pressures between 90 and 300 bar.

Then the compressed syngas pours into the MAS reactor, where the gas is heated up to temperatures between 280 and 320 ℃. The reactor is designed as a fixed bed reactor filled with an alkali-doped MoS_2 based catalyst. In the MAS reactor numerous reactions takes place to produce a mixed alcohols fuel.

After the MAS reactor, the gas flows through the condenser, where it is cooled down to approx. 10 ℃. At the bottom of the condensation pipe, the mixed alcohols can be drawn via a high-pressure needle valve. The non-reacted tail gas leaves the condenser at the top.

The tail gas goes through an expansion valve in order to relieve pressure to atmospheric pressure. The expansion valve is designed as a spring-loaded overflow valve. The inlet pressure is continuously adjustable.

Finally, the tail gas passes through a 3-way ball valve with a pneumatic actuator at the exit of the pilot plant. Also in this case the actuator is run by compressed-air over a 5/2-way solenoid valve, as well as at the syngas inlet. Depending on whether the CHP plant is working or not, the valve opens the tail gas pipe or the blow off pipe. The tail gas pipe goes back to the CHP, where the gas is burned in the combustion zone. The blow off pipe goes to an emergency chimney, where the gas is discharged to atmosphere.

4.3 Modes of operation

4.3.1 Start-up

4.3.1.1 Description of operation mode

Prior to starting up the MAS pilot plant, it has to be checked if all preconditions for a start-up are complied with. If so, each section is started up to reach the expected process conditions as quickly as possible.

4.3.1.2 Inlet & outlet pipes

Preconditions

- CHP release on
- CHP syngas valve open
- CHP tail gas valve open
- no signal errors
- all TI and TIC active
- all PI and PIC active
- RV1 manually opened at desired pressure
- RV2 manually opened at desired pressure
- BV-S1 manually opened
- BV-S2 manually opened
- V3 and BV-S3 automatically closed
- BV-S4 manually opened
- V3 automatically closed
- V6 and BV-S16 automatically in blow-off pipe position
- BV-S17 manually opened
- BV-S18 manually opened
- BV-S19 manually opened
- BV-S20 manually closed
- BV-S21 manually opened
- BV-S22 manually opened
- V7 and BV-S23 automatically opened at desired position
- BV-P6 manually closed
- P4 manually on
- H1 manually on

Process description

- V3 automatically opened
- V6 and BV-S16 automatically in blow-off pipe position

4.3.1.3 Steam Reformer

Preconditions

- no signal errors
- all TI and TIC active
- all PI and PIC active
- BV-P1 manually opened
- V1 automatically closed
- P1 automatically off

Process description

- H2 - heating-up to desired temperature
- H3 - heating-up to desired temperature
- H4 - heating-up to desired temperature
- H5 - heating-up to desired temperature
- H6 - heating-up to desired temperature

4.3.1.4 Scrubber

Preconditions

- no signal errors
- all TI and TIC active
- all PI and PIC active
- LIC active
- BV-S5 manually opened
- BV-S6 manually opened
- BV-S7 manually closed
- BV-P2 manually opened
- BV-P3 manually opened
- BV-P4 manually closed
- V4 automatically closed
- V5 automatically closed
- P2 automatically off
- P3 manually off

Process description

- P3 manually on

4.3.1.5 Compressor

Preconditions

- no signal errors
- all TI and TIC active
- all PI and PIC active
- compressor switchboard on
- BV-S8 manually opened
- BV-S9 manually opened
- BV-S10 manually closed
- BV-S11 manually opened
- BV-S12 manually opened
- NV2 manually opened at desired position

Process description

- compressor automatically on

4.3.1.6 MAS reactor & condenser

Preconditions

- no signal errors
- all TI and TIC active
- all PI and PIC active
- NV2 manually closed

Process description

- H7 - heating-up to desired temperature
- H8 - heating-up to desired temperature
- H9 - heating-up to desired temperature
- H10 - heating-up to desired temperature

4.3.1.7 Expansion

Preconditions

- no signal errors
- all TI and TIC active
- all PI and PIC active
- RV3 manually opened at desired pressure
- BV-S13 manually opened
- BV-S14 manually opened
- BV-S15 manually closed
- BV-P5 manually closed

4.3.2 Normal operation

4.3.2.1 Description of operation mode

In the normal operation mode, the MAS pilot plant is operated with syngas at the desired test parameters.

4.3.2.2 Inlet & outlet pipes

The syngas from the CHP enters the MAS pilot plant by passing valve BV-S3, which is actuated by solenoid valve V2 (operated with compressed air). The inlet pipe is equipped with a pressure sensor (M1) to avoid overload pressures higher than 200 mbar. The syngas pipe is heated up to approx. 70 ℃ to avoid condensation of aromatic compounds. The heating element H2 is controlled by thermocouple T2.

After expansion the tail gas passes valve BV-S15 towards the tail gas pipe back to the CHP. BV-S15 is actuated by solenoid valve V6 (operated with compressed air).

4.3.2.3 Steam reformer

As a first process step, the syngas flows into the steam reformer, where it is heated up to about 900 ℃. The heating elements H3, H4, H5 and H 6 are controlled by the thermocouples T14, T15, T16 and T17. For the purposes of an exact temperature measurement over the total length of the reformer, further thermocouples were installed (T3 - T13). The syngas passes through the preheating pipe from top to bottom and through the reaction pipe bottom-up.

For the steam addition high-purity water is pumped to the vaporiser part of the water pipe. Pump P1 and valve V1 are operated automatically by the PLC. The steam addition is started 5 minutes before switching from nitrogen to syngas mode to ensure that enough vapour is in the reformer.

4.3.2.4 Scrubber

After steam reforming, the syngas is cooled down to approx. 80 ℃ using an air heat exchanger. The temperature at the scrubber entrance is controlled by thermocouple T18. In order to avoid pressure higher than 200 mbar in the scrubber, a pressure sensor (M2) is mounted.

The addition of the fresh glycol is effected via pump P2 and valve V4. By means of previously determined time intervals fresh glycol is pumped into the scrubber. More precisely, P2 and V4 are alternately active/open or inactive/closed for a certain time.

The drain of the used glycol is controlled by level gauge L1. When L1 is active (i.e. the scrubber is filled up to approx. 80 %), valve V5 is open as long as the level is decreased to approx. 60 % of the scrubber volume. After one drain loop V5 is closed until L1 is active again.

4.3.2.5 Compressor

After the scrubber, the syngas flows through a gas meter (F1) to the compressor. The gas meter is mounted for measuring the volume flow before the MAS reaction. Previous to the compressor, a pressure sensor (M3) and a thermocouple (T19) are installed to assure observing the technical specifications of the compressor. After compression a bypass is installed to adjust the desired volume flow.

4.3.2.6 MAS reactor & condenser

Next the compressed syngas flows into the MAS reactor. Previous to the reactor, a pressure sensor (M4) is mounted. In addition a thermocouple (T20) is installed to control the heating element (H7) previous to the reactor. In the piping before the MAS reactor the syngas is heated up to temperatures between 280 and 320 °C, according to the required experiments. The heating elements H8, H9 and H10 are controlled by the thermocouples T21, T22 and T23. In order to measure temperature over the total length of the reformer, further thermocouples were installed (T24 – T26). The syngas flows through the reactor from top to bottom.

After the reactor the reacted syngas flow to the upper part of the condenser. Between reactor and condenser a pressure sensor (M5) and a thermocouple (T27) are installed. In the condenser the reacted gases are cooled down to about 10 °C to assure a total condensation of the mixed alcohols. The condensed alcohols are removed from the condenser over a high-pressure needle valve. The tail gas leaves the condenser at the top.

4.3.2.7 Expansion

As last process step, the tail gas passes through the overflow valve (RV-3), where it is expanded to atmospheric pressure. Pressure sensors are installed before and after the overflow valve. On the one hand, an analogue measuring instrument is installed to adjust the inlet pressure of the overflow valve, which is equivalent to the operating pressure of the compressor. On the other hand, two digital measuring instruments are installed to control the pressure before and after the expansion valve over the PLC. After the expansion, the gas flows through another gas meter (F2), where the volume flow at the exit of the pilot plant (after the MAS reaction) is measured.

4.3.3 Shut-down

4.3.3.1 Description of operation mode

The MAS pilot plant switches to the shut-down mode, if one of the following cases occurs:

- there is a plant shutdown in the CHP,
- the syngas system pressure from the CHP is too low, or
- a pressure, temperature or CO limit (yellow alert) is exceeded.

The shut-down mode equates to the normal operation mode with the distinction, that the plant is operated with nitrogen. The pressure and temperature parameters are the same like in the normal operation mode.

In order to stop the plant due to maintenance work or at the end of a test run, the plant is switched over to the shut-down mode. In this mode, the pilot plant is purged with nitrogen, while the heating elements cool down and the pressure decreases. When the pressures and temperatures achieve atmospheric conditions, the plant can be switched off.

4.3.3.2 Inlet & outlet pipes

- V2 and BV-S3 automatically closed
- V3 automatically opened
- after 15 minutes: V6 and BV-S16 automatically in blow-off pipe position
- H1 manually off

4.3.3.3 Steam Reformer

- H2 manually switched off
- H3 manually switched off
- H4 manually switched off
- H5 manually switched off
- H6 manually switched off
- P1 automatically switched off
- V1 automatically closed

4.3.3.4 Scrubber

- V4 automatically closed
- V5 automatically closed
- P2 automatically switched off
- P3 automatically switched off

4.3.3.5 Compressor

- compressor automatically switched off
- BV-S12 manually closed

4.3.3.6 MAS reactor & condenser

- H7 manually switched off
- H8 manually switched off
- H9 manually switched off
- H10 manually switched off

4.3.4 Emergency shut-down

4.3.4.1 Description of operation mode

The MAS pilot plant switches to the emergency shut-down mode, if one of the following cases occurs:

- one of the two emergency stop switches is pushed,
- a power failure occurs, or
- a pressure, temperature or CO maximum limit (red alert) is exceeded.

In the case of a pushed emergency stop switch, all pumps and heating elements are not working. In case of a power failure, the total electrical equipment is not working, because there is no emergency backup generator installed. For this reason, every valve is carried out in the respectively applicable safety position in the event of power failure (either currentless opened or currentless closed).

4.3.4.2 Inlet & outlet pipes

- V2 and BV-S3 automatically/currentless closed
- V3 automatically/currentless opened
- V6 and BV-S16 automatically/currentless in blow-off pipe position
- H1 automatically off

4.3.4.3 Steam Reformer

- H2 automatically switched off
- H3 automatically switched off
- H4 automatically switched off
- H5 automatically switched off
- H6 automatically switched off
- P1 automatically switched off
- V1 automatically/currentless closed

4.3.4.4 Scrubber

- V4 automatically/currentless closed
- V5 automatically/currentless closed
- P2 automatically switched off
- P3 automatically switched off

4.3.4.5 Compressor

- compressor automatically switched off
- BV-S12 manually closed

4.3.4.6 MAS reactor & condenser

- H7 automatically switched off
- H8 automatically switched off
- H9 automatically switched off
- H10 automatically switched off

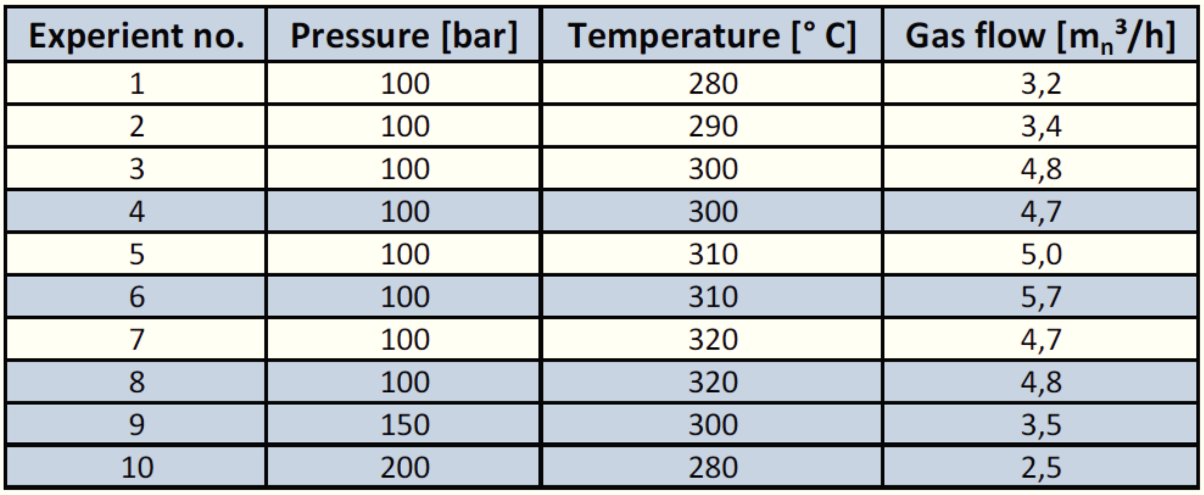
5 Results and discussion

5.1 Overview of experiments

5.1.1 Description of the experiments

The experiments on the MAS pilot plant were done with a MoS_2 catalyst. There are various test parameters which influences the MAS reactions. To simplify the complex chain of the synthesis, in this work only the influence of temperature and pressure on the MAS was investigated. The product distribution of the mixed alcohols, as well as the productivity of the MAS were further determined.

In the course of the first test series on the MAS pilot plant 10 experiments were carried out as can be seen in Table 5.1. The experiments no. 4, 6, 8, 9 and 10 will be further discussed in the subsequent sections.



Experient no.	Pressure [bar]	Temperature [° C]	Gas flow $[m_n^3/h]$
1	100	280	3,2
2	100	290	3,4
3	100	300	4,8
4	100	300	4,7
5	100	310	5,0
6	100	310	5,7
7	100	320	4,7
8	100	320	4,8
9	150	300	3,5
10	200	280	2,5

Table 5.1: Experimental setting data

5.1.2 Experiment no. 4

In experiment no. 4 the plant was run for two hours at a pressure of 100 bar and a temperature of 300 ℃. The volume flow amounts to a pprox. 4,7 m_n^3/h at the entrance of the pilot plant. In the contemplated measurement period approx. 410 ml of mixed alcohols were produced.

Figure 5.1 plots the pressure and temperature profiles of experiment no. 4. In the primary X-axis (left) the measured temperatures in ℃ can b e read. The temperatures of the heating elements ("TH MAS_R") and the temperature of the reactor ("T MAS_R") were measured respectively at the top, in the middle and at the bottom of the reactor. In the secondary X-axis (right) the measured pressures in bar can be read.

Hence, it can be seen that the compressor works very steady. The pressure peaks follow from the recurrent working condensate outlet device of the compressor. Moreover, the temperature profiles are very constant over the experiment time. With the exception of the temperature at the top of the MAS reactor (see "T MAS_R up" in Figure 5.1) all temperatures hit the requested temperature of 300 ℃. The reason s for this purpose are problems with assembling the respective thermocouple. This error in measurement occurs in every experiment of the first test series.

In addition it can be observed, that there is a difference between the temperature of the heating element and the temperature of the reactor at the bottom of the reactor. This temperature difference of approx. 12 ℃ results fro m the produced heat from the highly exothermic MAS reaction

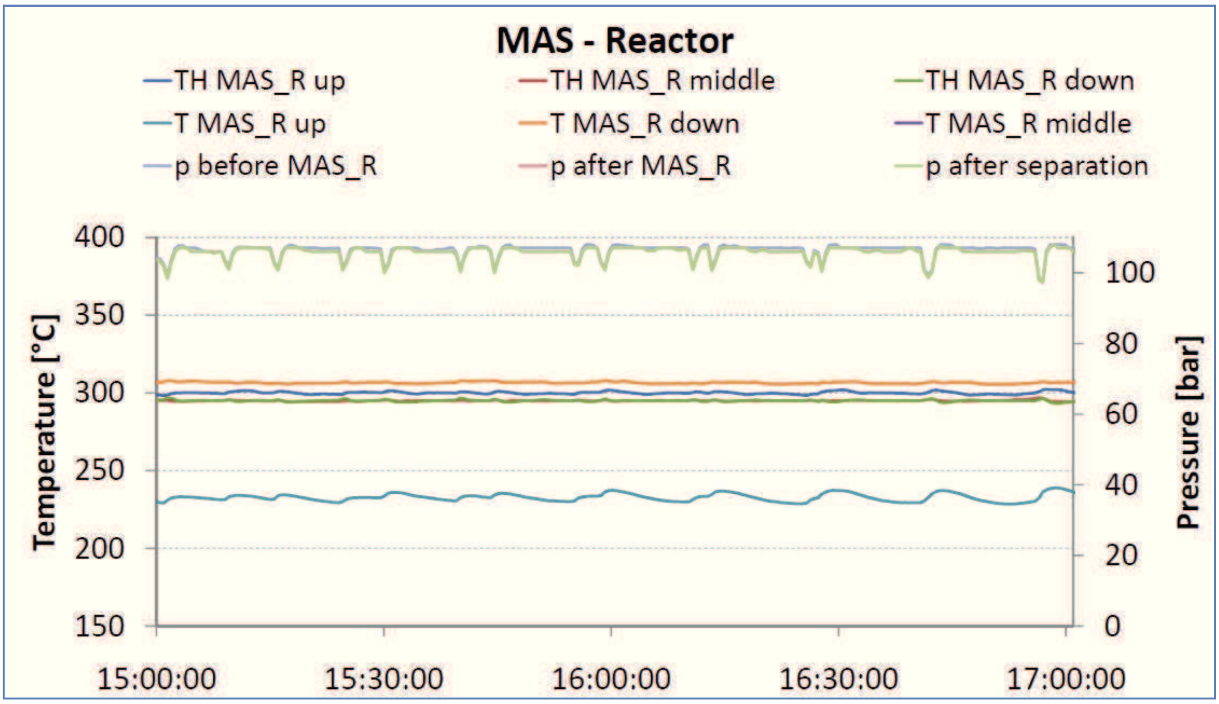


Figure 5.1: Test conditions for experiment no. 4 (100 bar, 300 ℃, 4,7 m_n^3/h)

5.1.3 Experiment no. 6

In experiment no. 6 the plant was run for two hours at a pressure of 100 bar and a temperature of 310 ℃. The volume flow amounts to approx. 5,7 m_n^3/h at the entrance of the pilot plant. In the contemplated measurement period approx. 360 ml of mixed alcohols were produced.

As noted above, the pressure and temperature profiles were also very steady at the desired test parameters (see Figure 5.2). Also in this experiment it can be clearly seen from the figure, that there is a difference between the temperature of the heating element and the temperature of the reactor at the bottom of the reactor. In this case, the temperature difference, due to the highly exothermic MAS reaction, amounts to approx. 12 ℃.

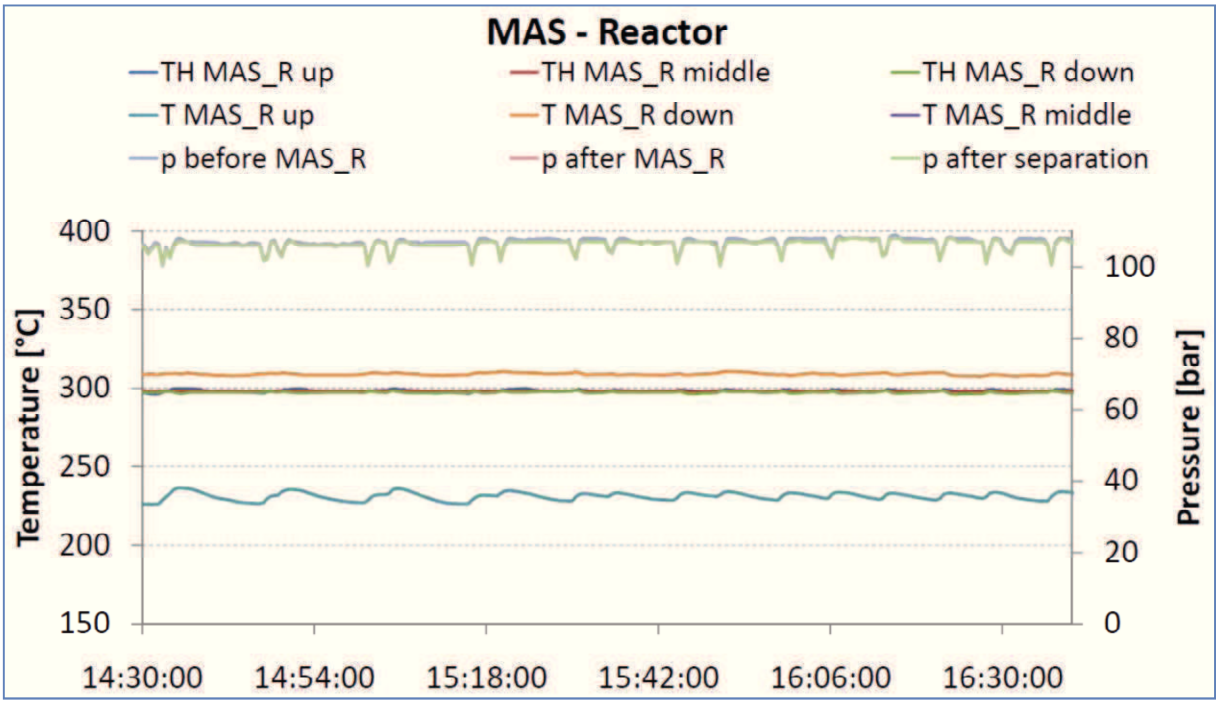


Figure 5.2: Test conditions for experiment no. 6 (100 bar, 310 ℃, 5,7 m_n^3/h)

5.1.4 Experiment no. 8

In experiment no. 8 the plant was run for one hour at a pressure of 100 bar and a temperature of 320 ℃. The volume flow amounts to approx. 4,8 m_n^3/h at the entrance of the pilot plant. In the contemplated measurement period approx. 215 ml of mixed alcohols were produced.

Very steady pressure and temperature profiles at the desired test parameters can be found in Figure 5.3 too. In this experiment there is also a difference in temperature at the bottom of the reactor, as already mentioned above. The difference between the temperature of the heating element and the temperature of the reactor at the bottom is about 12 ℃, which is equal to the two other experiments at 100 bar.

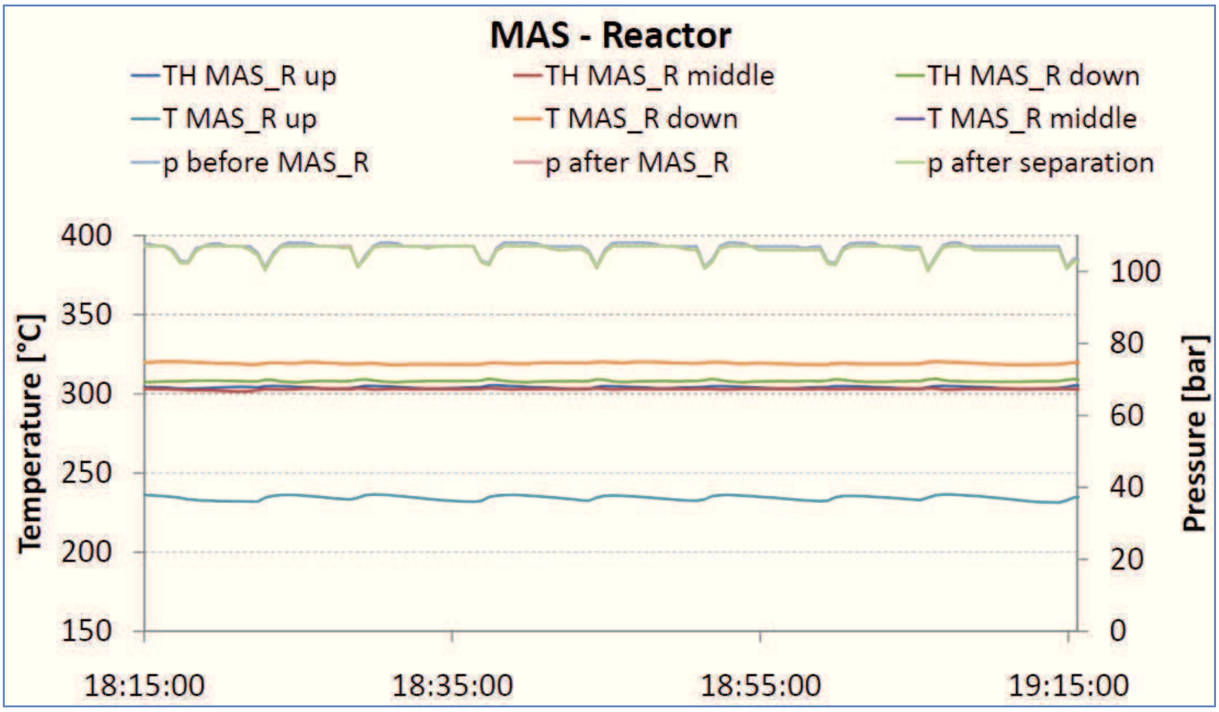


Figure 5.3: Test conditions for experiment no. 8 (100 bar, 320 ℃, 4,8 m_n^3/h)

5.1.5 Experiment no. 9

In experiment no. 9 the plant was run for two hours at a pressure of 150 bar and a temperature of 280 ℃. The volume flow amounts to approx. 3,5 m_n^3/h at the entrance of the pilot plant. In the contemplated measurement period approx. 220 ml of mixed alcohols were produced.

From Figure 5.4 it can be seen that the pressure and temperature profiles were rather steady at the desired test parameters. Similar to the experiments above-mentioned, a difference in temperature between the heating element and the reactor at the bottom can be seen from the figure. At a pressure of 150 bar, the temperature difference, due to the highly exothermic MAS reaction, amounts to approx. 10 ℃. Hence, the temperature difference is marginally lower than those of the experiments operated with 100 bar.

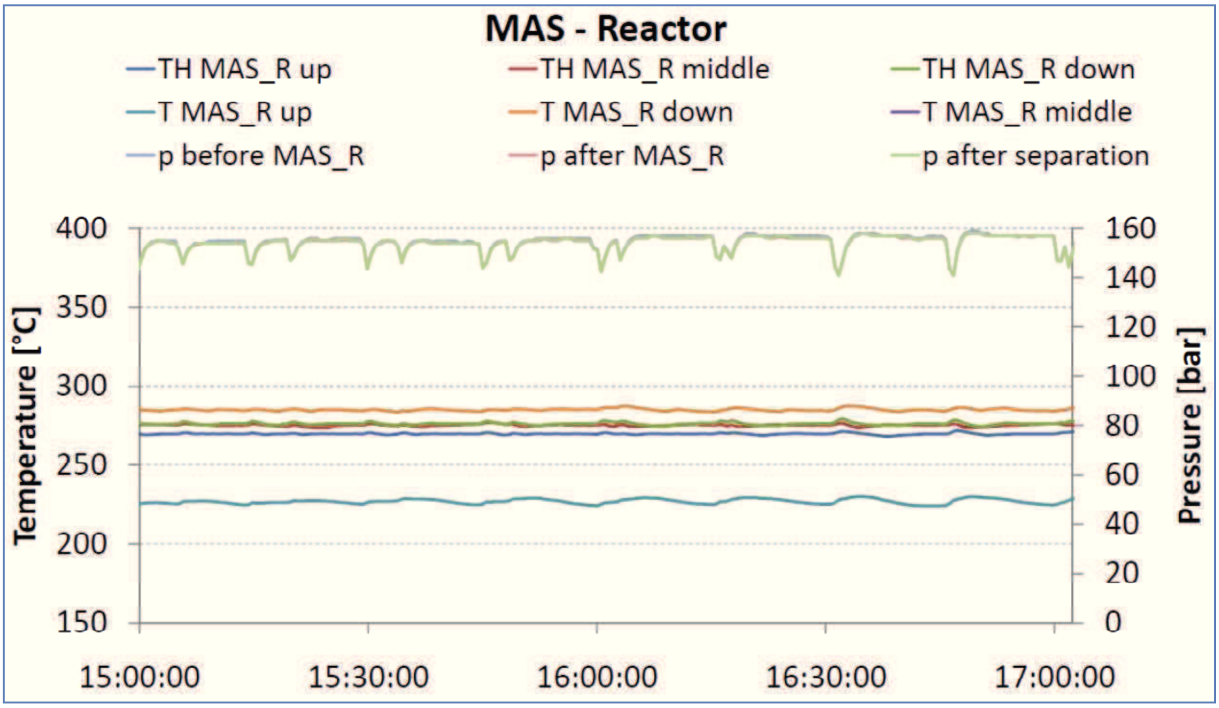


Figure 5.4: Test conditions for experiment no. 9 (150 bar, 280 ℃, 3,5 m_n^3/h)

5.1.6 Experiment no. 10

In experiment no. 10 the plant was run for approx. five hours at a pressure of 200 bar and a temperature of 280 ℃. The volume flow amounts to a pprox. 2,5 m_n^3/h at the entrance of the pilot plant. In the contemplated measurement period no alcohols were produced. Due to problems with temperature controlling at this high pressure, a steady test procedure was not possible.

Figure 5.5 shows the pressure and temperature profiles of experiment no. 10. Like in the other experiments, a difference in temperature between the heating element and the reactor at the bottom can be found in the figure. At 200 bar, the temperature difference, due to the highly exothermic MAS reaction, amounts to approx. 7 ℃. Hence, the temperature difference is marginally lower than those of the experiments operated with 150 bar.

It can be observed that by exceeding a temperature of approx. 280 ℃ a thermal runaway of the reactor occurred. To avoid a total runaway of the reactor the plant was run with nitrogen to cool down the reactor. Additionally the air cooling of the reactor was started. After the temperatures stabilised again at approx. 280 ℃, th e plant was run again with synthesis gas. By exceeding this temperature, the reactor started to run away again. At this time the pilot plant switched over to nitrogen because of technical problems of the CHP Güssing.

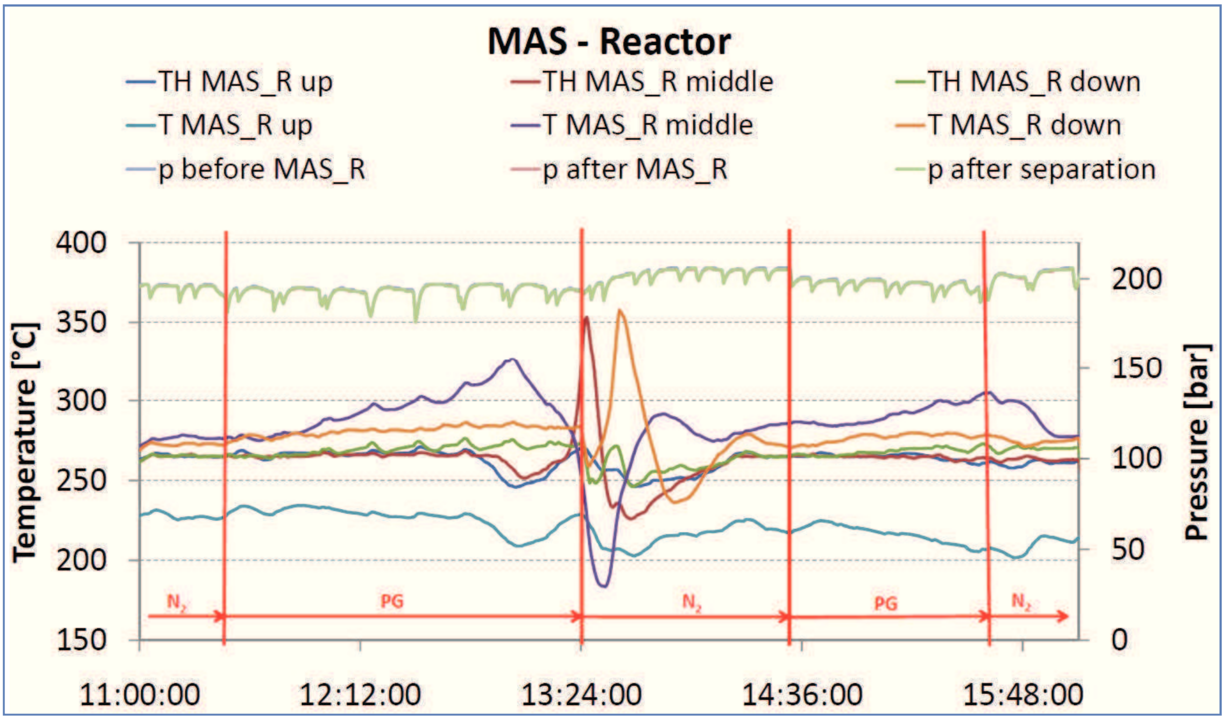


Figure 5.5: Test conditions for experiment no. 10 (200 bar, 280 ℃, 2,5 m_n^3/h)

5.2 Key results

5.2.1 Gas analysis

5.2.1.1 Analysis method

The composition of the syngas is determined by discontinuous measurements using gas chromatography. The syngas is filled in plastic bags from the test points and then injected into the gas chromatograph (GC) Clarus® 500 from "Perkin Elmer". The GC is equipped with three different columns – 2 apolar (Porapak®) and 1 molar sieve, connected with 2 automated valves and an injection loop of 500 µl. As carrier gas helium is used.

Two types of detectors are used:

- FID ... flame ionisation detector
  detection of hydrocarbons CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6
- TCD ... thermal conductivity detector
  detection of the permanent gases: O_2, N_2, CO, CO_2

Primarily, the syngas which has to be analysed, is entering in the first Porapak® column for pre-separation. After this, CO_2 and the hydrocarbons are going to the second Porapak® column, while O_2, H_2, N_2, CO and CH_4 are going to the molar sieve. The components are first detected by the TCD at 200 °C and after that by the FID at 300 °C.

The hydrogen concentration is calculated as 100 minus the sum of the gas concentration given by the two detectors.

Equipment:

- GC: Clarus® 500 "Perkin Elmer"
- Injection: manual
- Detectors: FID and TCD
- Columns: 6 feet Porapak® Q 50/80 Mesh
  10 feet Porapak® N 50/80 Mesh
  10 feet Molecular Sieve 5 Å
- Carrier: A – 23 ml/min He 5.0
  B – 30 ml/min He 5.0

Conditions:

- Oven: Initial – 45 °C, hold 20 min;
  Ramp 1 – 4 °C/min, from 45 °C to 100 °C, hold 5 min;
  Ramp 2 - 15 °C/min, from 100 °C to 180 °C, hold 45 min
- Injectors: A – 80 °C
  B – 80 °C
- Detectors: FID – 300 °C
  TCD – 200 °C

Calibration:

The calibration is realized with a calibration gas which includes 7 components:

- CH_4 – 10.010 %
- C_2H_4 – 3.010 %
- C_2H_6 – 0.497 %
- C_3H_8 – 0.493 %
- CO – 25.100 %
- CO_2 – 19.920 %
- N_2 – 2.007 %
- H_2 – 38.963 %

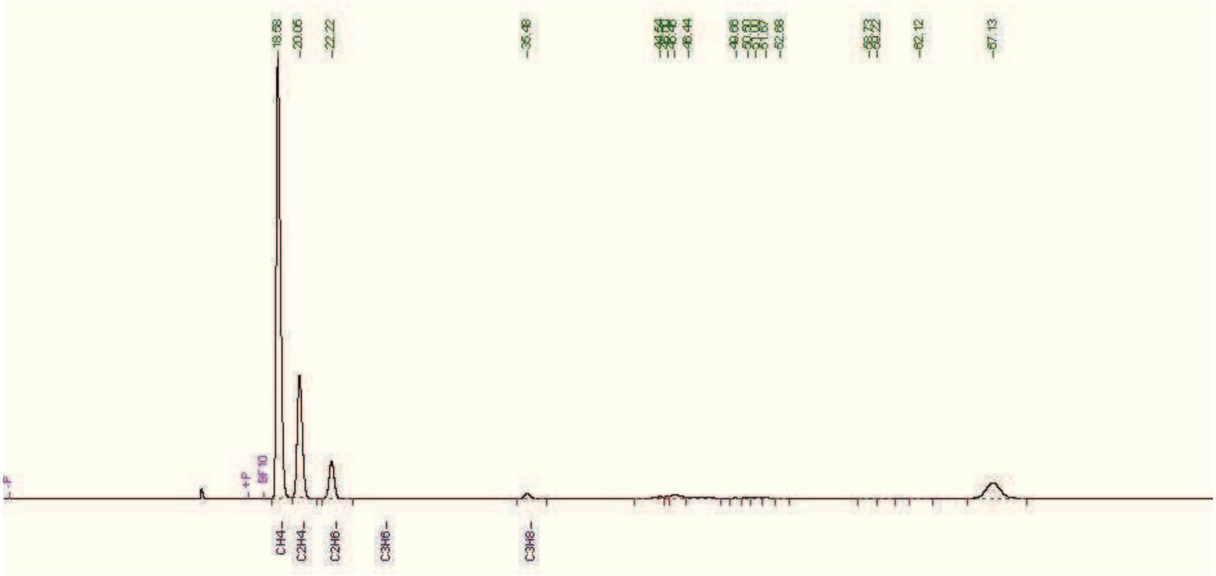


Figure 5.6: Chromatogram of gas composition on FID

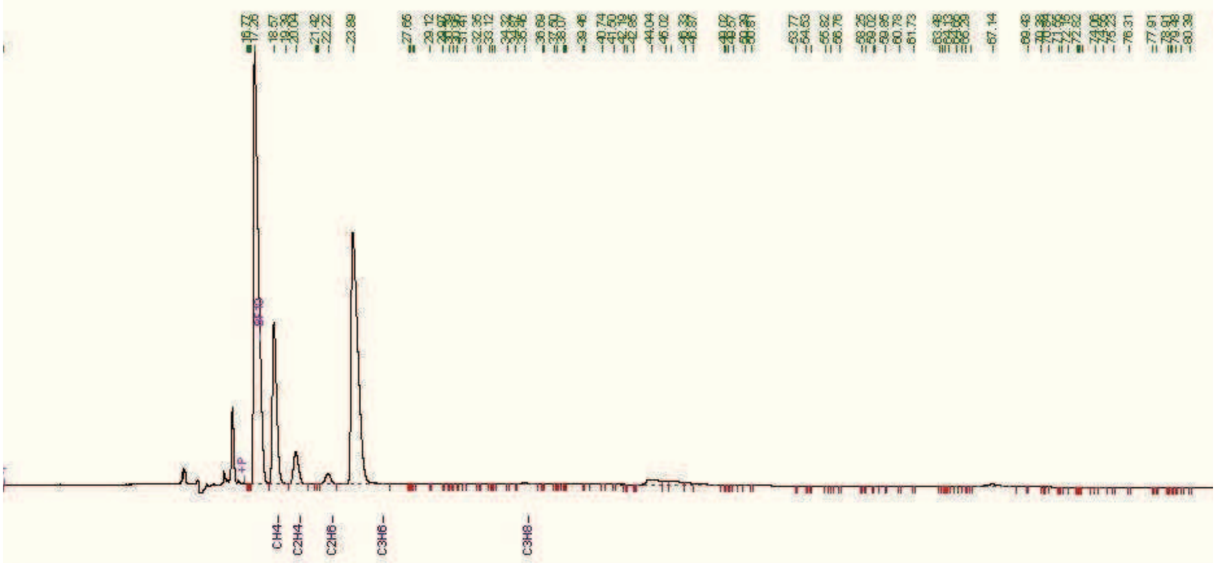


Figure 5.7: Chromatogram of gas composition on TCD

5.2.1.2 Analytical results

The determination of the gas composition was carried out for an experimental period of six days. The analysis comprises the gas components H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, O_2 and N_2. In Table 5.2, the results of the gas analyses are summarised.

Sample	Gas composition [vol%]									
	H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	O_2	N_2
Experiments 2011-05-18										
SG after scrubber	37.1697	23.6492	22.3297	10.8351	3.5989	0.2655	0.2392	0.0336	0.2671	1.6120
Sample 1	34.6338	19.1240	16.3415	9.3324	2.2490	0.3533	0.0000	0.0300	0.0034	17.9326
Sample 2	36.1351	21.9814	24.7574	11.5031	1.8439	0.7398	0.0000	0.0747	0.0657	2.8989
Sample 3	36.3854	21.7896	25.4543	11.6763	1.8636	0.7549	0.0000	0.0710	0.0521	1.9528
Sample 4	33.3771	19.8039	27.8658	13.3717	0.8931	1.3088	0.0000	0.2108	0.0641	3.1047
Experiments 2011-06-20										
SG after scrubber	38.7221	22.2022	24.5958	9.0552	2.9320	0.2296	0.1458	0.0268	0.1390	1.9515
Sample 1	37.5751	20.7901	26.7722	8.9092	2.1515	0.3531	0.0000	0.0331	0.2151	3.2006
Sample 2	34.8264	22.8662	26.7957	9.6779	2.5067	0.4474	0.0000	0.0467	0.1149	2.7181
Sample 3	36.9004	22.6546	26.9029	9.9182	0.0000	0.5727	0.0000	0.0619	0.1695	2.8198
Experiments 2011-06-21										
SG after scrubber 1	36.9988	21.9420	24.3334	8.7560	2.8608	0.2521	0.1471	0.0288	0.2622	4.4188
SG after scrubber 2	38.8307	21.6114	24.6597	8.6264	2.8498	0.2482	0.1499	0.0279	0.2611	2.7349
Sample 1	36.4581	22.2956	25.4880	9.2399	2.3883	0.4602	0.0000	0.0001	0.2397	3.4301
Sample 2	37.2352	22.2219	25.4596	9.2828	2.4233	0.4593	0.0000	0.0431	0.0980	2.7768
Sample 3	36.6982	22.2555	25.2329	9.5990	2.3804	0.5062	0.0000	0.0475	0.2704	3.0099
Experiments 2011-06-22										
SG after scrubber	41.0458	21.9295	23.8049	8.2770	2.7194	0.2437	0.1387	0.0230	0.1557	1.6623
Sample 1	38.4931	21.7225	24.8087	8.4270	2.3563	0.4050	0.0000	0.0370	0.3602	3.3902
Sample 2	39.1881	20.8769	24.7203	8.2084	2.2726	0.4034	0.0000	0.0347	0.0782	4.2174
Experiments 2011-06-28										
SG after scrubber	41.7285	20.5879	22.6574	7.4334	2.3567	0.2399	0.0977	0.0240	0.5769	4.2976
Sample 1	41.1809	21.1133	23.7630	7.7023	1.9856	0.3612	0.0000	0.0296	0.4480	3.4161
Sample 2	41.3903	21.1075	24.3711	8.1067	2.0889	0.3838	0.0000	0.0316	0.1525	2.3676
Experiments 2011-06-29										
SG after scrubber	40.2920	20.7769	23.5580	8.3327	2.6829	0.2562	0.1231	0.0287	0.4845	3.4650

Table 5.2: Summary of the gas analysis

For each experiment, gas samples were taken after water condensation ("SG after scrubber") and after expansion ("Sample"), as can be seen from Figure 5.8. The test point before steam reforming was not used due to the fact that the steam reformer was not operated during this work.

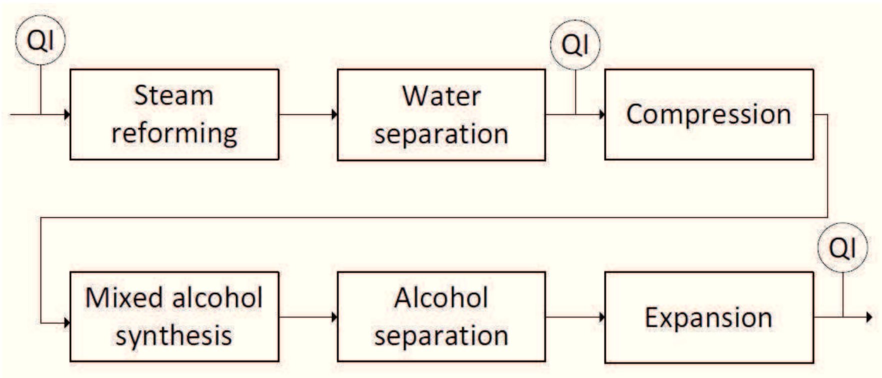


Figure 5.8: Location of test points

5.2.2 Sulphur analysis

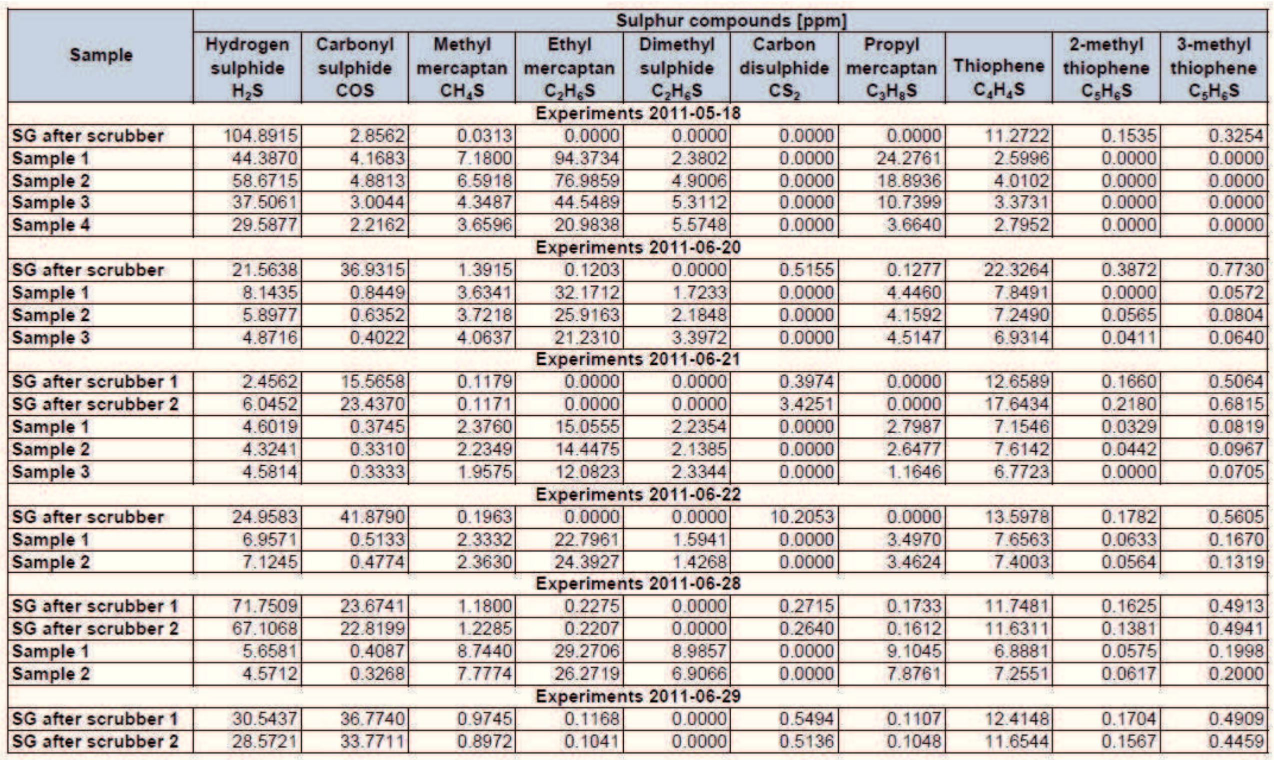
5.2.2.1 Analysis method

The analysis of the sulphur compounds in the syngas is determined by discontinuous measurements similarly to the gas analysis. Also in this case the GC Clarus® 500 was used, though with a different detector. For sulphur analysis, a SCD (sulphur chemiluminescence detector) with helium as carrier gas was utilised.

5.2.2.2 Analytical results

The measurement of the sulphur compounds was carried out for the same experimental period like for the gas analysis. The analysis comprises the sulphur compounds hydrogen sulphide, carbonyl sulphide, methyl mercaptan, ethyl mercaptan, dimethyl sulphide, carbon disulphide, propyl mercaptan, thiophene, 2-methyl thiophene and 3-methyl thiophene.

The results of the gas analysis are summarised in Table 5.3.



Sample	Sulphur compounds [ppm]									
	Hydrogen sulphide H_2S	Carbonyl sulphide COS	Methyl mercaptan CH_4S	Ethyl mercaptan C_2H_6S	Dimethyl sulphide C_2H_6S	Carbon disulphide CS_2	Propyl mercaptan C_3H_8S	Thiophene C_4H_4S	2-methyl thiophene C_5H_6S	3-methyl thiophene C_5H_6S
Experiments 2011-05-18										
SG after scrubber	104.8915	2.8562	0.0313	0.0000	0.0000	0.0000	0.0000	11.2722	0.1535	0.3254
Sample 1	44.3870	4.1683	7.1800	94.3734	2.3802	0.0000	24.2761	2.5996	0.0000	0.0000
Sample 2	58.6715	4.8813	6.5918	76.9859	4.9006	0.0000	18.8936	4.0102	0.0000	0.0000
Sample 3	37.5061	3.0044	4.3487	44.5489	5.3112	0.0000	10.7399	3.3731	0.0000	0.0000
Sample 4	29.5877	2.2162	3.6596	20.9838	5.5748	0.0000	3.6640	2.7952	0.0000	0.0000
Experiments 2011-06-20										
SG after scrubber	21.5638	36.9315	1.3915	0.1203	0.0000	0.5155	0.1277	22.3264	0.3872	0.7730
Sample 1	8.1435	0.8449	3.6341	32.1712	1.7233	0.0000	4.4460	7.8491	0.0000	0.0572
Sample 2	5.8977	0.6352	3.7218	25.9163	2.1848	0.0000	4.1592	7.2490	0.0565	0.0804
Sample 3	4.8716	0.4022	4.0637	21.2310	3.3972	0.0000	4.5147	6.9314	0.0411	0.0640
Experiments 2011-06-21										
SG after scrubber 1	2.4562	15.5658	0.1179	0.0000	0.0000	0.3974	0.0000	12.6589	0.1660	0.5064
SG after scrubber 2	6.0452	23.4370	0.1171	0.0000	0.0000	3.4251	0.0000	17.6434	0.2180	0.6815
Sample 1	4.6019	0.3745	2.3760	15.0555	2.2354	0.0000	2.7987	7.1546	0.0329	0.0819
Sample 2	4.3241	0.3310	2.2349	14.4475	2.1385	0.0000	2.6477	7.6142	0.0442	0.0967
Sample 3	4.5814	0.3333	1.9575	12.0823	2.3344	0.0000	1.1646	6.7723	0.0000	0.0705
Experiments 2011-06-22										
SG after scrubber	24.9583	41.8790	0.1963	0.0000	0.0000	10.2053	0.0000	13.5978	0.1782	0.5605
Sample 1	6.9571	0.5133	2.3332	22.7961	1.5941	0.0000	3.4970	7.6563	0.0633	0.1670
Sample 2	7.1245	0.4774	2.3630	24.3927	1.4268	0.0000	3.4624	7.4003	0.0564	0.1319
Experiments 2011-06-28										
SG after scrubber 1	71.7509	23.6741	1.1800	0.2275	0.0000	0.2715	0.1733	11.7481	0.1625	0.4913
SG after scrubber 2	67.1068	22.8199	1.2285	0.2207	0.0000	0.2640	0.1612	11.6311	0.1381	0.4941
Sample 1	5.6581	0.4087	8.7440	29.2706	8.9857	0.0000	9.1045	6.8881	0.0575	0.1998
Sample 2	4.5712	0.3268	7.7774	26.2719	6.9066	0.0000	7.8761	7.2551	0.0617	0.2000
Experiments 2011-06-29										
SG after scrubber 1	30.5437	36.7740	0.9745	0.1168	0.0000	0.5494	0.1107	12.4148	0.1704	0.4909
SG after scrubber 2	28.5721	33.7711	0.8972	0.1041	0.0000	0.5136	0.1048	11.6544	0.1567	0.4459

Table 5.3: Summary of the sulphur measurement

5.2.3 Product analysis

5.2.3.1 Analysis method

For the analysis of the MAS product, a method was applied in which the analysis of the alcohols C1-C5 as well as the aromatic compounds benzene and toluene were included.

Materials:

- methanol
- ethanol
- 1-propanol
- 1-butanol
- 1-pentanol
- benzene
- toluene
- distilled water

Equipment:

- GC: Clarus 500 “Perkin Elmer”
- Injection: manual
- Detectors: FID (for alcohols detection) and TCD (for water detection)
- Column: 10 feet Porapak N 50/80 Mesh
  6 feet Porapak Q 50/80 Mesh

- Carrier: A – 30 ml/min He 5.0
  B – 25 ml/min He 5.0

Conditions:

- Oven: Initial – 80 °C, hold 5 min;
  Ramp 1 – 5 °C/min, from 80 °C to 110 °C, hold 10 min;
  Ramp 2 – 15 °C/min, from 110 °C to 180 °C, hold 80 min
- Injectors: A – 150 °C
  B – 150 °C
- Detectors: FID – 300 °C
  TCD – 200 °C

Sample analysis:

1 µl of pure sample was injected in the A injector.

Calibration:

For calibration, a mixture of methanol, ethanol, propanol, butanol, pentanol, benzene, toluene and water was prepared (Table 5.4). For each component, the same volume of 200 µl was added and subsequently mixed well. From the mixture, 1 µl were injected directly in the GC, using injector A.

Calibration mixture	Volume of component [µl]	Density [mg/µl]	Mass [mg]
Methanol	200	0.7918	158.36
Ethanol		0.7890	157.80
Propanol		0.8034	160.68
Butanol		0.8100	162.00
Pentanol		0.8144	162.88
Benzene		0.8765	175.30
Toluene		0.8669	173.38
Water		1.0000	200.00
TOTAL	1600	0.8440	1350.40

Table 5.4: Composition of calibration mixture

For each volume of the mixture, volume, density and mass was calculated, as can be seen in Table 5.5.

	Volume of component injected	Density	Mass	FID Area	TCD Area
	µl	mg/µl	mg	µV*s	µV*s
Methanol	0.0375	0.7918	0.030	1246966	677516
Ethanol		0.789	0.030	1745273	639336
Propanol		0.8034	0.030	2396172	643727
Butanol		0.81	0.030	2546978	606814
Pentanol		0.8144	0.031	2500435	441499
Benzene		0.8765	0.033	4698757	643566
Toluene		0.8669	0.033	4483177	634602
Water		1	0.038	0	408766
TOTAL	0.3	0.844	0.253	19617758	4695826

Table 5.5: FID and TCD areas based on the chromatographic analysis

On the basis of the mass and the FID respectively TCD areas, for each component calibration curves have been established (see Figure 5.9 and Figure 5.10).

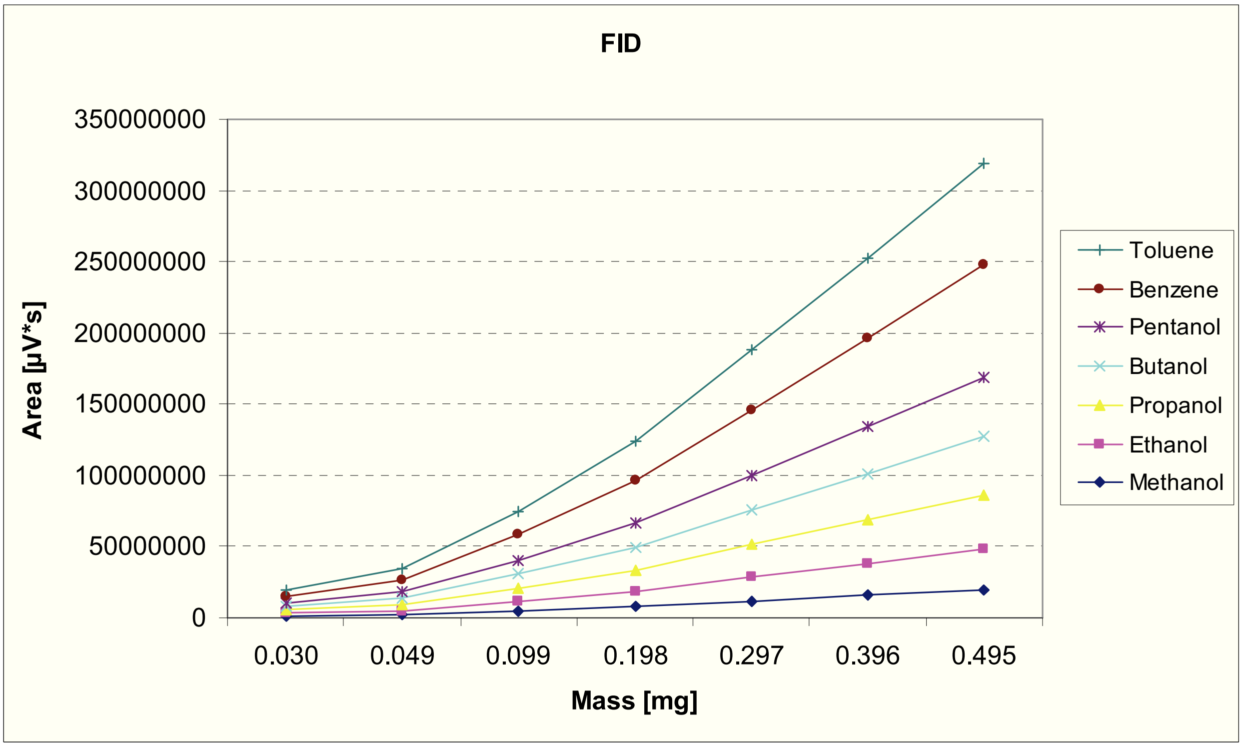


Figure 5.9: Calibration on the FID channel

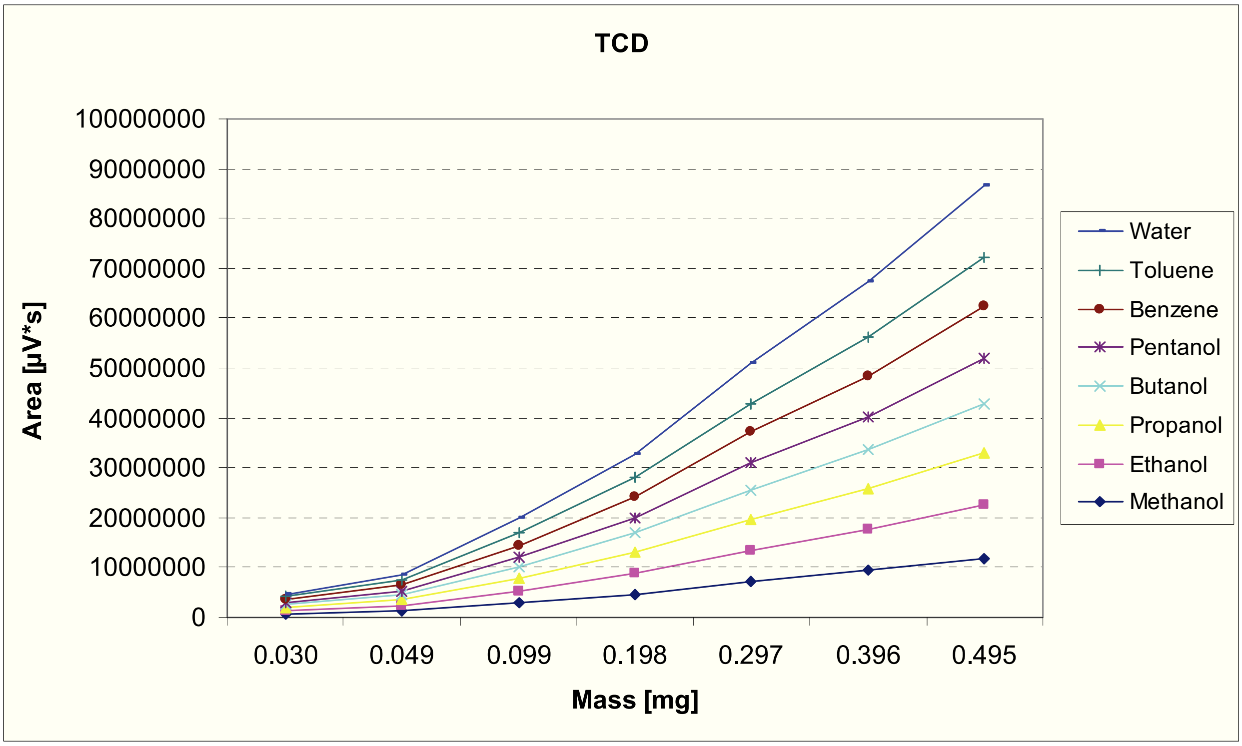
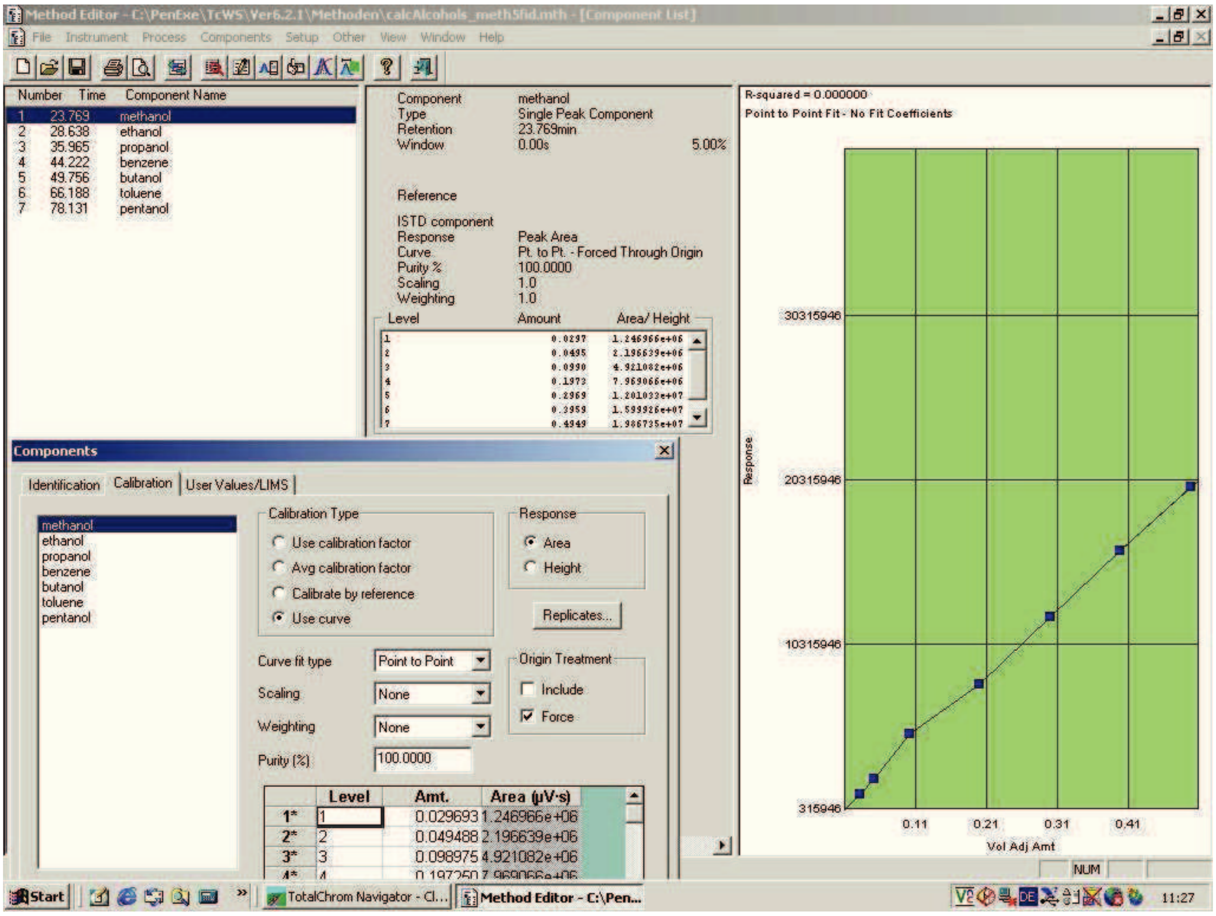


Figure 5.10: Calibration on the TCD channel

The calibration method for the two channels has been realised with the previous determined results. The calibration curves for the components have been made by point to point method and plotted using the software Origin for both FID and TCD. Figure 5.11 displays the calibration method for the FID channel. The same calibration method was carried out for the TCD channel (figure not shown).


Method Editor - C:\PenExe\TcWS\Ver6.2.1\Methoden\calcAlcohols_meth5fid.mth - [Component List]

Number	Time	Component Name
1	23.769	methanol
2	28.638	ethanol
3	35.965	propanol
4	44.222	benzene
5	49.756	butanol
6	66.188	toluene
7	78.131	pentanol

Component	methanol	
Type	Single Peak Component	
Retention	23.769min	
Window	0.00s	5.00%
Reference		
ISTD component		
Response	Peak Area	
Curve	Pt. to Pt. - Forced Through Origin	
Purity %	100.0000	
Scaling	1.0	
Weighting	1.0	

Level	Amount	Area/ Height
1	0.0297	1.246966e+06
2	0.0495	2.196639e+06
3	0.0990	4.921082e+06
4	0.1973	7.969066e+06
5	0.2969	1.201033e+07
6	0.3959	1.599926e+07
7	0.4949	1.986735e+07

Components

methanol
ethanol
propanol
benzene
butanol
toluene
pentanol

Calibration Type
○ Use calibration factor
○ Avg calibration factor
○ Calibrate by reference
● Use curve

Response
● Area
○ Height

Curve fit type: Point to Point
Scaling: None
Weighting: None
Purity (%): 100.0000

Origin Treatment
☐ Include
☑ Force

	Level	Amt.	Area (µV·s)
1*	1	0.029693	1.246966e+06
2*	2	0.049488	2.196639e+06
3*	3	0.098975	4.921082e+06
4*	4	0.197250	7.969066e+06

R-squared = 0.000000
Point to Point Fit - No Fit Coefficients

Figure 5.11: Calibration method for FID channel

In Figure 5.12 and Figure 5.13 the samples can be compared with the calibration mixtures both for FID and TCD.

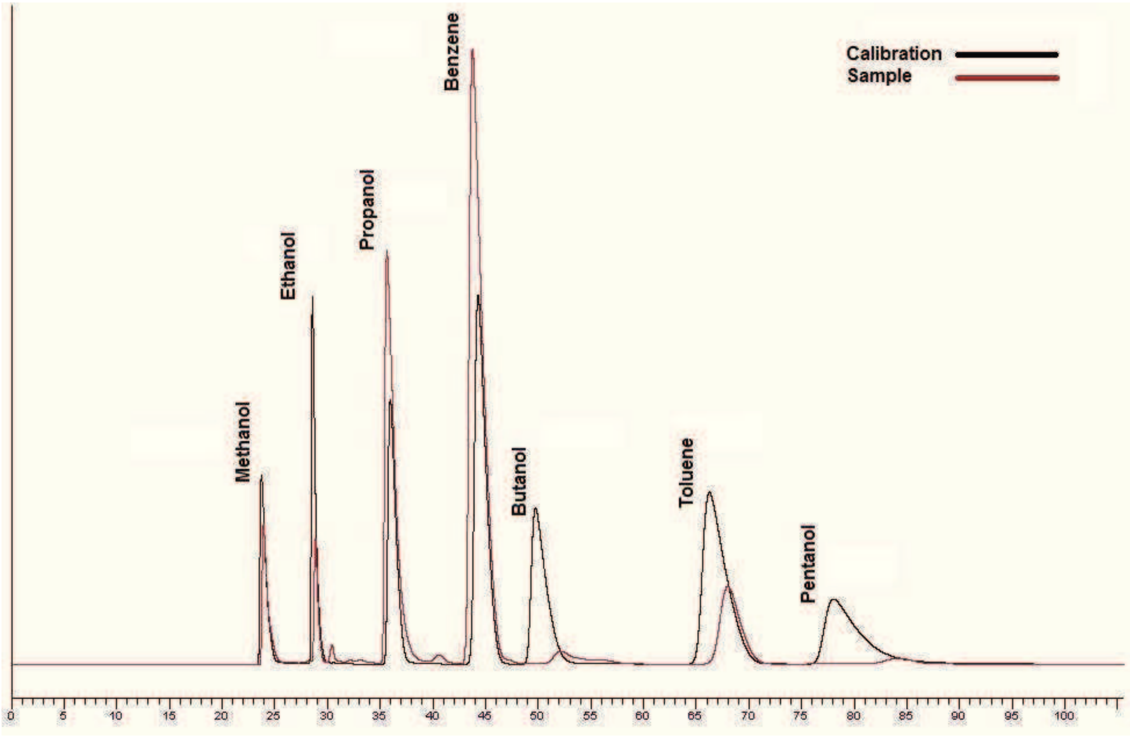


Figure 5.12: Chromatogram of sample and calibration mixture on FID

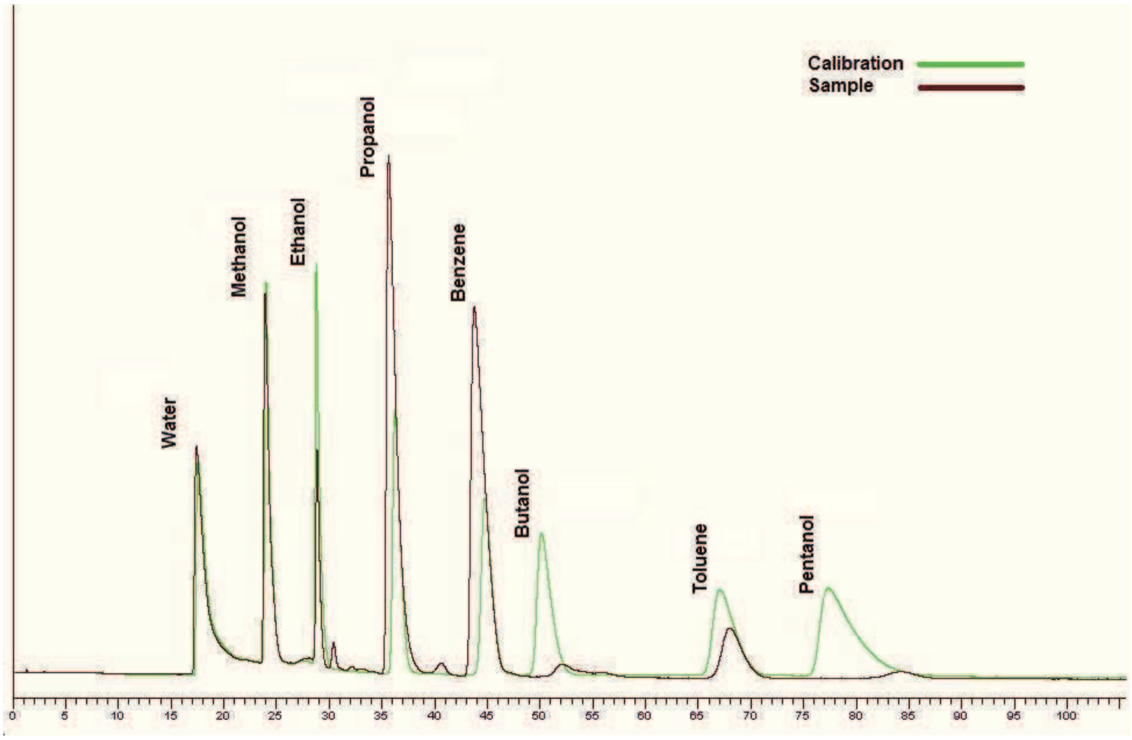


Figure 5.13: Chromatogram of sample and calibration mixture on TCD

5.2.3.2 Analytical results

In the test run described in this work, over five litres of mixed alcohols were produced. An overview of the produced amount is given in Table 5.6. For further product analysis, only these samples were taken, which were withdrawn at the desired temperatures (blue marked).

Sample number	Date	Temperature [°C]	Pressure [bar]	Amount [ml]	Test duration [min]
MA01	2011-05-12	230	100	120	
MA02	2011-05-12	250	100	260	
MA03	2011-05-12	290	100	100	
MA04	2011-05-12	280	100	60	
MA05	2011-05-18	up to 280	100	120	
MA06	2011-05-18	280	100	160	60
MA07	2011-05-18	285	100	220	
MA08	2011-05-18	290	100	310	60
MA09	2011-06-01	up to 290	100	120	
MA10	2011-06-01	290	100	100	
MA11	2011-06-01	up to 380	100	300	
MA12	2011-06-20	up to 300	100	200	
MA13	2011-06-20	300	100	90	30
MA14	2011-06-20	up to 310	100	150	
MA15	2011-06-20	310	100	100	30
MA16	2011-06-20	up to 320	100	120	
MA17	2011-06-20	320	100	120	30
MA18	2011-06-21	up to 315	100	520	
MA19	2011-06-21	315	100	410	120
MA20	2011-06-21	up to 320	100	300	
MA21	2011-06-21	320	100	215	60
MA22	2011-06-22	up to 310	100	130	
MA23	2011-06-22	310	100	360	120
MA24	2011-06-28	up to 300	150	200	
MA25	2011-06-28	300	150	220	120
MA26	2011-06-29	290	200	250	300
MA27	2011-06-30	270	100	90	
Sum				**5,345**	

Table 5.6: Overview of mixed alcohols amount produced

The mixed alcohols products obtained during the plant operation are given in Table 5.7.

	Components [m%]																	
	Methanol		**Ethanol**		**Propanol**		**Butanol**		**Pentanol**		**Benzene**		**Toluene**		**Water**		**Rest**	
	FID	***TCD***	**FID**	***TCD***	**FID**	***TCD***	**FID**	***TCD***	**FID**	***TCD***	**FID**	***TCD***	**FID**	***TCD***	**FID**	***TCD***	**FID**	***TCD***
MA04	8.79	*9.00*	4.14	*4.19*	28.65	*28.21*	1.13	*0.81*	0.91	*1.21*	31.21	*30.75*	5.81	*5.95*	0.00	*11.52*	7.84	*8.36*
MA06	11.53	*11.84*	6.06	*6.26*	38.21	*38.04*	1.21	*0.65*	1.54	*2.00*	12.48	*12.61*	3.10	*3.01*	0.00	*10.09*	15.80	*15.50*
MA07	10.58	*10.86*	5.37	*5.41*	35.86	*35.53*	0.58	*0.47*	1.88	*2.54*	13.56	*13.13*	2.81	*2.92*	0.00	*8.54*	20.83	*20.59*
MA08	9.61	*9.53*	6.10	*5.97*	38.80	*38.02*	0.91	*0.85*	1.95	*2.44*	12.69	*11.73*	2.59	*2.49*	0.00	*11.99*	15.36	*16.99*
MA08	11.82	*11.29*	5.53	*5.49*	38.30	*37.10*	1.04	*0.94*	1.94	*2.29*	15.13	*13.71*	2.50	*2.51*	0.00	*14.26*	9.48	*12.41*
MA10	9.15	*9.07*	4.47	*4.36*	43.87	*42.59*	1.51	*0.98*	2.17	*2.75*	11.38	*10.56*	3.63	*3.53*	0.00	*9.57*	14.26	*16.58*
MA13	12.13	*11.65*	2.23	*2.20*	31.12	*29.92*	1.43	*1.25*	1.28	*1.41*	19.93	*18.46*	5.28	*5.15*	0.00	*11.61*	14.99	*18.36*
MA15	13.73	*13.22*	2.97	*2.91*	36.50	*34.95*	2.14	*1.52*	1.55	*1.71*	17.32	*15.85*	4.12	*4.10*	0.00	*6.14*	15.53	*19.59*
MA17	15.65	*15.07*	4.02	*3.98*	42.79	*40.75*	1.66	*1.38*	1.78	*1.79*	13.78	*11.82*	2.55	*2.40*	0.00	*5.84*	11.92	*16.97*
MA19	15.97	*15.25*	3.03	*3.06*	34.38	*33.01*	1.28	*1.09*	1.29	*1.32*	17.93	*16.50*	3.78	*3.71*	0.00	*8.29*	14.05	*17.77*
MA21	16.47	*15.74*	3.52	*3.51*	37.19	*35.44*	1.27	*1.15*	1.46	*1.63*	17.93	*16.35*	3.81	*3.77*	0.00	*7.91*	10.44	*14.50*
MA23	14.80	*14.20*	2.43	*2.53*	30.87	*30.01*	1.38	*1.34*	1.28	*1.14*	15.96	*14.84*	4.13	*3.99*	0.00	*15.25*	13.88	*16.71*
MA25	19.58	*18.87*	3.30	*3.33*	33.18	*31.98*	1.15	*1.09*	1.38	*1.24*	8.49	*6.88*	2.72	*2.89*	0.00	*12.28*	17.90	*21.44*
MA27	15.42	*14.70*	4.00	*3.97*	35.66	*34.71*	1.38	*1.37*	1.84	*2.33*	12.32	*10.67*	2.82	*2.83*	0.00	*10.44*	16.12	*18.98*

Table 5.7: Mixed alcohols product analysis in m%

In Figure 5.14, a picture of the produced alcohols at different temperatures is shown.

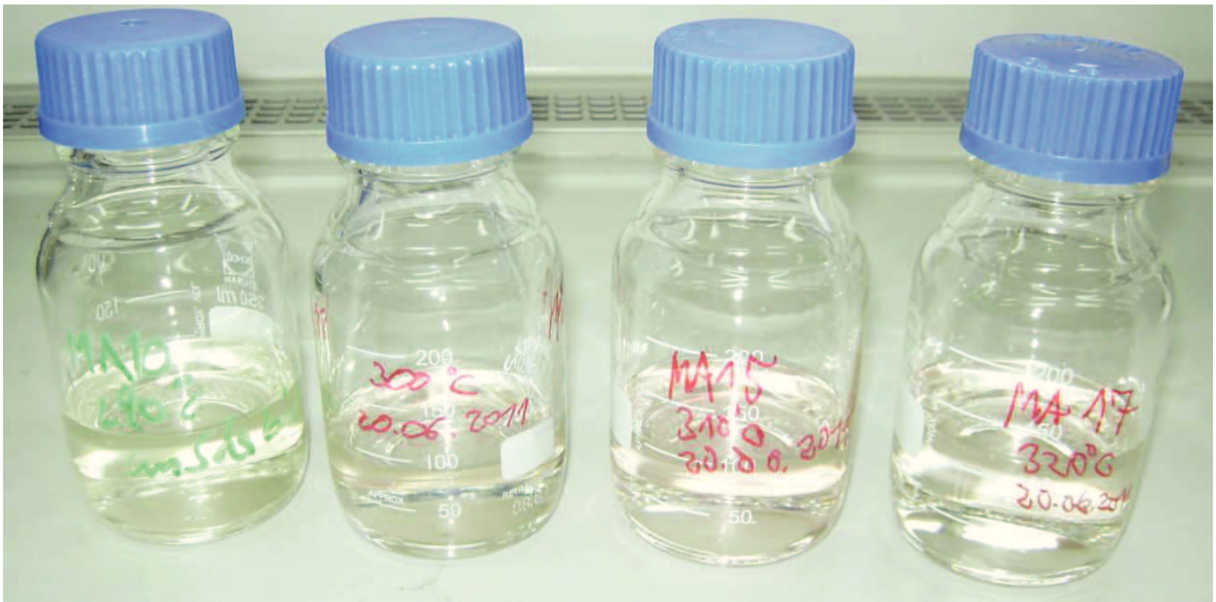


Figure 5.14: Picture of the produced alcohols

5.2.4 Productivity

In order to estimate the performance of the MAS pilot plant, the productivity of the MAS was calculated. In the following figures, the productivities of alcohols with respect to space velocity (SV) are illustrated. In Figure 5.15 the productivity is given in g product/Nm³/h gas and in Figure 5.16 in ml product/Nm³/h gas. In the figures, two space velocities are highlighted (SV: 2233 h^{-1} and 3267 h^{-1}). As can be obviously seen from the figures, the productivity is increasing with rising temperature at a certain space velocity.

The productivity of each alcohol at a space velocity of 3267 h^{-1} is shown in Figure 5.17. Inspection of this figure indicates that the productivity of methanol and propanol rises comparatively strong with increasing temperatures. In contrast, the productivity of ethanol, butanol and pentanol is just slightly increasing with respect to temperature.

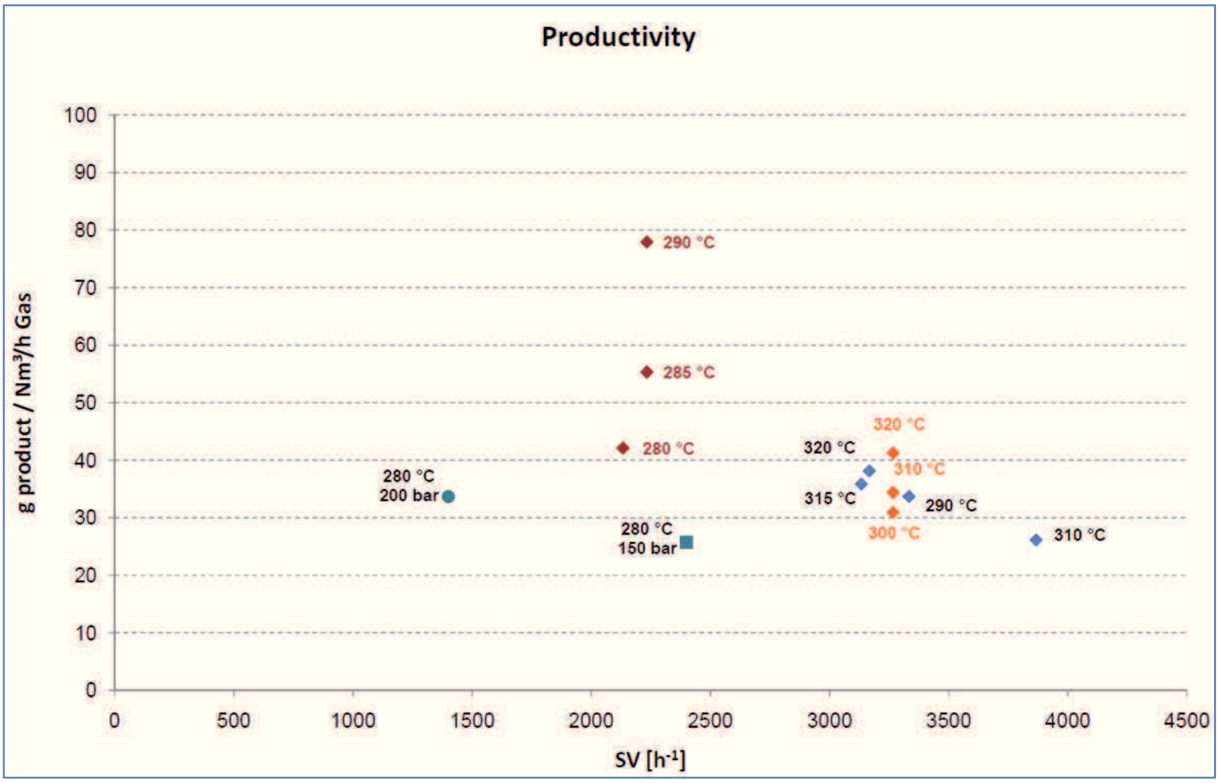


Figure 5.15: Productivity of alcohols in g according to SV

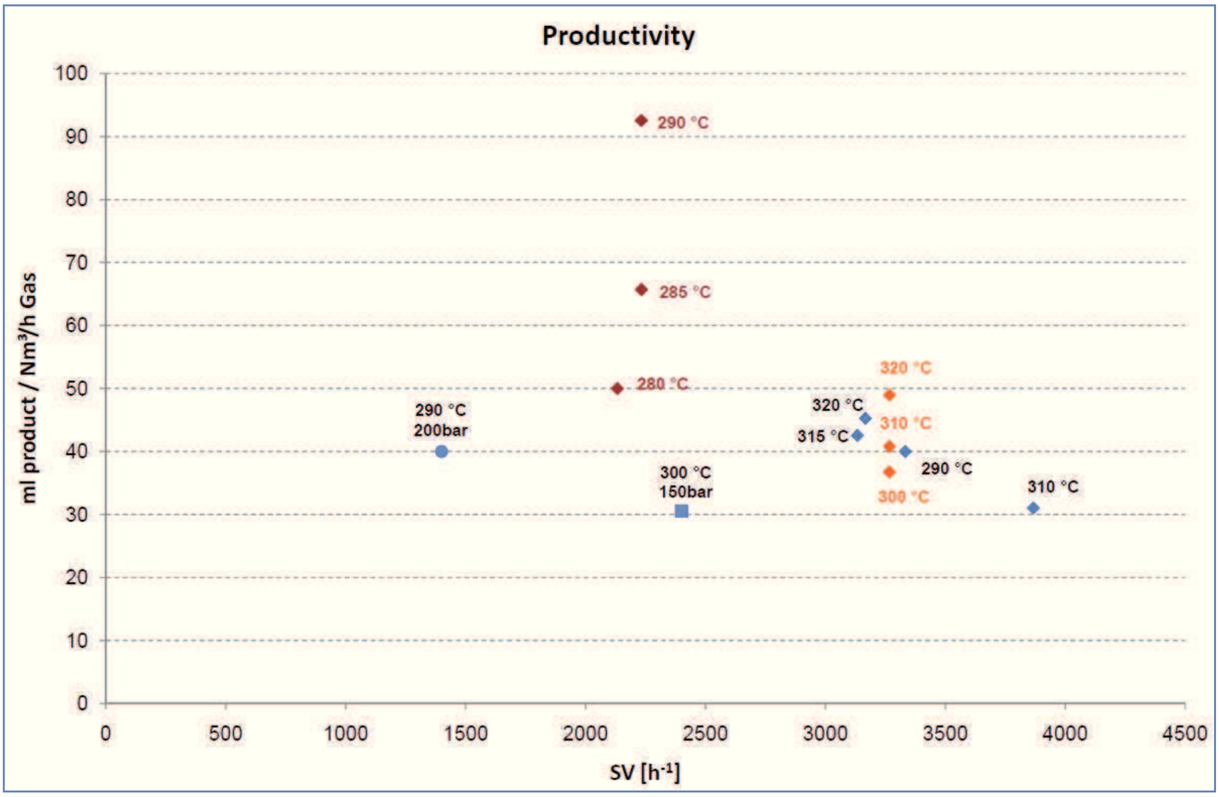


Figure 5.16: Productivity of alcohols in ml according to SV

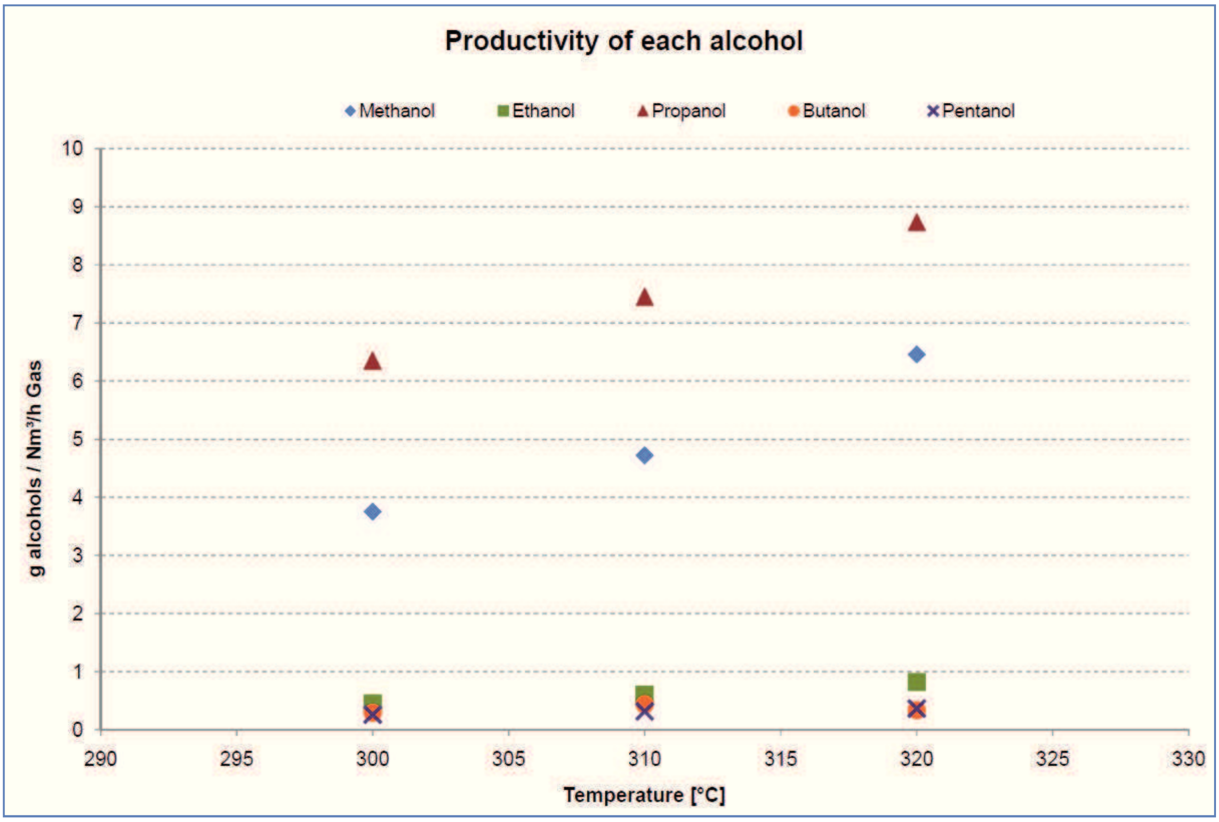


Figure 5.17: Productivity of each alcohol at a space velocity of 3267 h^{-1} (100 bar)

5.3 Comparison with results in other research

In the field of MAS, there are only few research papers and studies available. Among these different research works, a great deal of them engages in kinetic analysis or syngas application using syngas from gas bottles. In contrast, the experiments discussed in this work were carried out on a pilot plant with real syngas from a biomass gasifier.

In Figure 5.18 the effect of temperature on CO conversion as well as on alcohols selectivity is shown. The definition of the alcohol selectivity is given below.

$$selectivity\ S = \frac{produced\ amount}{converted\ amount} = \frac{\Sigma alcohols}{\Sigma CO}$$

It can be observed that CO conversion increases with higher temperatures while the alcohol selectivity decreases. The realised experiments do not agree with this effect. A possible explanation for this non-conformity could be the gas measurement at different times (see also chapter 5.4.4).

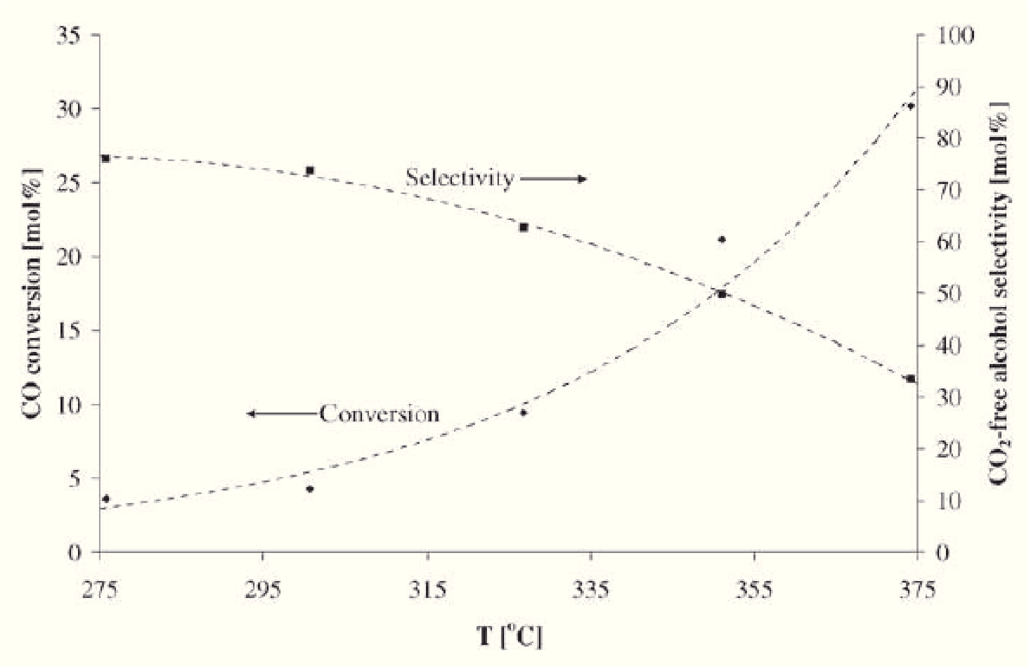


Figure 5.18: CO conversion and alcohol selectivity with respect to reactor temperature at 100 bar, GHSV = 5600 h^{-1} and a feed of 48.6 vol% H_2 and 51.3 vol% CO [59]

The effect of variation of temperature can be found in Figure 5.19 as well as in Figure 5.20. In Figure 5.19 it can be clearly observed that formation of alcohols peaks at a temperature of about 600 K at a pressure of 90 atm.

This is in good agreement with the findings in this work. In the realised experiments, the formation of alcohols reaches its peak value at a temperature of 320 ℃ by a pressure of 100 bar.

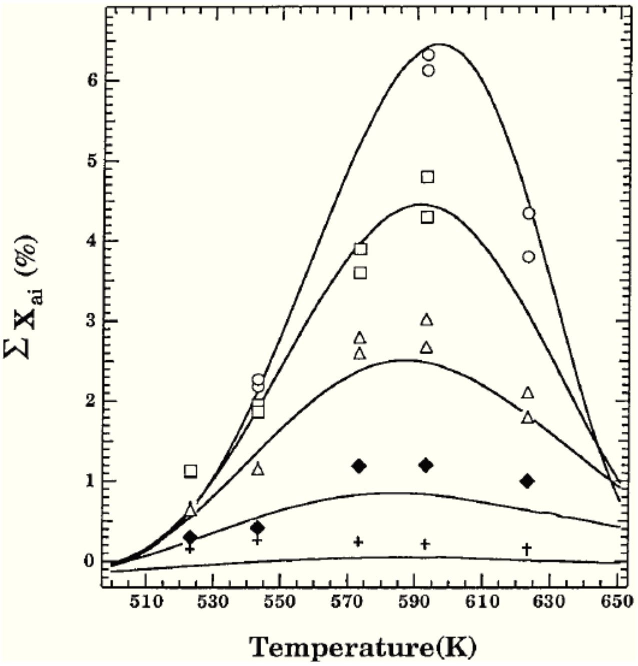


Figure 5.19: Alcohol formation according to reaction temperature for 15 (+), 30 (♦), 50 (Δ), 70 (□) and 90 (o) atm at Θ_{H2} = 1.01 and τ = 17.1 g-cat*h/mol; symbols experimental, lines simulated [53]

Figure 5.20 represents CO conversion, CO_2 formation, mixed alcohol formation and paraffin formation according to reaction temperatures. Inspection of the figure indicates that the formation of mixed alcohols tops out at about 590 K. The CO conversion as well as the formation rate of CO_2 and paraffins increase with increasing temperatures.

Also this relation compares well with the results in this work. As already mentioned above, the formation of alcohols reaches its peak value at a temperature of 320 ℃ by 100 bar. The CO_2 formation rises with higher temperatures (see also Table 5.2) and is, thus, consistent with the tendency shown in the figure.

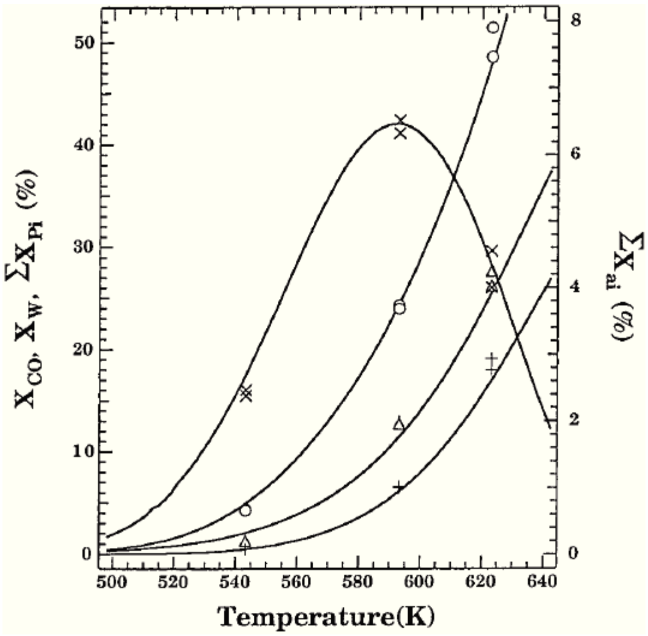


Figure 5.20: CO conversion (o), CO_2 formation (Δ), mixed alcohol formation (x) and paraffin formation (+) according to reaction temperatures at 90 atm, $\Theta_{H2} = 1.01$ and $\tau = 17.1$ g-cat*h/mol; symbols experimental, lines simulated [53]

The influence of pressure on the formation of mixed alcohols and paraffins is given in Figure 5.21. It can be seen from the figure that the formation of mixed alcohols is steeply increasing when pressure is getting higher. Due to a lack of experiments at higher pressures (150 and 200 bar), this pressure influence cannot be confirmed yet.

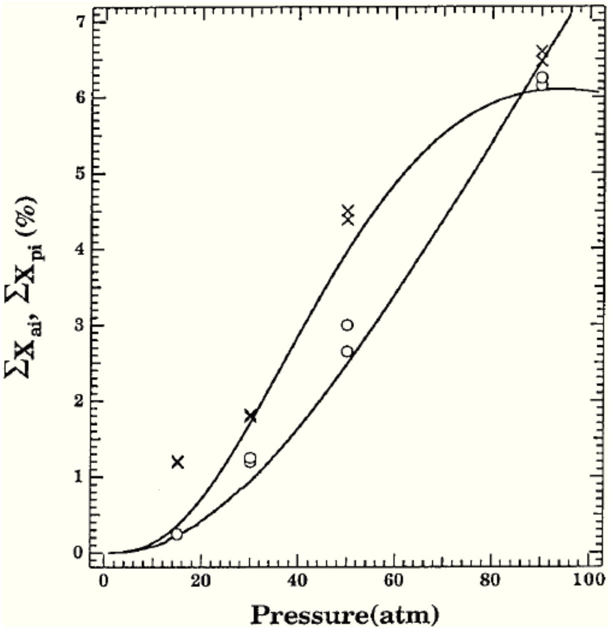


Figure 5.21: Influence of pressure on the formation of mixed alcohols (o) and paraffins (x) at $\Theta_{H2} = 1.01$ and $\tau = 17.1$ g-cat*h/mol; symbols experimental, lines simulated [53]

The influence of the H_2/CO molar feed ratio on CO conversion, CO_2 formation, mixed alcohol formation and paraffin formation as well as on the formation of methanol, ethanol, propanol and butanol is illustrated in Figure 5.22.

From Figure 5.22 it can be seen that the formation of mixed alcohols reaches its optimum value at a H_2/CO molar feed ratio of about 3. The test runs, carried out on the pilot plant, was run at a H_2/CO ratio of 2 which should be a quite good value for an optimal alcohol formation.

As can be founded in Figure 5.22b, the formation of methanol is strongly increasing with higher H_2/CO ratio. The ethanol formation curve has its peak at a ratio of approx. 1 and is subsequently decreasing. Concerning the propanol and butanol formation, there is also a small peak at about 0.5 with a following slight decrease.

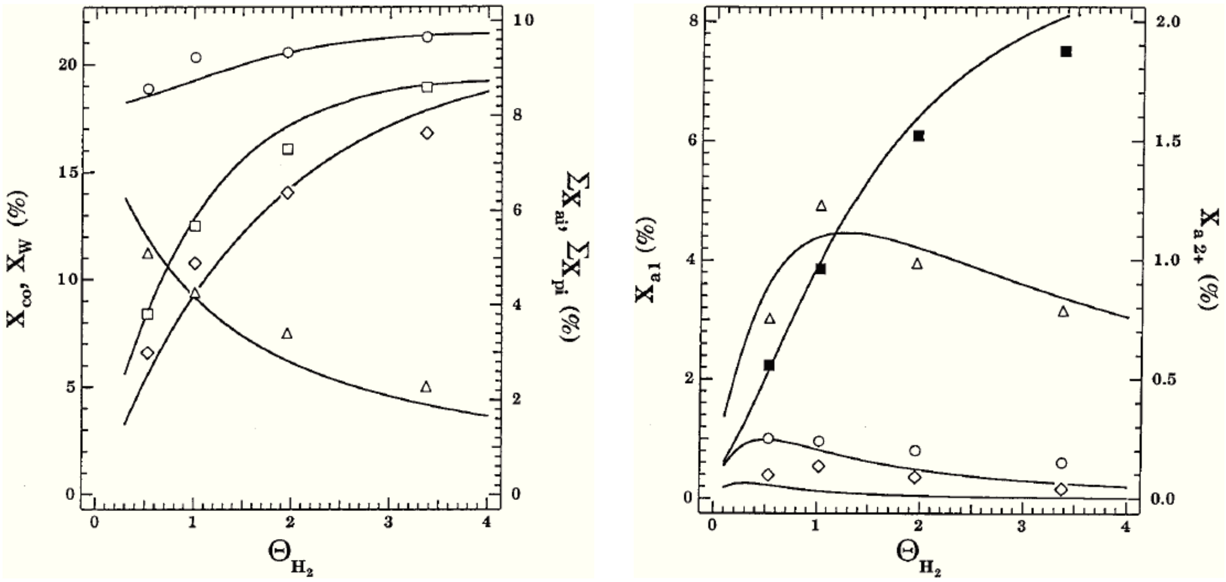


Figure 5.22: Influence of H_2/CO molar feed ratio on CO conversion (o), CO_2 formation (Δ), mixed alcohol formation (□) and paraffin formation (◇)(a) and on formation of methanol (■), ethanol (Δ), propanol (o) and butanol (◇) (b) at 320 ℃, 90 atm and τ = 12.5 g-cat*h/mol; symbols experimental, lines simulated [53]

5.4 Discussion of results

5.4.1 General

One general problem within this test run is the relatively bad comparability of the realised experiments due to the varying flows. At the pilot plant, the flow is not controlled directly. From the design the flow should be given by the compressor. The gas flow in the compressor is mainly given by the inlet pressure. As this was not constant, also the flow of the compressor changed from day to day. The approximate volume flow can only be determined by reading off the values of the gas meter and subsequent calculation. Hence, an exact adjustment of the volume flow is not possible.

Another problem is the lack of experiments at higher pressures (150 and 200 bar) because of the very difficult temperature control of the highly exothermic reactor. Thus, it is not possible to make a statement relating to the dependency of MAS on pressure.

5.4.2 Gas analysis

In Figure 5.23, the gas composition of the test runs carried out on 21st June 2011 can be found. The red bars represent the gas composition before and the green bars the gas composition after the MAS reaction. It can be seen, that the gas composition before MAS is not steady. Actually, the problem is that there is no online measurement system installed at the MAS pilot plant. Thus, the components before and after MAS cannot be measured at the same time. However, there is an online measurement system installed at the CHP in order to measure the CO and CO_2 concentration of the raw gas (see also Figure 5.24).

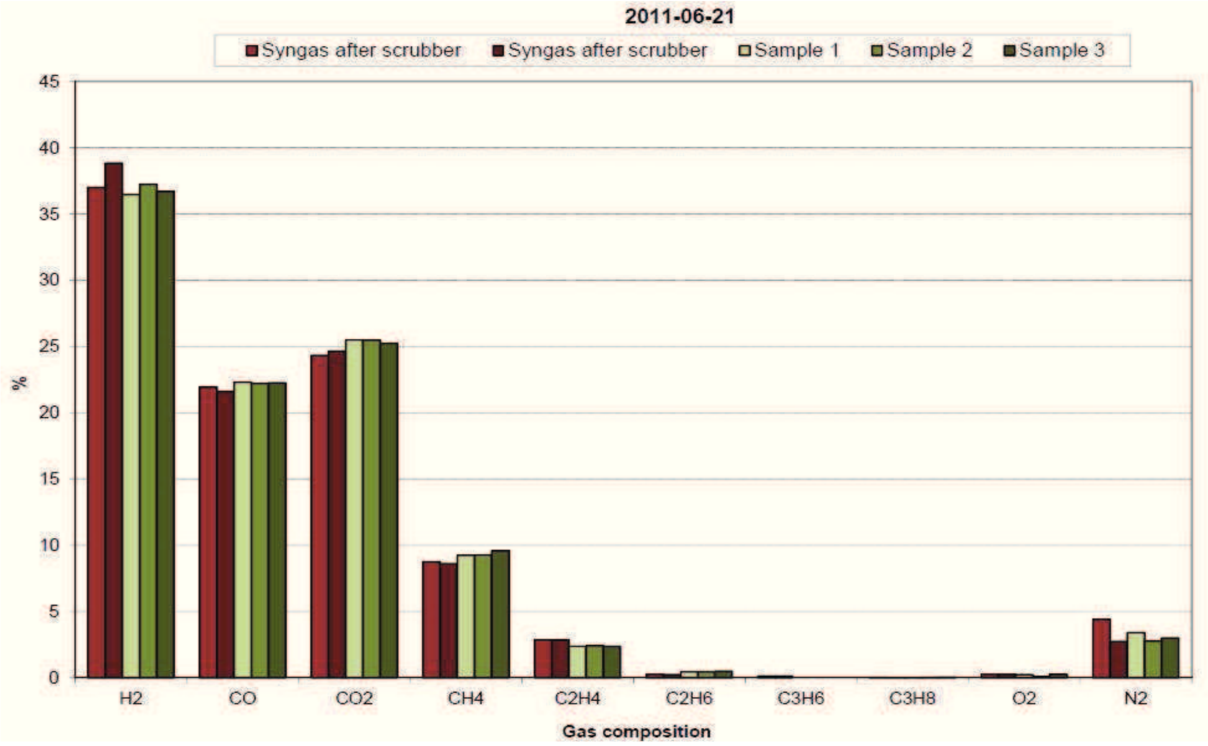


Figure 5.23: Gas composition of test runs on 21st June 2011

The minor deviations in the gas composition before MAS results from the variable gas composition from the gasifier of the CHP. The raw gas data from the CHP across one day are shown in Figure 5.24. As evident from the figure, the CO and CO_2 concentrations fluctuate slightly during the course of the day. By reason of the unsteady biomass feed, occasionally larger fluctuations can occur (see Figure 5.24 at about 11 p.m.).

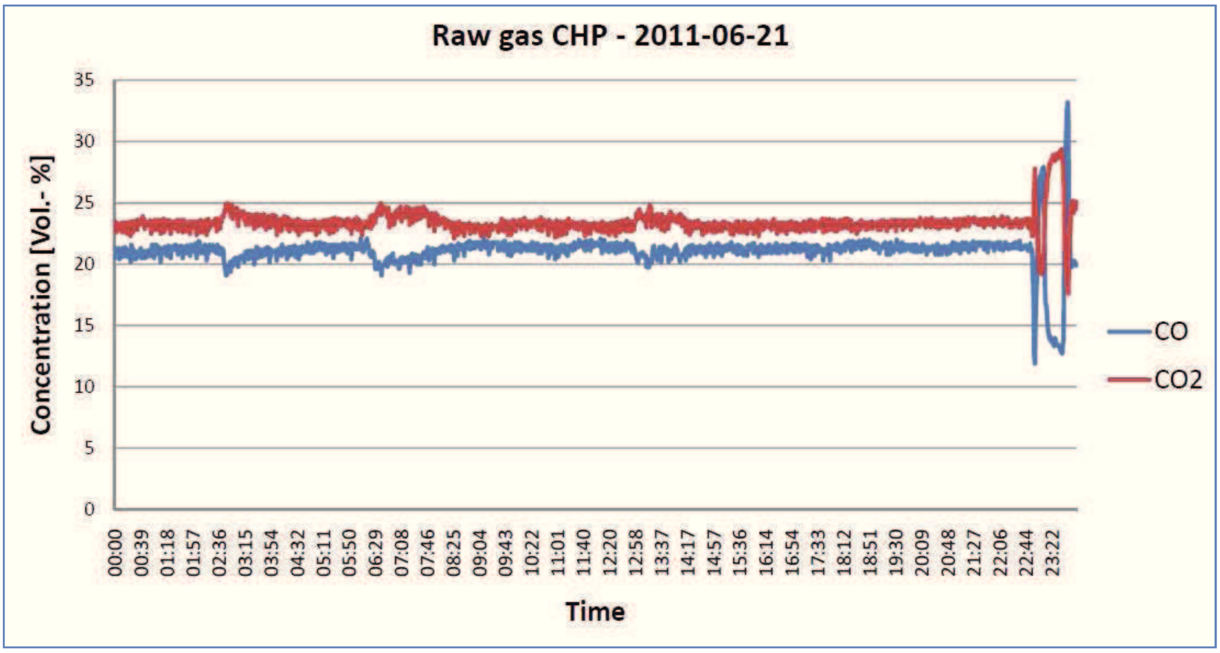


Figure 5.24: CHP raw gas data on 21st June 2011

5.4.3 Sulphur analysis

In the following figures, the concentrations of the different sulphur compounds are pictured.

Figure 5.25 reveals the dependency of mercaptan concentration on temperature after the MAS reactor. As can be clearly seen from the figure, the concentration of ethyl mercaptan strongly decreases with increasing temperature. Also the concentrations of methyl and propyl mercaptan slightly decrease with higher temperatures. Hence, it can be observed that by using process temperature above 300 ℃, only low am ounts of mercaptans will be produced.

An analogue dependency of concentration and temperature can be found for the sulphides. From Figure 5.26 it can be seen that the concentration of hydrogen sulphide considerably decreases when the temperature is getting higher. For carbonyl and dimethyl sulphide a similar behaviour can be noticed, even though the decrease is only slight. The concentration of carbon disulphide is zero after MAS independent of reaction temperature.

In Figure 5.27 the concentrations of thiophenes with respect to reaction temperature are shown. From the figure there is no explicit correlation of thiophene concentration and temperature observable.

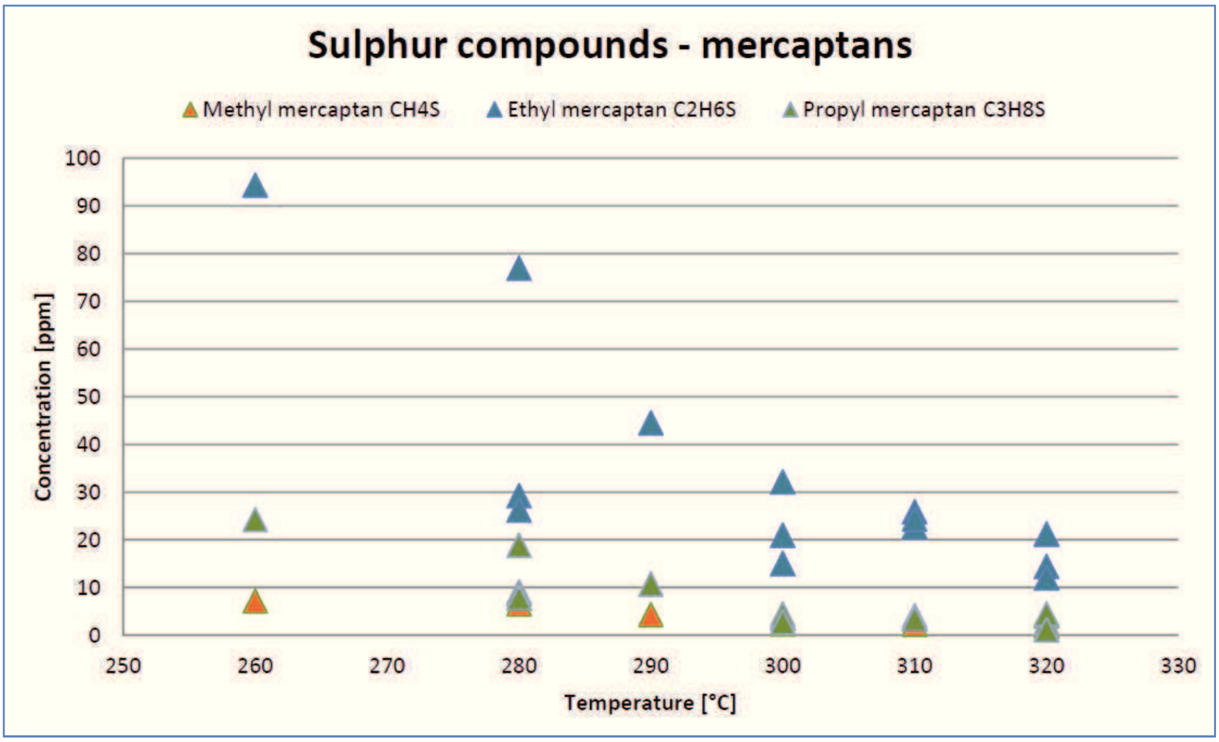


Figure 5.25: Concentrations of mercaptans according to reaction temperature

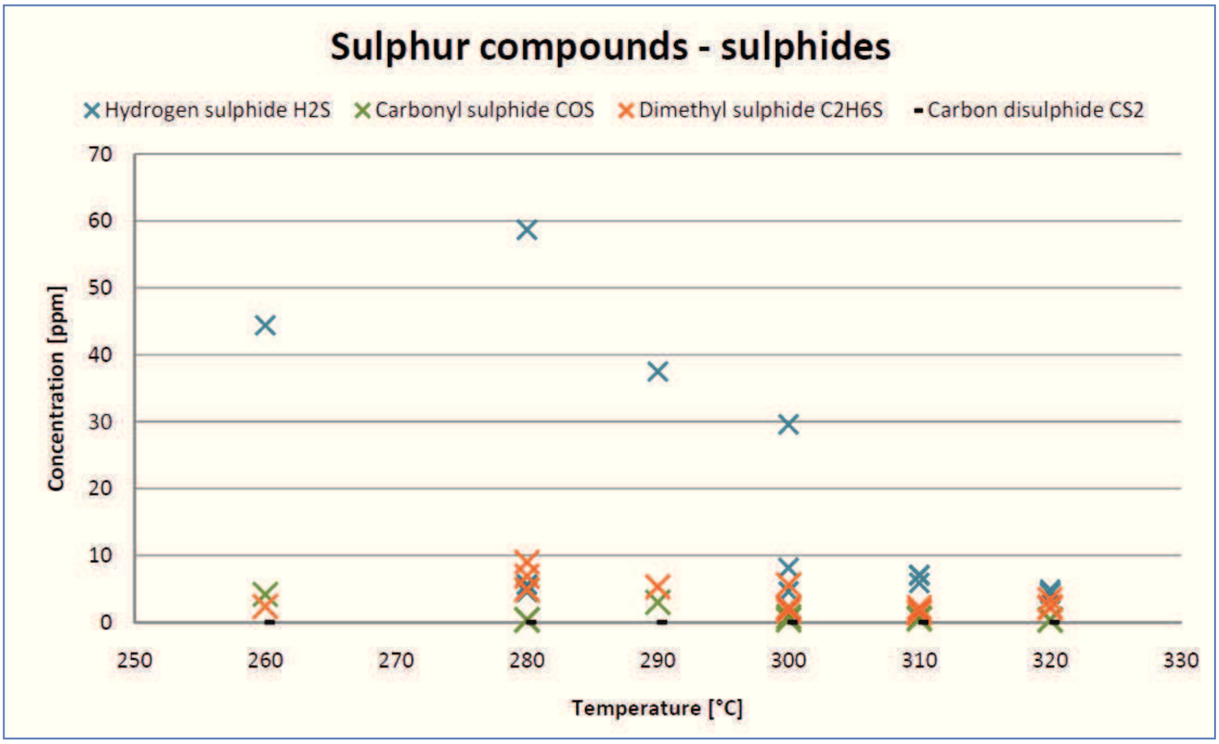


Figure 5.26: Concentrations of sulphides according to reaction temperature

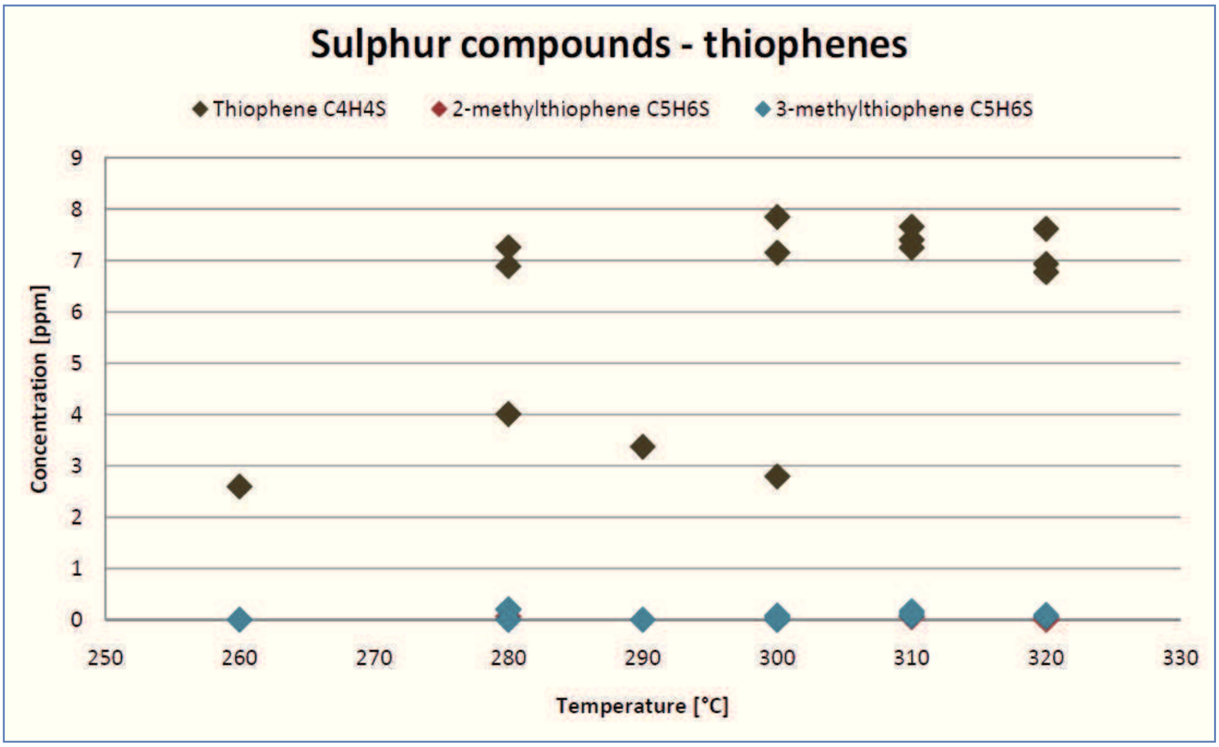


Figure 5.27: Concentrations of thiophenes according to reaction temperature

5.4.4 Product analysis

In the produced mixed alcohols, plenty of different compounds are contained, which could not be determined yet. The main components are methanol, ethanol, propanol, butanol, benzene and toluene. By using the TCD for gas chromatography, the water content could be determined additionally. However, there is also a number of other oxygenates in the mixed alcohols fuel that have to be still defined. Altogether, approx. 85 % of the MAS product could be analysed.

The difficulty concerning the product analysis is that there is no applicable chemical analysis device available in the laboratory at the Technikum in Güssing, except the gas chromatograph. So as to solve this problem, the product analysis will be contracted out to an analytical laboratory. There the mixed alcohols samples will be analysed using a GC-MS (GC with mass spectrometer) in order to analyse all components contained in the samples.

5.5 Conclusion of results

In this work, the MAS over a Mo_2S catalyst have been investigated in a pilot plant. As feed gas, real syngas from the biomass CHP in Güssing was used. The total plant was constructed and the start-up was carried out.

With the objective of an unmanned operation, the pilot plant is equipped with an automation system. Due to the highly exothermic MAS reaction, the temperature of the reactor is very difficult to control. Hence, to achieve unmanned operation of the plant, further improvements of the automation systems have to be carried out in future.

In the course of this work, ten experiments were realised at different process parameters. In the test run, a temperature variation between 280 and 320 °C and a pressure variation between 100 and 200 bar were carried out at varying volume flows. At the 100 bar experiments, the plant was working without problems at the desired temperatures. With increasing pressure, the control of the reactor temperature becomes more and more difficult and only a temperature of 290 °C could be achieved. Over all experiments, the steam reformer could not be operated due to the excessive pressure loss. So as to solve this problem, a new reformer catalyst will be used, which causes a lower pressure loss.

The key results of the experiment comprise gas analysis, sulphur analysis as well as analysis of the product. Furthermore, the product distribution of the mixed alcohols and the productivity of the MAS were determined. As expected, the formation of mixed alcohols increases with increasing temperatures. An influence of pressure on the alcohol formation could not be observed because not enough experiments have been carried out.

The mass balance for the MAS could not be calculated due to some problems. On the one hand, the fluctuations of the gas composition do not allow a reliable calculation. On the other hand the conversion rate was too small for a mass balance study.

In order to improve the whole MAS process, further research and development will be done on the MAS pilot plant. For the future the objectives will be the calculation of the mass- and energy balances and the production of larger amounts of mixed alcohols.

6 Summary and Perspectives

Today the transportation sector is addicted to fuels from fossil sources in most instances. The demand of liquid fuels is increasing and therefore, alternatives have been found to replace these fossil fuels with biofuels from renewable sources. At the moment, several pathways for producing biofuels from biomass feedstocks are investigated such as methanol from methanol synthesis or diesel from Fischer-Tropsch synthesis. In the last years, there were hardly any research activities in the area of mixed alcohols from synthesis gas in Europe, contrary to the US.

The synthesis of mixed alcohols from syngas using MoS_2-based catalysts has the major advantage that this catalyst is resistant against sulphur poisoning. Hence, the gas cleaning requirements are much simpler in comparison with other syntheses. The possibility to convert the produced mixed alcohols to high quality fuels using dehydration with subsequent oligomerisation is another advantage of this synthesis.

Summing up, it can be stated that the production of mixed alcohols from syngas for application as a fuel are a process with good prospects. The product from mixed alcohol synthesis can be used directly as blending component for gasoline without any modification of the engine. The octane number is higher compared to those of ethanol. Moreover, the tolerance to water is better due to ability of mixed alcohols to act as solubiliser.

The target of this thesis is the investigation of the mixed alcohols synthesis in pilot scale. For this purpose a pilot plant was built at the location of the combined heat and power plant Güssing. The required syngas was taken from the CHP after the gas cleaning section.

The main components of the MAS pilot plant are

- the steam reforming unit,
- the gas drying unit,
- the gas compression unit,
- the MAS fixed-bed reactor and
- the product separation unit.

The technical equipment of the mixed alcohols plant is shown in the following figure.

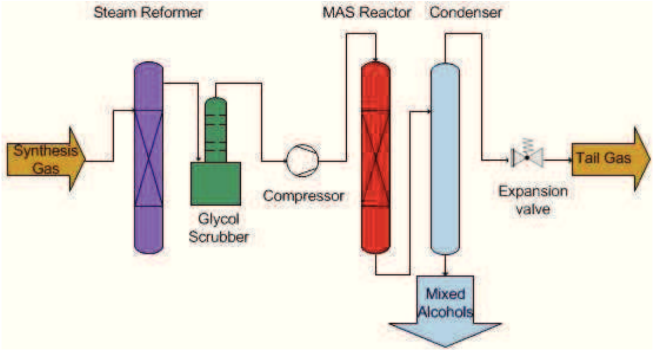


Figure 6.1: Flow diagram of the MAS pilot plant

At first, the syngas from the CHP goes to the steam reformer in which the hydrocarbons are converted into H_2 and CO and the H_2/CO ratio for the synthesis is adjusted. By using the steam reformer, a H_2/CO ratio of 2:1 should be achieved. The steam reformer is made up of two electrically heated tubes. In the first tube the gas is heated up to about 900 °C. The second tube is the reforming reactor, where the catalyst is filled in.

For gas drying a glycol scrubber is used in which the syngas is cooled down to approx. 2 °C so the most of the water in the syngas is removed.

For achieving the high pressure required for the MAS, a compressor is installed, which is capable to compress an amount of gas of approx. 5 Nm^3/h up to pressures between 90 and 300 bar.

For the synthesis itself a fixed bed reactor is used, designed as a long seamless tube made from stainless steel. The reaction temperature ranges between 280-320 °C and is achieved by an electric trace heating system.

The separation of the mixed alcohols from the unreacted tail gas is done directly after the reactor at the operating pressure of the MAS, using a condenser tube.

The catalysts used for MAS are mainly alkali-doped oxides (zinc and chromium oxides) or alkali-doped sulphides (molybdenum sulphides). At the MAS pilot plant Güssing, a molybdenum sulphide (MoS2) catalyst is used.

The temperatures over the steam reformer were very steady during the realised experiments. However, the steam reformer did not show the expected performance because of the high pressure loss of the steam reforming catalyst of approximately 20 mbar. Therefore the experiments were carried out without catalyst at lower temperatures. Another catalyst will be ordered and installed for the next experiences, which shows lower pressure losses.

The pressures before and after the MAS reactor are roughly constant. The small pressure fluctuations results from the condensate outlet device of the compressor which opens every 15 minutes for a short period. From there a small pressure drop occurs.

The temperatures of the MAS reactor were very difficult to control due to the strongly exothermic reaction of the synthesis. Up to temperatures of 310 °C the experiments could carried out without problems. By increasing the temperature the reactor temperature rises rapidly and a control of the synthesis was not possible any more. In that case, the plant had to be shut down and the reactor had to be cooled down.

The CO content before and after MAS reactor could not be measured at the same time. The CO value before MAS reactor is measured only once (no online measurement installed) and thus the temporal fluctuation of the CO values cannot be measured. Under these circumstances, the expected decrease of CO could not be shown in this work.

The composition of the MAS product had been analysed by gas chromatography. The MAS product contains higher alcohols with carbon numbers in the range of C1 to C5. Due to the fact that the composition of the produced alcohols is not typical further R&D would be necessary. In the future additional test runs will be carried out in the MAS pilot plant. Furthermore, the analytic methods will be examined and a suitable method will be established.

In the scope of this work, it could be worked out that MAS operated at a temperature of 320 ℃ at 100 bar achieved the highest productivity . The operation at higher pressures gave no practical results due to problems with controlling the temperature of the reactor. Due to the fact that no flow measurement is installed at the MAS pilot plant, it was not possible to adjust the same flow value for all experiments. Hence, finding the optimum process parameters by accomplishment of further experiments should be considered for the future work.

To conclude it should be mentioned that the construction and the start-up of the MAS pilot plant went according to plan without any larger problems. In the course of the first experiments over 5 l of mixed alcohols could be produced and analysed. In summary the first test run proceeded very successful.

Seeing that there are practically no research activities in Europe at the moment, the MAS pilot plant in Güssing will be a leading project in the field of alcohol synthesis in the future.

7 References

[1] Exxon Mobile, "Outlook for Energy - A view to 2030," Texas, 2009.

[2] Kjell Aleklet, "IEA accepts Peak Oil - An analysis of Chapter 3 of the World Energy Outlook 2004," 2004.

[3] I. Bolter, D. Bacovsky, and M. Wörgetter, "Biofuels in the European Union: An overview on the European biofuels policy.," IEA Task 39 Report T39-B7 2007.

[4] M. Wörgetter, "Biotreibstoffe der ersten und zweiten Generation - ein technischer Überblick," in *Central European Biomass Conference 2008*, Graz, 2008.

[5] S.N. Naik, V. V. Goud, P. K. Rout, and A.K. Dalai, "Production of first and second generation biofuels: A comprehensive review," *Revewable and Sustainable Energy Reviews*, vol. 14, pp. 578-597, 2010.

[6] EBTP. (2011, October) European Biofuels TECHNOLOGY PLATFORM. [Online]. www.biofuelstp.eu

[7] European Biodiesel Board. (2011, October) EBB European Biodiesel Board. [Online]. www.ebb-eu.org

[8] U. Schuchardt, R. Sercheli, and R.M. Vargas, "Transesterification of Vegetable Oils: a Review," *J. Braz. Chem. Soc.*, vol. Vol. 9, no. No. 1, pp. 199-210, 1998.

[9] Refuel/ECN. (2011, October) refuel. [Online]. www.refuel.eu

[10] R. Sims, M. Taylor, J. Saddler, and W. Mabee. (2008, November) From 1st- to 2nd-generation biofuel technologies; An overview of current industry and RD&D activities. IEA report.

[11] M. Enguídanos, A. Soria, B. Kavalov, and P. Jensen, "Techno-economic analysis of Bio-alcohol production in the EU: a short summary for decision-makers," Institute for Prospective Technological Studies, Report EUR 20280 EN 2002.

[12] A. Demirbas, "Competitive liquid biofuels from biomass," *Applied Energy*, no. 88, pp. 17-28, 2011.

[13] ENERS Energy Concept. (2011, October) Biofuels Platform. [Online]. www.biofuels-platform.ch

[14] R.E.H. Sims, M. Warren, J.N. Saddler, and M. Taylor, "An overview of second generation biofuel technologies," *Bioresource Technology* , no. 101, pp. 1570-1580, 2010.

[15] Fachagentur Nachwachsende Rohstoffe e.V. (FNR). (2011, October) BtL-Plattform. [Online]. www.btl-plattform.de

[16] Fachagentur Nachwachsende Rohstoffe e.V. (FNR). (2011, October) Biokraftstoffe - Pflanzen, Rohstoffe, Produkte. Brochure.

[17] I. Olofsson, A. Nordin, and U. Söderlind, "Initial Reviw and Evaluation of Process Technologies and Systems Suitable for Cost-Efficient Medium-Scale Gasification for Biomass to Liquid Fuels," Energy Technology & Thermal Process Chemistry, University of Umea, Sweden, ETPC Report ISSN 1653-0551, 2005.

[18] Paul Scherrer Institur (PSI), Conzepte Technik Umwelt (CTU), TU Wien, repotec. (2009, January) Demonstration der Produktion von synthetischem Erdgas aus Holz im Massstab 1 MW am Biomassekraftwerk Güssing. Document. [Online]. http://www.raonline.ch

[19] Paul Scherrer Institute (PSI), "The SNG Technology Platform in Güssing, A - Status report of Bio-SNG project," in *European Biofuels Technology Platform, 2nd Stakeholder Plenary Meeting - Implementing the Strategic Research Agenda for sustainable biofuels: From pilots to demonstration plants*, Brussel, 2009, p. Poster, Poster (http://www.biofuelstp.eu).

[20] K. Nath and D. Das, "Hydrogen from biomass," *Current Science*, vol. No. 3, no. Vol.85, pp. 265-271, August 2003.

[21] K.-H. Tetzlaff, *Bio-Wasserstoff - Eine Strategie zur Befreiung aus der selbstverschuldeten Abhängigkeit von Öl*. Norderstedt, Deutschland: Books on Demand GmbH, 2005.

[22] Hannes Wagner and Martin Kaltschmitt, "Pathways for synthesis of liquid bio fuels - Review on conversion, efficiency, selectivity and by-products," in *ICPC - 10th International Conference on Polygeneration Strategies with special Focus on Integrated Biorefineries*, Leipzig, 2010, p. 12.

[23] P.L. Spath and D.C. Dayton, "Preliminary Screening - Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas (NREL/TP-510-34929)," Colorado, 2003.

[24] G.W. Huber, S. Iborra, and A. Corma, "Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering," *Chem. Rev.*, no. 106, pp. 4044-4098, 2006.

[25] J. R. Rostrup-Nielsen, "New aspects of syngas production and use," *Catalysis Today*, vol. 63, no. 2-4, pp. 159-164.

[26] B. Davenport, "Methanol," SRI International, Menlo Park, CA, Chemical Economics Handbook Marketing Research Report Report number 674.5000, 2002.

[27] E.G. Hancock, "The manufacture of gasoline ant the chemistry of its components," *Critical Reports on Applied Chemistry*, no. 10, pp. 20-56, 1985.

[28] ExxonMobil Research & Engineering (EMRE) Hindman M., "Methanol to Gasoline (MTG) Technology - An Alternative for Liquid Fuel Production," in *World CTL Conference*, Beijing, China, 2010.

[29] I. Wender, "Reactions of synthesis gas," *Fuel Processing Technology*, vol. 48, no. 3, pp. 189-297, 1996.

[30] S. Joseph and Y.T. Shah. (2011, November) I-A Methanol to Gasoline Process; Fischer-Tropsch Archive. [Online]. www.fischer-tropsch.org

[31] F.J. Keil, "Methanol-to-hydrocarbons: process technology (Review)," *Microporous and Mesoporous Materials*, no. 29, pp. 49-66, 1999.

[32] UOP LLC. (2011, November) uop - A Honeywell Company. [Online]. www.uop.com

[33] S. Han and C.D. Chang, "Fuels, Synthetic, Liquid Fuels," in *Kirk-Othmer Encyclopedia of Chemical Technology*, Kirk-Othmer, Ed., 2000, ch. 42.

[34] S.A. Tabak, A.A. Avidan, and F.J. Krambeck, "Production of synthetic gasoline and diesel fuel from non-petroleum resources," in *191. American Chemical Society national meeting*, New York, USA, April 1986, pp. 293-299.

[35] K.-W. Jun, H.-S. Lee, H.-S. Roh, and S.-E. Park, "Catalytic Dehydration of Methanol to Dimethyl Ether (DME) over Soli-Acid Catalysts," *Bull. Korean Chem. Soc.*, vol. 23, no. 6, 2002.

[36] X. D. Peng, B. A. Toseland, and P. J. A. Tijm, "Kinetic understanding of the chemical synergy under LPDME conditions - once-through applications," *Chemical Engineering Science*, vol. 54, no. 13-14, pp. 2787-2792, 1999.

[37] J. B. Hansen and F. Joensen, "High conversion of synthesis gas into oxygenates," *Studies in Surface Science and Catalysis*, vol. 61, pp. 457-467, 1991.

[38] ZeaChem Inc. (2011, November) ZeaChem. [Online]. www.zeachem.com

[39] J.J. Spivey and A. Egbebi, "Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas," *Chem. Soc. Rev.*, no. 36, pp. 1514-1528, 2007.

[40] R. Schnepf, "CRS Report for Congress: Agriculture-Based Renewable Energy Production," in *Energy: Ethanol*, TheCapitol.Net, Ed., 2010, ch. Chapter 5.

[41] P.C. Badger, "Ethanol From Cellulose: A General Review," in *Trends in new crops and new uses*.: ASHS Press, 2002.

[42] H.H. Szmant, *Organic building blocks of the chemical industry*. Canada, 1989.

[43] A.F. Zobaa and R. Bansal, *Handbook of Renewable Energy Technology*. Singapore: World Scientific Publishing Co., 2011.

[44] R. Rauch, H. Hofbauer, S. Sacareanu, and A. Chiru, "From gasification to synthetic fuels via Fischer-Tropsch synthesis," *Bulletin of the Transilvania Univerity of Brasov*, vol. 3, no. 52, 2010.

[45] Z. Abosteif, "Variation of Fischer-Tropsch synthesis parameters using steam gasifier product gas," Karlsruher Institute of Technology (KIT), Diplomarbeit 2011.

[46] S. Fürnsinn and H. Hofbauer, "Synthetische Kraftstoffe aus Biomasse: Technik, Entwicklungen, Perspektiven," *Chemie Ingenieur Technik*, vol. 79, no. 5, 2007.

[47] L.P. Dancuart and A.P. Steynberg, "Fischer-Tropsch Based GTL Technology: A New Process?," in *studies in surface science and catalysis: 163 - Fischer-Tropsch synthesis, catalysts and catalysis*, First edition ed., B.H. Davis and M.L. Occelli, Eds. Amsterdam, The Netherlands: Elsevier B.V., 2007, pp. 379-400.

[48] H. Schablitzky et al., "Investigations on hydrotreating of Fischer Tropsch- biowaxes for generation of bio-products from lignocellulosic biomass," in *Proceedings of the ICPS 11 (International Conference on Polygeneration Strategies)*, Vienna, 2011, pp. 197-209.

[49] G. Falk, G. Weber, R. Rauch, H. Hofbauer, and C. Weiß, "Mixed Alcohols from Biomass Steam Gasification," in *Proceeding of the International Conference on Polygeneration Strategies 11 (ICPS)*, Vienna, 2011, pp. 281-288.

[50] G.J. Quarderer, "Mixed Alcohols from Synthesis Gas," in *78th National AICHE Meeting*, New Orleans, 1986.

[51] G.J. Hutchings, R.G. Copperthwaite, and N.J. Coville, "Catalysis for hydrocarbon formation and transformations," *South African Journal of Science*, vol. 1, no. 84, pp. 12-16, 1988.

[52] S.F. Wong, M.S. Patel, and D.A. Storm, "Retrofitting Methanol Plants For Higher Alcohols," in *78th American Institute of Chemical Engineers spring national meeting*, New Orleans, LA, 1986.

[53] T.Y. Park, I. Nam, and Y.G. Kim, "Kinetic Analysis of Mixed Alcohol Synthesis from Syngas over K/MoS2 Catalyst," *Ind. Eng. Chem. Res.*, no. 36, pp. 5246-5257, 1997.

[54] R. Herman, "Classical and Non-Classical Routes for Alcohols Synthesis," in *New Trends in CO Activation*. New York: Elsevier, 1991, ch. Chapter 7, pp. 265-349.

[55] W.S. Epling, "Reaction and surface characterization studies of K- and Cs-promoted, Zn/Cr spinel, higher alcohol synthesis catalysts," University of Florida, Gainesville, FL, Ph.D. Dissertation 1997.

[56] V.R. Surisetty, A.K. Dalai, and J. Kozinski, "Alcohols as alteranative fuels: An overview," *Applied Catalysis A: General*, no. 404, pp. 1-11, 2011.

[57] M.E. Dry, "High quality diesel via the Fischer-Tropsch process - a review," *Journal of Chemical Technology and Biotechnology*, vol. 77, no. 1, pp. 43-50, 2001.

[58] P. Courty, P. Chaumette, C. Raimbault, and P. Travers, "Production of methanol-higher alcohol mixtures from natural gas via syngas chemistry," *Revue de l'Institut Francais du Petrole*, vol. 45, no. 4, pp. 561-578, 1990.

[59] J.M. Christensen, P.M. Mortensen, R. Trane, P.A. Jensen, and A.D. Jensen, "Effects of H2S and process conditions in the synthesis of mixed alcohols from syngas over alkali promoted cobalt-molybdenum sulfide," *Applied Catalysis A: General*, no. 366, pp. 29-43, 2009.

[60] Nexant Inc., "Equipment Desing and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup, and Oxygen Separation Equipment; Task 9: Mixed Alcohols From Syngas - State of Technology," National Renewable Energy Laboratory (NREL), San Francisco, Subsontract Report NREL/SR-510-39947, 2006.

[61] (2011, November) Engineers Guide - Information on Engineering, Science and Technology. [Online]. www.inclusive-science-engineering.com

[62] H. Botha, "Synthetic Fuels," in *SAE Fuels and Emissions Conference Cape Town*, 2007.

[63] S.-B. Qiu, W.-W. Huang, Y. Xu, L. Liu, and Q.-X. Li, "Production of Mixed Alcohols from Bio-syngas over Mo-based Catalyst," *Chinese Journal of Chemical Physics*, vol. 24, no. 1, 2011.

[64] Y. Yang et al., "Mo-Co-K Sulfide-Based Catalysts Promoted by Rare Earth Salts for Selective Synthesis of Ethanol and Mixed Alcohols from Syngas," *Chinese Journal of Catalysis*, vol. 28, no. 12, pp. 1028-1030, 2007.

[65] X. Zhang, Z. Li, Q. Guo, H. Zheng, and K. Xie, "Selective synthesis of mixed alcohols from syngas over catalyst Fe2O3/Al2O3 in slurry reactor," *Fuel Processing Technology*, no. 91, pp. 379-382, 2010.

[66] G.J. Quarderer and G.A. Cochran, "Catalytic process for producing mixed alcohols from hydrogen and carbon monoxide," *PCT Int. Appl. (Dow Chemical Co., USA)*, p. 40 pp., 1984.

[67] D.G. Taylor, "A process to produce EcaleneTM DE ® Denatured Ethanol from synthesis gas Utilizing Catalytic Thermal Reforming (CTR) and the "Power Energy Process"," 2002.

[68] R. Rauch et al., "Steam gasification of biomass at CHP plant Güssing - Status of the demonstration plant," in *2nd World Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection*, Rome, 2004, p. 4.

[69] A. Potetz, "Synthetic Biofuels made in Güssing," in *3. BTL-Kongress* , Berlin, 2008, p. 40.

[70] R. Rauch and H. Hofbauer, "Wirbelschicht-Wasserdampfvergasung in der Anlage Güssing," in *9. Int. Fachtagung "Energetische Nutzung nachwachsender Rohstoffe"*, 2003, pp. 2-5.

[71] M. Bolhàr-Nordenkampf et al., "Scale-up of a 100 kWth pilot FICFB-gasifier to a 8 MWth FICFB-gasifier demonstration plant in Güssing (Austria)," in *1st International Ukrainian Conference on BIOMASS FOR ENERGY*, Kyiv, 2002, p. 4.

[72] M. Bolhàr-Nordenkampf, R. Rauch, K. Bosch, C. Aichernig, and H. Hofbauer, "Biomass CHP Plant Güssing - Using Gasification for Power Generation," in *Int. Conference on Biomass Utilisation*, Thailand, 2002.

[73] C. Wegst and M. Wegst, *Stahlschlüssel-Taschenbuch*. Marbach/N.: Stahlschlüssel Wegst GmbH, 2010.

[74] (2011, August) M.WOITE Sonderwerstoffe Edelstähle - Website. [Online]. http://www.m-woite.de/en/download/14841.pdf

[75] (2011, August) QVF Process Systems. [Online]. www.qvf.com

[76] Sulzer Chemtech Ltd. (2010) Structured Packings for Distillation, Absorption and Reactive Distillation. Document.

[77] Armacell Enterprise GmbH. (2011, September) Armacell Enterprise GmbH. [Online]. www.armacell.com

[78] Bauer Kompressoren GmbH. (2010) Betriebsanleitung und Ersatzteilliste, Industrie-Hochdruckkompressoranlagen. Document.

[79] Wolfgang Tietze, *Handbuch Dichtungspraxis*, 3rd ed. Essen: Vulkan Verlag, 2003.

[80] Temperature Control. (2011, August) Temperature Control-Website. [Online]. www.temperaturecontrol.de

[81] J. Fraden, *Handbook of Modern Sensors: Physics, Design, and Applications*, 4th ed. New York, USA: Springer New York, 2010.

[82] TC Ltd. (2011, September) TC Thermocouple Design. [Online]. www.thermocouplesensors.co.uk

[83] tecsis GmbH. (2011, August) tecsis-Website. [Online]. www.tecsis.de

[84] tecsis GmbH. (2011, February) Operating Instructions - Pressure sensor Model P3297. Document.

[85] Endress+Hauser, Inc. (2010) Liquipoint T FTW31/32 - Level limit switch for multiple point detection in conductive liquids. Document.

[86] Bernecker + Rainer Industrie-Elektronik GmbH. (2011, September) B&R Perfection in Automation. [Online]. www.br-automation.com

[87] National Instruments Corporation. (2011, September) National Instruments. [Online]. www.ni.com

[88] J. Vessman et al., "Selectivity in analytical chemistry (IUPAC Recommendations 2001)," *Pure Appl. Chem.*, vol. Vol. 73, no. No. 8, pp. 1381-1386, 2001.

[89] ENERS Energy Concept. (2011, November) Biofuels Platform. [Online]. www.biofuels-platform.ch

[90] G.P. van der Laan, "Kinetics, Selectivity and Scale Up of the Fischer-Tropsch Synthesis," University of Groningen, Dissertation 1999.

[91] D. Taschler, "Optimization of a Biomass-based Fischer-Tropsch Synthesis - Location Güssing," Fachhochschulstudiengänge Burgenland GmbH, Pinkafeld, Diplomarbeit 2009.

[92] McGraw-Hill. (2011, November) Access Science. [Online]. www.accessscience.com

7.1 Nomenclature

a	year (annum)
A	area
approx.	approximately
bn	billion
BtL	biomass to liquid
BV	ball valve
BV-P	plastic ball valve
BV-S	steel ball valve
cal	calorie
CFC	chlorofluorocarbon
CHP	combined heat and power (plant)
CNG	compressed natural gas
CPU	central processing unit
DFB	dual fluidized bed
DIN	Deutsches Institut für Normung
DME	dimethylether
DN	nominal size
e.g.	for example (exempli gratia)
ETBE	ethyl-tertio-butyl-ether
EU	European Union
F	flow meter
FAD	Förderkreis Abgasnachbehandlungstechnologien für Dieselmotoren e.V.
FAME	fatty acid methyl ester
FFV	flexible fuel vehicle
FICFB	fast internal circulating fluidized bed
FID	flame ionisation detector
FT	Fischer-Tropsch
FTS	Fischer-Tropsch synthesis

GHSV	gas hourly space velocity
GTL	Gas-to-Liquid
H	heating
HB	Brinell hardness
HP	high pressure
HT	high temperature
I/O	input/output
ID	inner diameter
IUPAC	International Union of Pure and Applied Chemistry
L	length
LIC	level indicator controller
LNG	liquefied natural gas
LP	low pressure
LPG	liquefied petroleum gas
LT	low temperature
M	manometer
MAS	mixed alcohol synthesis
mat.	material
MS	mass spectrometer
MTBE	methyl-tertiary butylether
MWh	megawatt hour
NBR	nitrile butadiene rubber
NG	natural gas
no.	number
NV	needle valve
OD	outer diameter
OLE	object linking and embedding
OPC	OLE for process control
P	pump
PEFI	Power Fuels, Inc.
PI	pressure indicator

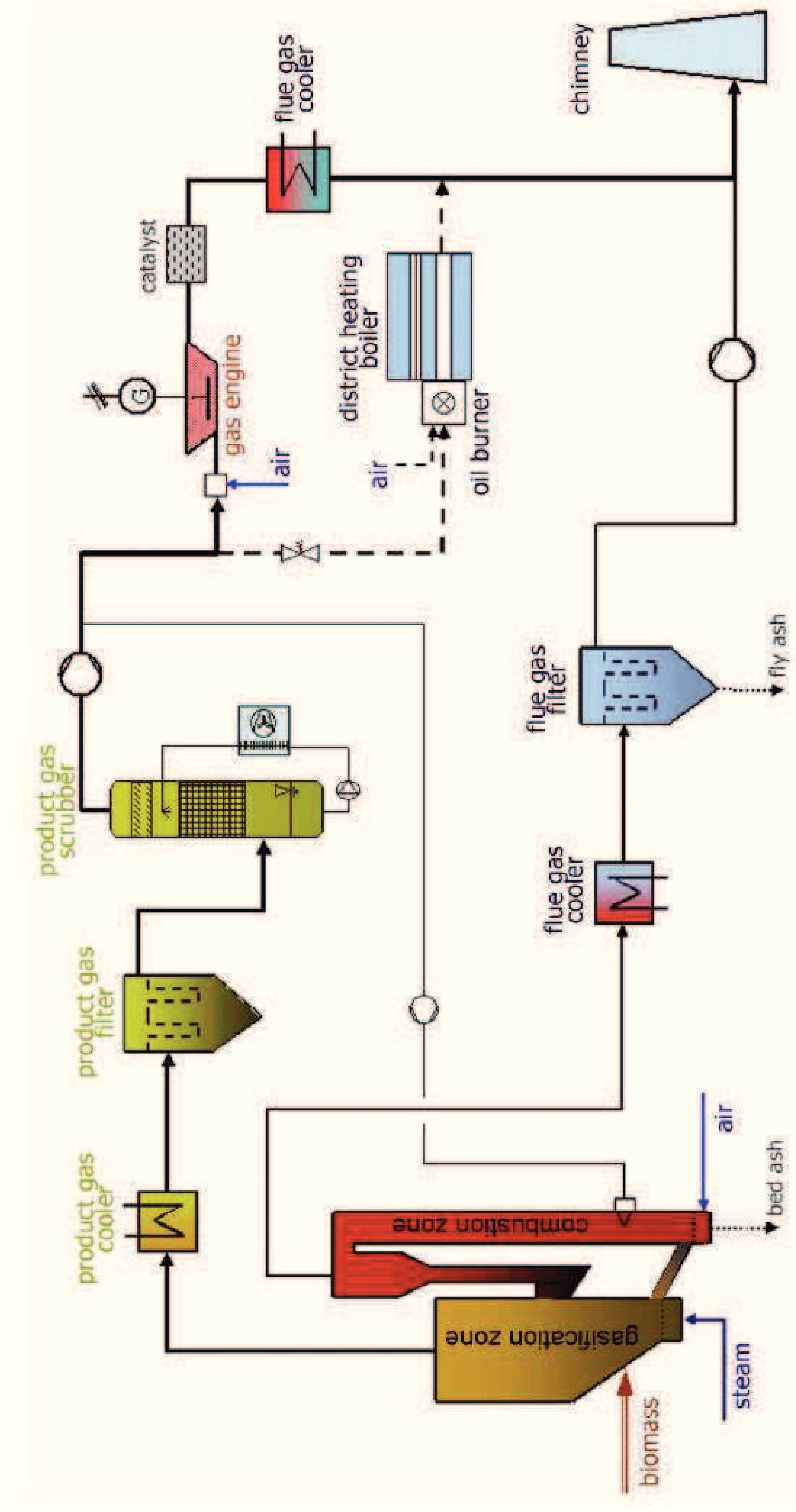
PIC	pressure indicator controller
PLC	programmable logic controller
PSA	pressure swing adsorption
PTFE	polytetrafluoroethylene
PVO	pure vegetable oils
QI	quality indicator
RME	rapeseed methyl ester
RV	reducing valve
SCD	sulphur chemiluminescence detector
SG (syngas)	synthesis gas
SNG	synthetic natural gas
SP	set point
SR	steam reformer
SV	space velocity
SVO	straight vegetable oils
T	thermocouple
TCD	thermal conductivity detector
TH	trace heating
TI	temperature indicator
TIC	temperature indicator controller
UFO	used frying oils
UK	United Kingdom
US	United States
V	volume
VDMA	Verband Deutscher Maschinen- und Anlagenbau
WD	wall thickness
WGS	water-gas-shift
WRI	Western Research Institute
WVO	waste vegetable oils
θ_i	molar feed ratio of species i to CO
τ	space time

7.2 Tables

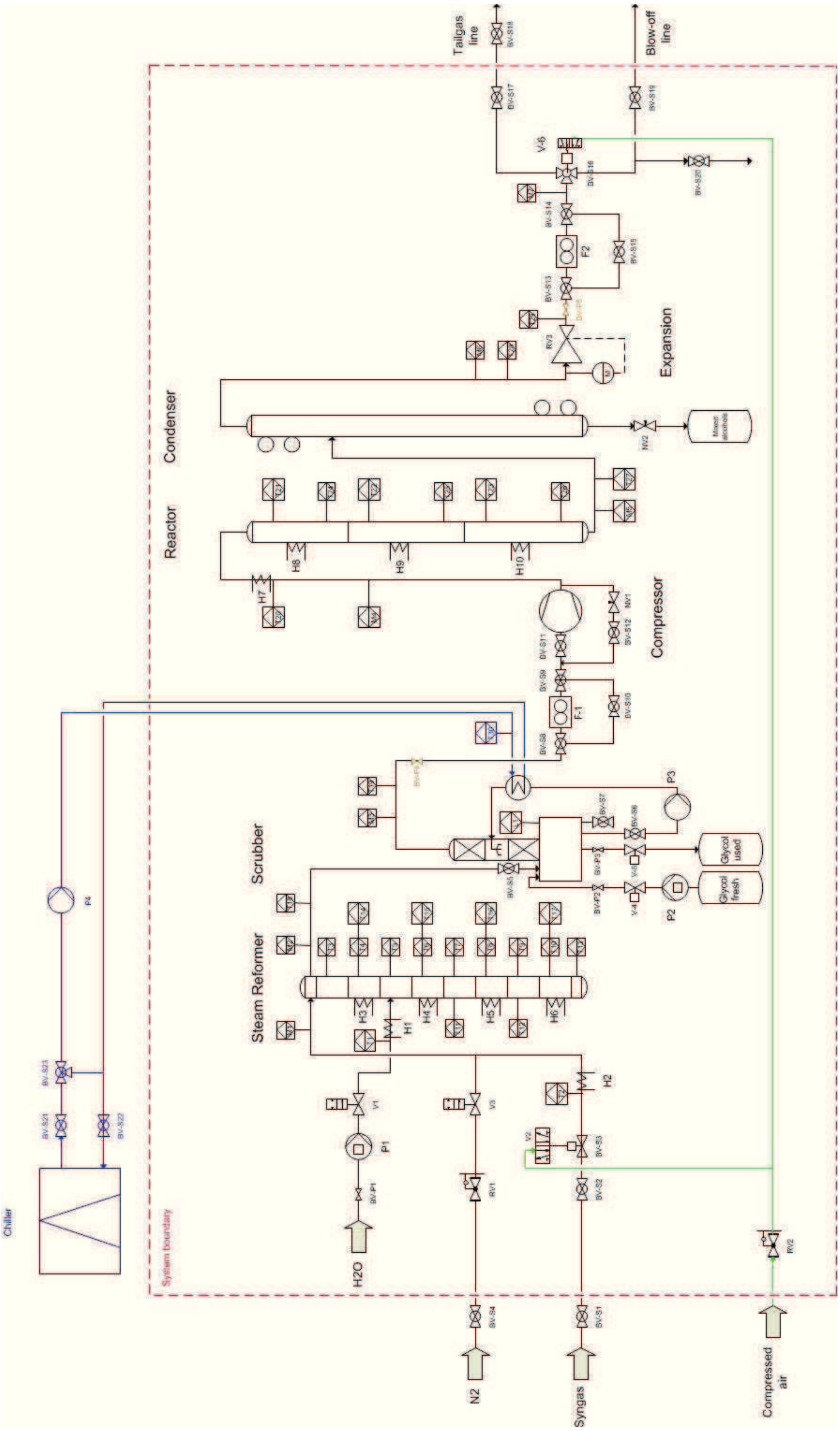
7.3 Figures

8 Appendix

8.1 Flow sheet CHP plant Güssing



8.2 Flow sheet MAS pilot plant



8.3 MSR specifications

Tag-No	Function code	Function	Sensor type	Sensor position	Connection	Medium	Temperatur [°C]			Pressure [bar]			measuring method	material	ATEX	Signal
							min	operating	max	min	operating	max				
TEMPERATURE																
T1	TIC	temperatur measuring & control	thermocouple type K	water IN	6 mm	steam	-200	300	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T2	TIC	temperatur measuring & control	thermocouple type K	product gas IN	6 mm	product gas	-200	80	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T3	TI	temperatur measuring	thermocouple type K	steam reformer M1	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T4	TI	temperatur measuring	thermocouple type K	steam reformer M2	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T5	TI	temperatur measuring	thermocouple type K	steam reformer M3	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T6	TI	temperatur measuring	thermocouple type K	steam reformer M4	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T7	TI	temperatur measuring	thermocouple type K	steam reformer M5	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T8	TI	temperatur measuring	thermocouple type K	steam reformer M6	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T9	TI	temperatur measuring	thermocouple type K	steam reformer M7	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T10	TI	temperatur measuring	thermocouple type K	steam reformer M8	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T11	TI	temperatur measuring	thermocouple type K	steam reformer M9	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T12	TI	temperatur measuring	thermocouple type K	steam reformer M10	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T13	TI	temperatur measuring	thermocouple type K	steam reformer M11	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T14	TIC	temperatur measuring & control	thermocouple type K	steam reformer C1	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T15	TIC	temperatur measuring & control	thermocouple type K	steam reformer C2	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T16	TIC	temperatur measuring & control	thermocouple type K	steam reformer C3	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T17	TIC	temperatur measuring & control	thermocouple type K	steam reformer C4	6 mm	syngas	-200	900	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T18	TI	temperatur measuring	thermocouple type K	previous to scrubber	6 mm	syngas	-200	90	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T19	TI	temperatur measuring	thermocouple type K	previous to compressor	6 mm	syngas	-200	20	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T20	TIC	temperatur measuring & control	thermocouple type K	previous to reactor	6 mm	syngas	-200	300	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T21	TIC	temperatur measuring & control	thermocouple type K	reactor C1	6 mm	syngas	-200	300	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T22	TIC	temperatur measuring & control	thermocouple type K	reactor C2	6 mm	syngas	-200	300	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T23	TIC	temperatur measuring & control	thermocouple type K	reactor C3	6 mm	syngas	-200	300	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T24	TI	temperatur measuring	thermocouple type K	reactor M1	6 mm	syngas	-200	300	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T25	TI	temperatur measuring	thermocouple type K	reactor M2	6 mm	syngas	-200	300	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T26	TI	temperatur measuring	thermocouple type K	reactor M3	6 mm	syngas	-200	300	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T27	TI	temperatur measuring	thermocouple type K	previous to condenser	6 mm	syngas	-200	250	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T28	TI	temperatur measuring	thermocouple type K	after condenser	6 mm	syngas	-200	20	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T29	TI	temperatur measuring	thermocouple type K	after expansion valve	6 mm	syngas	-200	3	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
T30	TIC	temperatur measuring & control	thermocouple type K	refrigerant circuit	6 mm	glycol	-200	-3	1200	0	0	40	resistance measurement	NiCr-Ni (silicone wire)	N	digital
PRESSURE																
M1	PI	pressure measuring	pressure sensor	previous to steam reformer	G 1/4 "	product gas	-40	80	125	0	0.08	0.6	piezo-resistive	stainless steel	N	analog
M2	PI	pressure measuring	pressure sensor	previous to scrubber	G 1/4 "	syngas	-40	90	125	0	0.06	0.6	piezo-resistive	stainless steel	N	analog
M3	PI	pressure measuring	pressure sensor	previous to compressor	G 1/4 "	syngas	-40	20	125	0	0.06	0.6	piezo-resistive	stainless steel	N	analog
M4	PIC	pressure measuring & control	pressure sensor	after compressor	1/4 "	syngas	-40	20	125	0	100	400	piezo-resistive	stainless steel	N	analog
M5	PI	pressure measuring	pressure sensor	after reactor	1/4 "	syngas	-40	300	125	0	100	400	piezo-resistive	stainless steel	N	analog
M6	PI	pressure measuring	pressure sensor	previous to expansion valve	1/4 "	syngas	-40	20	125	0	100	400	piezo-resistive	stainless steel	N	analog
M7	PI	pressure measuring	pressure sensor	after expansion valve	G 1/4 "	syngas	-40	3	125	0	0.01	0.6	piezo-resistive	stainless steel	N	analog
LEVEL																
L1	LZ+	overfill protection	two-rod probe	scrubber	G 1 "	glycol+water	-40	0	70	0	0	10	capacitive	stainless steel	N	digital
FLOW																
F1	FI	indirect flow measuring	gas meter	previous to compressor	G 1 "	syngas	-25	20	40	1	0	1.5	residential diaphragma	aluminium powder-coated	N	digital
F2	FI	indirect flow measuring	gas meter	after expansion valve	G 1 "	syngas	-25	3	40	1	0	1.5	residential diaphragma	aluminium powder-coated	N	digital
CO reading																
G1	GI	gas concentration measurment	gas sensor	compressor	-	CO	-10	25	40	-	-	-	electrochemical reaction	-	N	analog
G2	GI	gas concentration measurment	gas sensor	switching cabinet	-	CO	-10	25	40	-	-	-	electrochemical reaction	-	N	analog

pressure is equivalent to gauge pressure

8.4 Valve list

Part 1

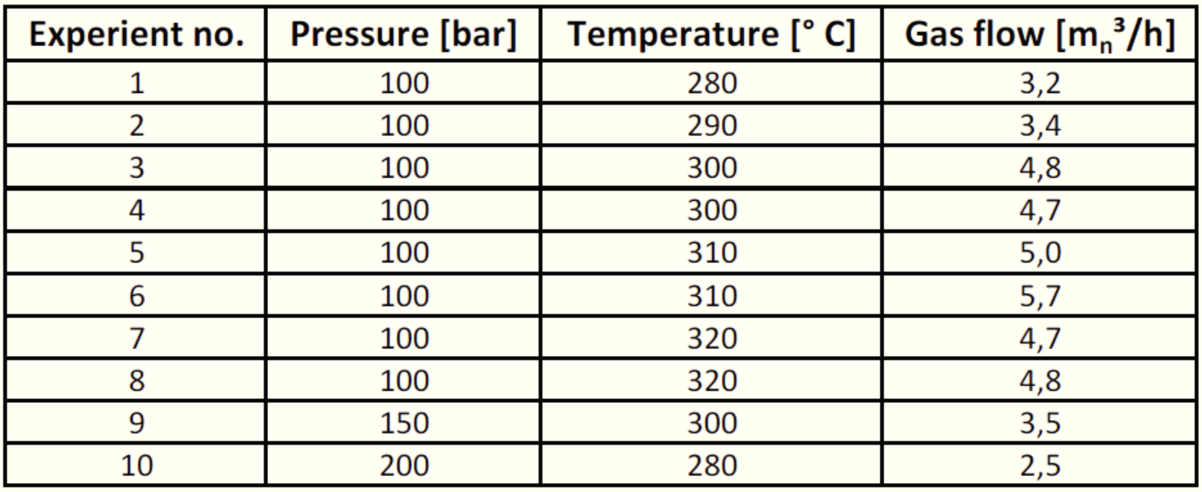
Valve-No.		Description	Typ	Function	Cleartext	Pipe	Medium	Temperatur [°C]			Pressure [bar]		
								min	operating	max	min	operating	max
Solenoid valves													
	V1	water inlet	automatic	flow regulation	regulation of water for steam reformer	6 mm	de-ionised water	-30	20	80	-	0.1	10
	V2	syngas inlet	automatic	flow regulation	regulation of syngas	1"	syngas	-10	20	70	3	4	10
	V3	nitrogen inlet	automatic	flow regulation	regulation of nitrogen	8 mm	nitrogen	-10	20	130	-	0.1	15
	V4	glycol fresh	automatic	flow regulation	regulation of fresh glycol for scrubber	6 mm	glycol fresh	-30	20	80	-	0.1	10
	V5	glycol used	automatic	flow regulation	regulation of used glycol from scrubber	6 mm	glycol used	-30	20	80	-	0.1	10
	V6	tailgas / blow-off	automatic	changeover switch	shift between tailgas and blow-off line	1"	tailgas	-10	20	70	3	4	10
	V7	refrigerant circuit	automatic	changeover switch	shift between fresh and used refrigerant	22 mm	refrigerant	-	3	120	-	-	-
Ball Valves													
	BV-S1	syngas main pipe	manual	open-close valve	shut-off valve after main syngas pipe	2 "	syngas	-	70	130	-	0.1	25
	BV-S2	syngas pipe MAS	manual	open-close valve	shut-off valve before Mixed Alcohols plant	1 "	syngas	-	70	130	-	0.1	25
	BV-S3	syngas inlet	automatic	open-close valve	shut-off valve syngas inlet	1 "	syngas	-30	70	110	0	0.1	16
	BV-S4	nitrogen pipe MAS	manual	open-close valve	shut-off valve nitrogen inlet	8 mm	nitrogen	-	20	130	-	0.1	25
	BV-S5	scrubber inlet pipe	manual	open-close valve	shut-off valve before Scrubber	1 "	syngas	-	90	130	-	0.1	25
	BV-S6	scrubber circuit pipe	manual	open-close valve	shut-off valve before Glycol circuit	1 "	glycol used	-	3	130	-	0.1	25
	BV-S7	scrubber drain pipe	manual	open-close valve	shut-off valve to drain scrubber	1 "	glycol used	-	3	130	-	0.1	25
	BV-S8	gas meter 1 - inlet	manual	open-close valve	shut-off valve before gas meter 1	1 "	syngas	-	5	130	-	0.1	25
	BV-S9	gas meter 1 - outlet	manual	open-close valve	shut-off valve after gas meter 1	1 "	syngas	-	5	130	-	0.1	25
	BV-S10	gas meter 1 - bypass	manual	open-close valve	shut-off valve for removing of gas meter 1	1 "	syngas	-	5	130	-	0.1	25
	BV-S11	compressor inlet pipe	manual	open-close valve	shut-off valve before compressor	1 "	syngas	-	5	130	-	0.1	25
	BV-S12	compressor bypass pipe	manual	open-close valve	shut-off valve compressor bypass pipe	6 mm	syngas	-40	20	150	0	100	415
	BV-S13	gas meter 2 - inlet	manual	open-close valve	shut-off valve before gas meter 2	1 "	syngas	-	5	130	-	0.1	25
	BV-S14	gas meter 2 - outlet	manual	open-close valve	shut-off valve after gas meter 2	1 "	syngas	-	5	130	-	0.1	25
	BV-S15	gas meter 2 - bypass	manual	open-close valve	shut-off valve for removing of gas meter 2	1 "	syngas	-	5	130	-	0.1	25
	BV-S16	tailgas / blow-off pipes	automatic	3-way valve	switch valve to switch between tailgas and blow-off pipe	1 "	tailgas	-30	5	110	0	0.1	16
	BV-S17	tailgas pipe	manual	open-close valve	shut-off valve before tailgas pipe	1 "	tailgas	-	20	130	-	0.1	25
	BV-S18	tailgas main pipe	manual	open-close valve	shut-off valve before tailgas main pipe	2 "	tailgas	-	20	130	-	0.1	25
	BV-S19	blow-off pipe	manual	open-close valve	shut-off valve before blow-off pipe	1 "	tailgas	-	20	130	-	0.1	25
	BV-S20	blow-off drain pipe	manual	open-close valve	shut-off valve to drain the blow-off line	1 "	tailgas	-	20	130	-	0.1	25
	BV-S21	refrigerant circuit inlet	manual	open-close valve	shut-off valve before refrigerant circuit	22 mm	refrigerant	-	-3	130	-	0	25
	BV-S22	refrigerant circuit outlet	manual	open-close valve	shut-off valve after refrigerant circuit	22 mm	refrigerant	-	20	130	-	0	25
	BV-S23	refrigerant circuit mixer	manual	3-way valve	switch valve to switch between fresh and used refrigerant	22 mm	refrigerant	n.s.	n.s.	n.s.	n.s.	0	n.s.
	BV-P1	water inlet	manual	open-close valve	shut-off valve water before steam reformer	6 mm	water	0	20	60	0	0	10
	BV-P2	glycol fresh	manual	open-close valve	shut-off valve glycol fresh before scrubber	6 mm	glycol fresh	0	20	60	0	0	10
	BV-P3	glycol used	manual	open-close valve	shut-off valve glycol used after scrubber	6 mm	glycol used	0	10	60	0	0	10
	BV-P4	gasometry pipe after scrubber	manual	open-close valve	shut-off valve gasometry after scrubber	6 mm	syngas	0	10	60	0	0	10
	BV-P5	gasometry pipe after expansion	manual	open-close valve	shut-off valve gasometry after expansion	6 mm	syngas	0	3	60	0	0	10
	BV-P6	gasometry main pipe before FT	manual	open-close valve	shut-off valve before FT gasometry	6 mm	syngas	n.s.	20	n.s.	n.s.	0	n.s.
Reducing Valves													
	RV1	nitrogen inlet	manual	infinitely variable	pressure reducing valve nitrogen inlet	1 "	nitrogen	n.s.	20	n.s.	n.s.	0.2	n.s.
	RV2	compressed air	manual	infinitely variable	pressure reducing valve compressed air	6 mm	compressed air		20	60	0.5	4	10
	RV3	overflow valve	manual	infinitely variable	pressure reducing valve tail gas	6 mm	tail gas	-10	3	80	50	100	300
Needle Valves													
	NV1	compressor bypass pipe	manual	infinitely variable	needle valve to adjust volume flow	6 mm	syngas	-53	20	p.c.	0	100	344
	NV2	Mixed alcohols removal	manual	infinitely variable	needle valve to discharge the mixed alcohols	6 mm	mixed alcohols	-53	3	p.c.	0	100	344
pressure is equivalent to gauge pressure													
p.c. ... pressure-controlled													
n.s. ... not stated													

Part 2

Valve-No.	Description	Typ	Function	Cleartext	Pipe	Medium	Temperatur [°C]			Pressure [bar]		
							min	operating	max	min	operating	max
Solenoid valves												
V1	water inlet	automatic	flow regulation	regulation of water for steam reformer	6 mm	de-ionised water	-30	20	80	-	0.1	10
V2	syngas inlet	automatic	flow regulation	regulation of syngas	1"	syngas	-10	20	70	3	4	10
V3	nitrogen inlet	automatic	flow regulation	regulation of nitrogen	8 mm	nitrogen	-10	20	130	-	0.1	15
V4	glycol fresh	automatic	flow regulation	regulation of fresh glycol for scrubber	6 mm	glycol fresh	-30	20	80	-	0.1	10
V5	glycol used	automatic	flow regulation	regulation of used glycol from scrubber	6 mm	glycol used	-30	20	80	-	0.1	10
V6	tailgas / blow-off	automatic	changeover switch	shift between tailgas and blow-off line	1"	tailgas	-10	20	70	3	4	10
V7	refrigerant circuit	automatic	changeover switch	shift between fresh and used refrigerant	22 mm	refrigerant	-	3	120	-	-	-
Ball Valves												
BV-S1	syngas main pipe	manual	open-close valve	shut-off valve after main syngas pipe	2 "	syngas	-	70	130	-	0.1	25
BV-S2	syngas pipe MAS	manual	open-close valve	shut-off valve before Mixed Alcohols plant	1 "	syngas	-	70	130	-	0.1	25
BV-S3	syngas inlet	automatic	open-close valve	shut-off valve syngas inlet	1 "	syngas	-30	70	110	0	0.1	16
BV-S4	nitrogen pipe MAS	manual	open-close valve	shut-off valve nitrogen inlet	8 mm	nitrogen	-	20	130	-	0.1	25
BV-S5	scrubber inlet pipe	manual	open-close valve	shut-off valve before Scrubber	1 "	syngas	-	90	130	-	0.1	25
BV-S6	scrubber circuit pipe	manual	open-close valve	shut-off valve before Glycol circuit	1 "	glycol used	-	3	130	-	0.1	25
BV-S7	scrubber drain pipe	manual	open-close valve	shut-off valve to drain scrubber	1 "	glycol used	-	3	130	-	0.1	25
BV-S8	gas meter 1 - inlet	manual	open-close valve	shut-off valve before gas meter 1	1 "	syngas	-	5	130	-	0.1	25
BV-S9	gas meter 1 - outlet	manual	open-close valve	shut-off valve after gas meter 1	1 "	syngas	-	5	130	-	0.1	25
BV-S10	gas meter 1 - bypass	manual	open-close valve	shut-off valve for removing of gas meter 1	1 "	syngas	-	5	130	-	0.1	25
BV-S11	compressor inlet pipe	manual	open-close valve	shut-off valve before compressor	1 "	syngas	-	5	130	-	0.1	25
BV-S12	compressor bypass pipe	manual	open-close valve	shut-off valve compressor bypass pipe	6 mm	syngas	-40	20	150	0	100	415
BV-S13	gas meter 2 - inlet	manual	open-close valve	shut-off valve before gas meter 2	1 "	syngas	-	5	130	-	0.1	25
BV-S14	gas meter 2 - outlet	manual	open-close valve	shut-off valve after gas meter 2	1 "	syngas	-	5	130	-	0.1	25
BV-S15	gas meter 2 - bypass	manual	open-close valve	shut-off valve for removing of gas meter 2	1 "	syngas	-	5	130	-	0.1	25
BV-S16	tailgas / blow-off pipes	automatic	3-way valve	switch valve to switch between tailgas and blow-off pipe	1 "	tailgas	-30	5	110	0	0.1	16
BV-S17	tailgas pipe	manual	open-close valve	shut-off valve before tailgas pipe	1 "	tailgas	-	20	130	-	0.1	25
BV-S18	tailgas main pipe	manual	open-close valve	shut-off valve before tailgas main pipe	2 "	tailgas	-	20	130	-	0.1	25
BV-S19	blow-off pipe	manual	open-close valve	shut-off valve before blow-off pipe	1 "	tailgas	-	20	130	-	0.1	25
BV-S20	blow-off drain pipe	manual	open-close valve	shut-off valve to drain the blow-off line	1 "	tailgas	-	20	130	-	0.1	25
BV-S21	refrigerant circuit inlet	manual	open-close valve	shut-off valve before refrigerant circuit	22 mm	refrigerant	-	-3	130	-	0	25
BV-S22	refrigerant circuit outlet	manual	open-close valve	shut-off valve after refrigerant circuit	22 mm	refrigerant	-	20	130	-	0	25
BV-S23	refrigerant circuit mixer	manual	3-way valve	switch valve to switch between fresh and used refrigerant	22 mm	refrigerant	n.s.	n.s.	n.s.	n.s.	0	n.s.
BV-P1	water inlet	manual	open-close valve	shut-off valve water before steam reformer	6 mm	water	0	20	60	0	0	10
BV-P2	glycol fresh	manual	open-close valve	shut-off valve glycol fresh before scrubber	6 mm	glycol fresh	0	20	60	0	0	10
BV-P3	glycol used	manual	open-close valve	shut-off valve glycol used after scrubber	6 mm	glycol used	0	10	60	0	0	10
BV-P4	gasometry pipe after scrubber	manual	open-close valve	shut-off valve gasometry after scrubber	6 mm	syngas	0	10	60	0	0	10
BV-P5	gasometry pipe after expansion	manual	open-close valve	shut-off valve gasometry after expansion	6 mm	syngas	0	3	60	0	0	10
BV-P6	gasometry main pipe before FT	manual	open-close valve	shut-off valve before FT gasometry	6 mm	syngas	n.s.	20	n.s.	n.s.	0	n.s.
Reducing Valves												
RV1	nitrogen inlet	manual	infinitely variable	pressure reducing valve nitrogen inlet	1 "	nitrogen	n.s.	20	n.s.	n.s.	0.2	n.s.
RV2	compressed air	manual	infinitely variable	pressure reducing valve compressed air	6 mm	compressed air		20	60	0.5	4	10
RV3	overflow valve	manual	infinitely variable	pressure reducing valve tail gas	6 mm	tail gas	-10	3	80	50	100	300
Needle Valves												
NV1	compressor bypass pipe	manual	infinitely variable	needle valve to adjust volume flow	6 mm	syngas	-53	20	p.c.	0	100	344
NV2	Mixed alcohols removal	manual	infinitely variable	needle valve to discharge the mixed alcohols	6 mm	mixed alcohols	-53	3	p.c.	0	100	344
pressure is equivalent to gauge pressure												
p.c. ... pressure-controlled												
n.s. ... not stated												

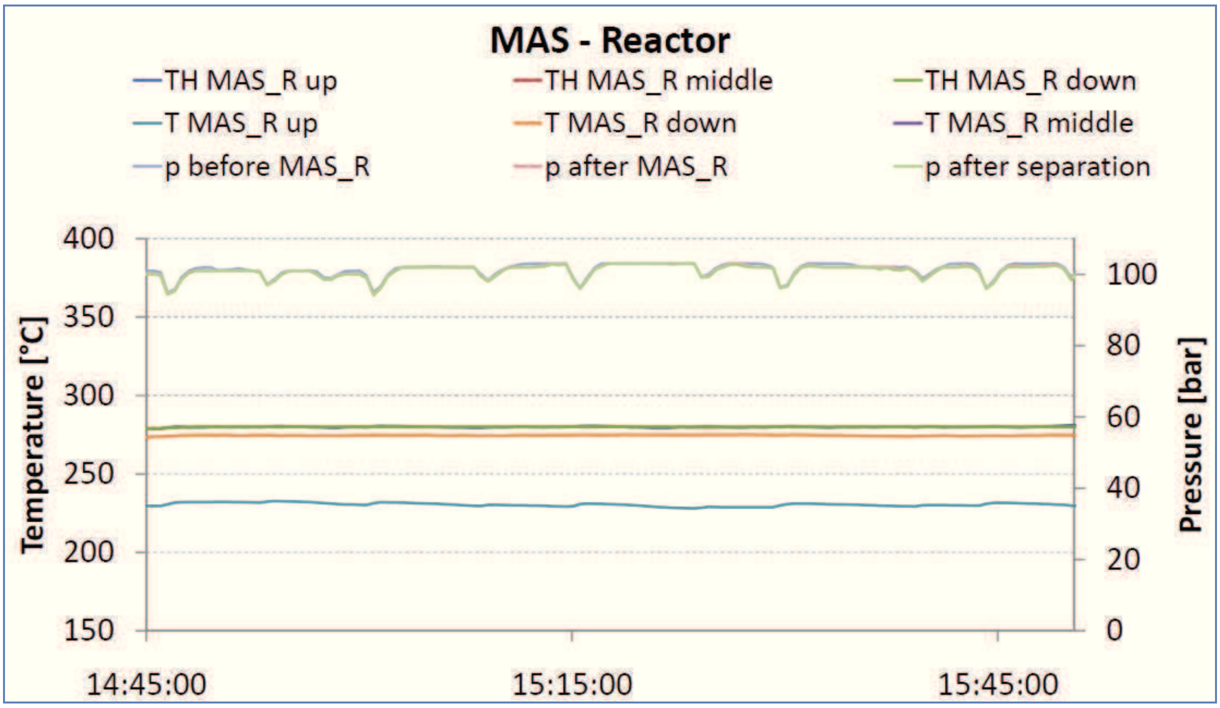
8.5 Experimental data

Experimental setting data

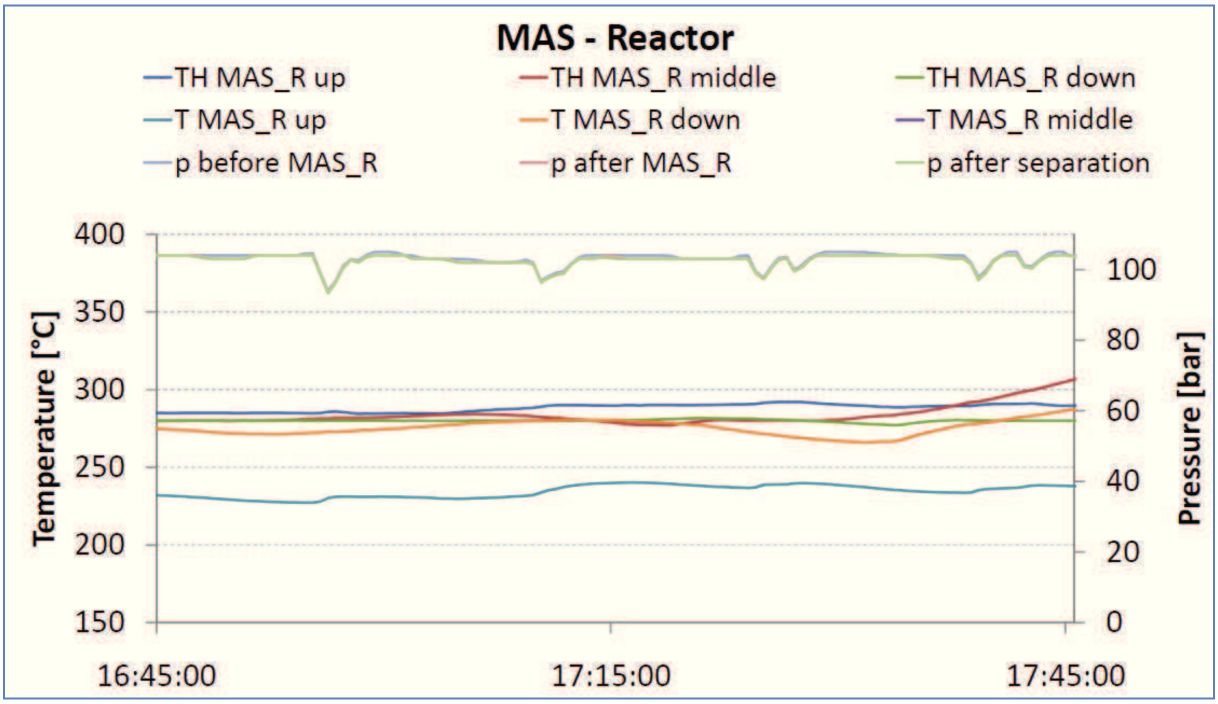


Experient no.	Pressure [bar]	Temperature [° C]	Gas flow [m_n^3/h]
1	100	280	3,2
2	100	290	3,4
3	100	300	4,8
4	100	300	4,7
5	100	310	5,0
6	100	310	5,7
7	100	320	4,7
8	100	320	4,8
9	150	300	3,5
10	200	280	2,5

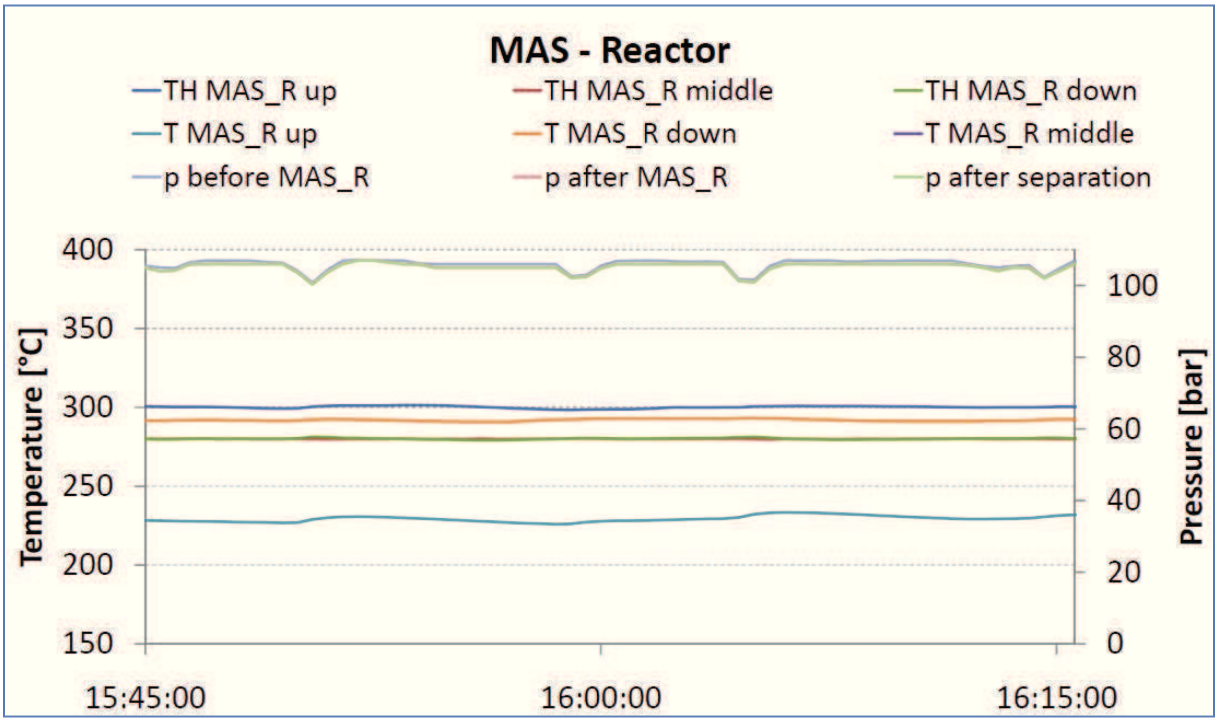
Experiment no. 1 (100 bar, 280 ℃, 3,2 m_n^3/h)



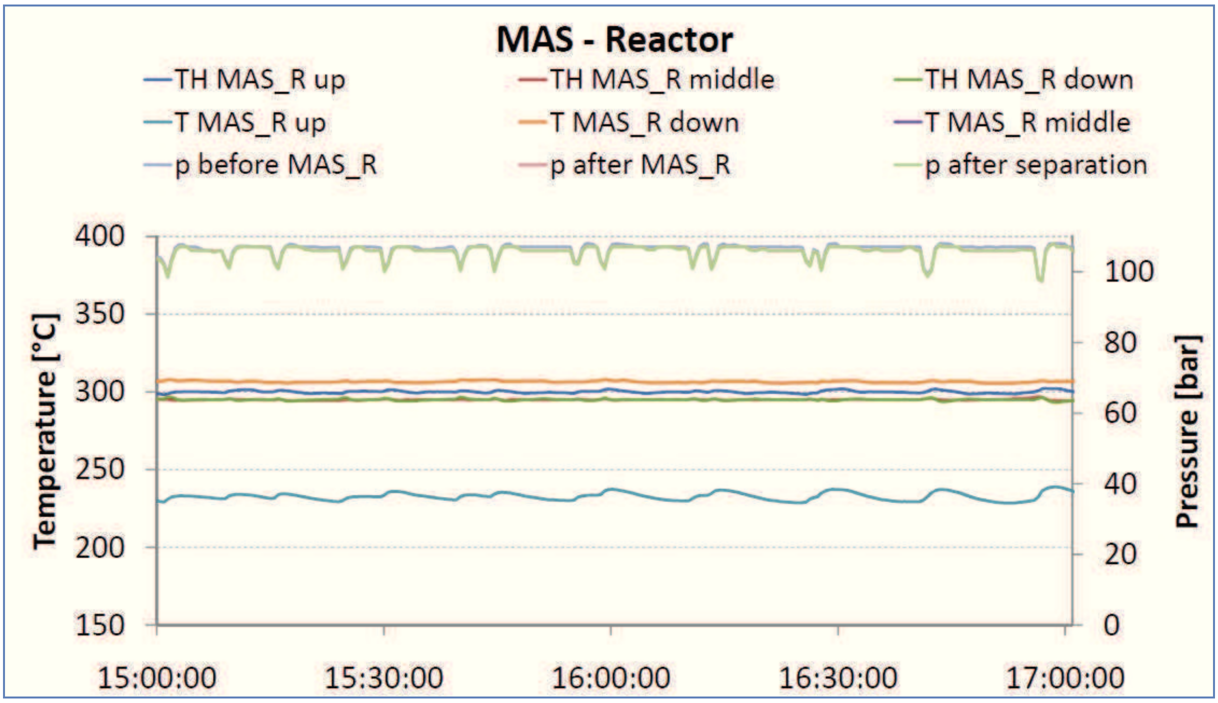
Experiment no. 2 (100 bar, 290 °C, 3,4 m$_n$³/h)



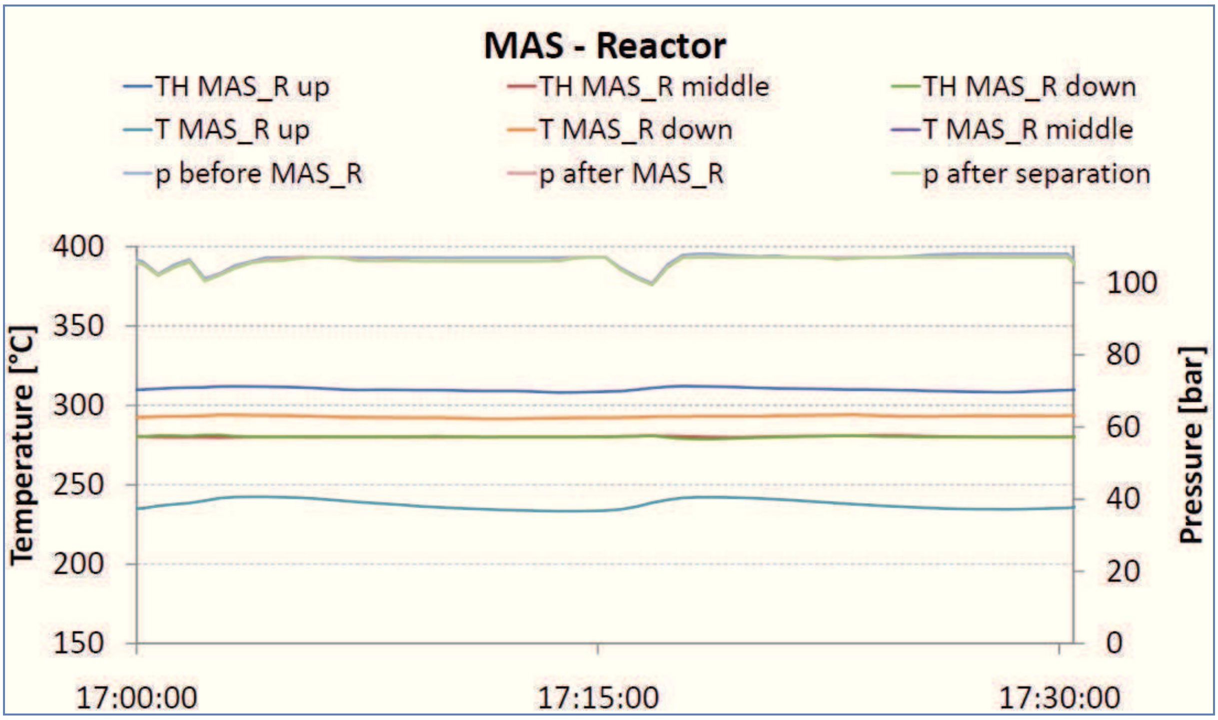
Experiment no. 3 (100 bar, 300 °C, 4,8 m$_n$³/h)



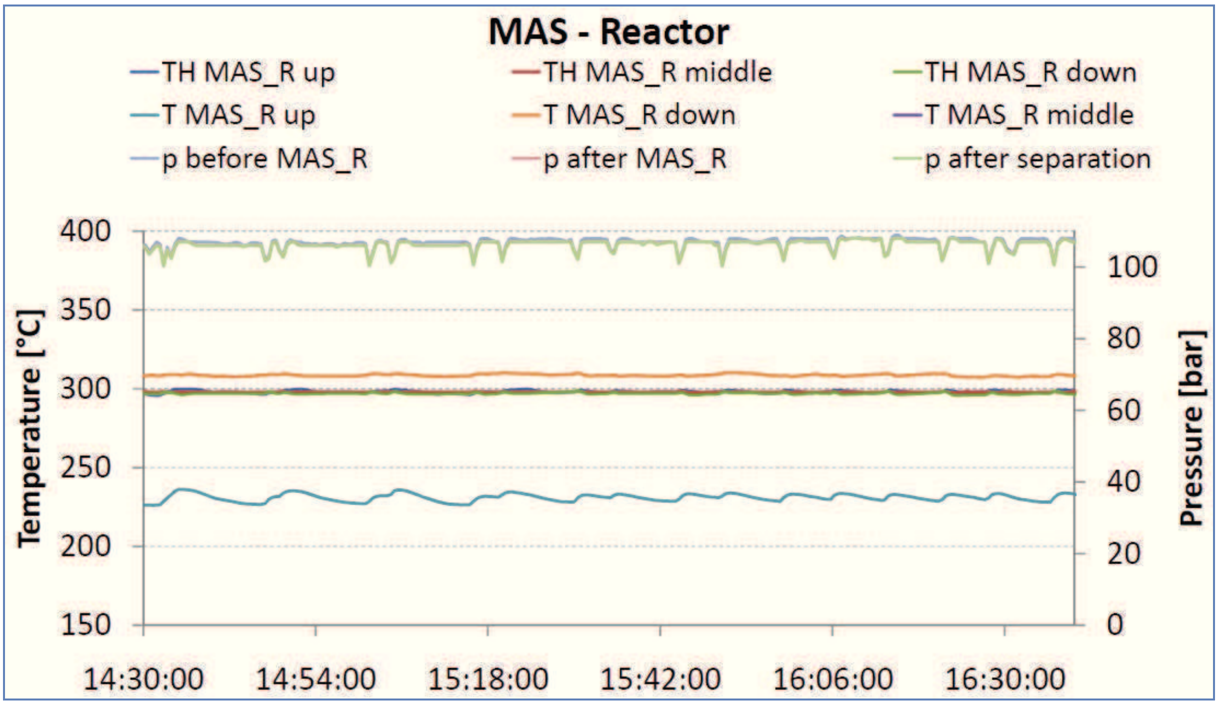
Experiment no. 4 (100 bar, 300 °C, 4,7 m$_n^3$/h)



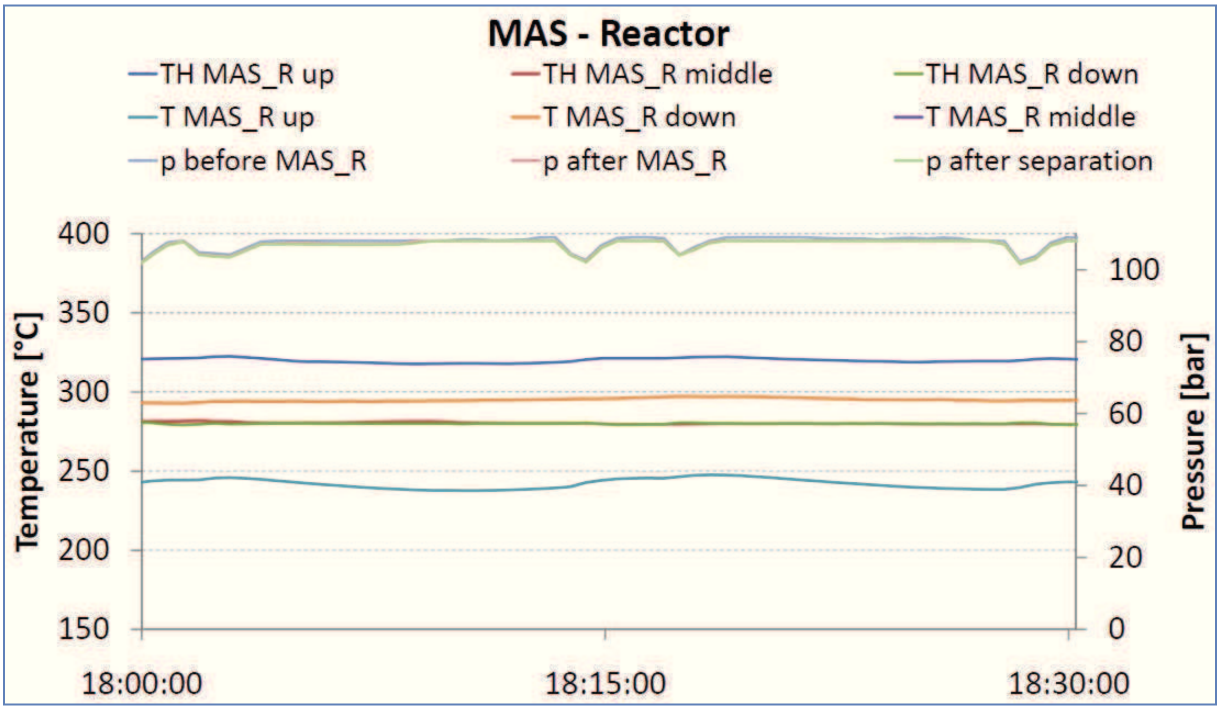
Experiment no. 5 (100 bar, 310 °C, 5,0 m$_n^3$/h)



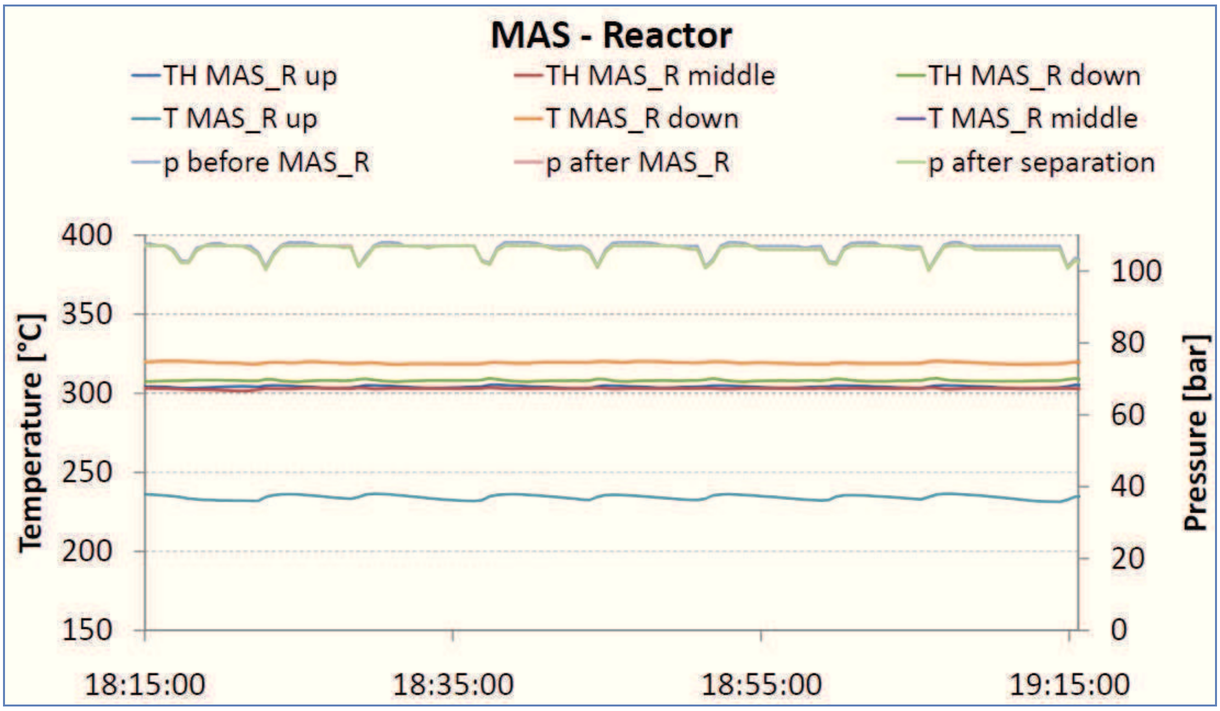
Experiment no. 6 (100 bar, 310 °C, 5,7 m_n^3/h)



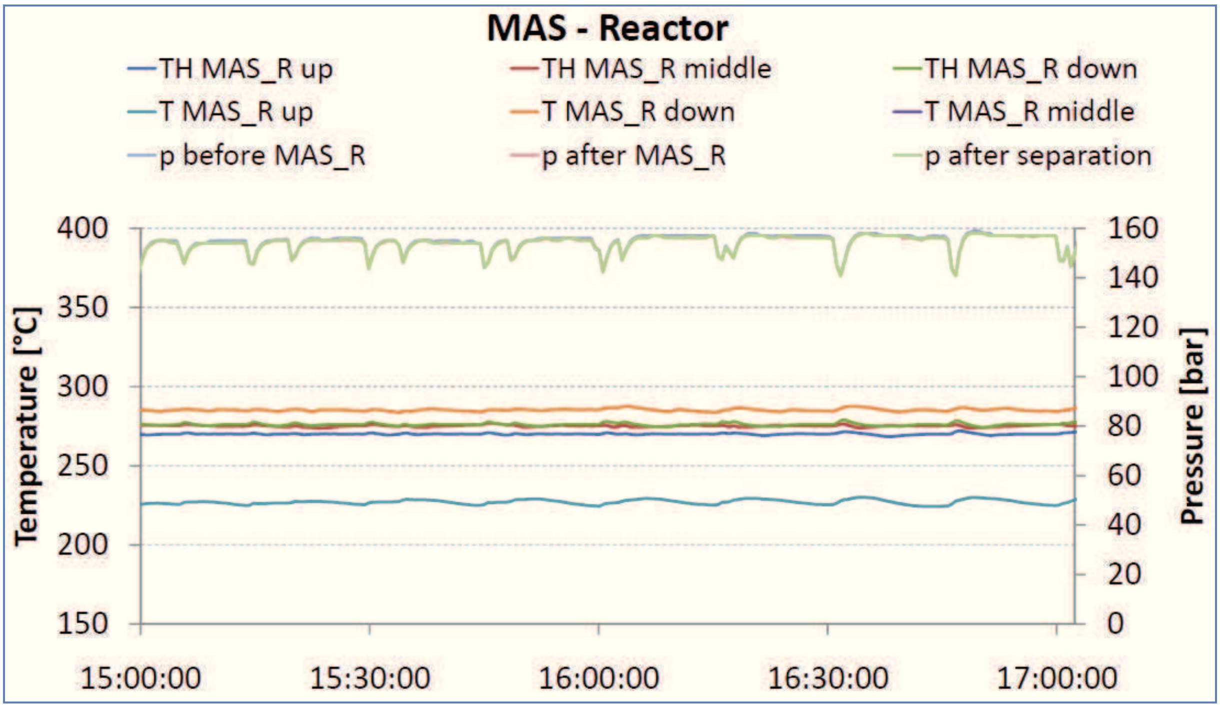
Experiment no. 7 (100 bar, 320 °C, 4,7 m_n^3/h)



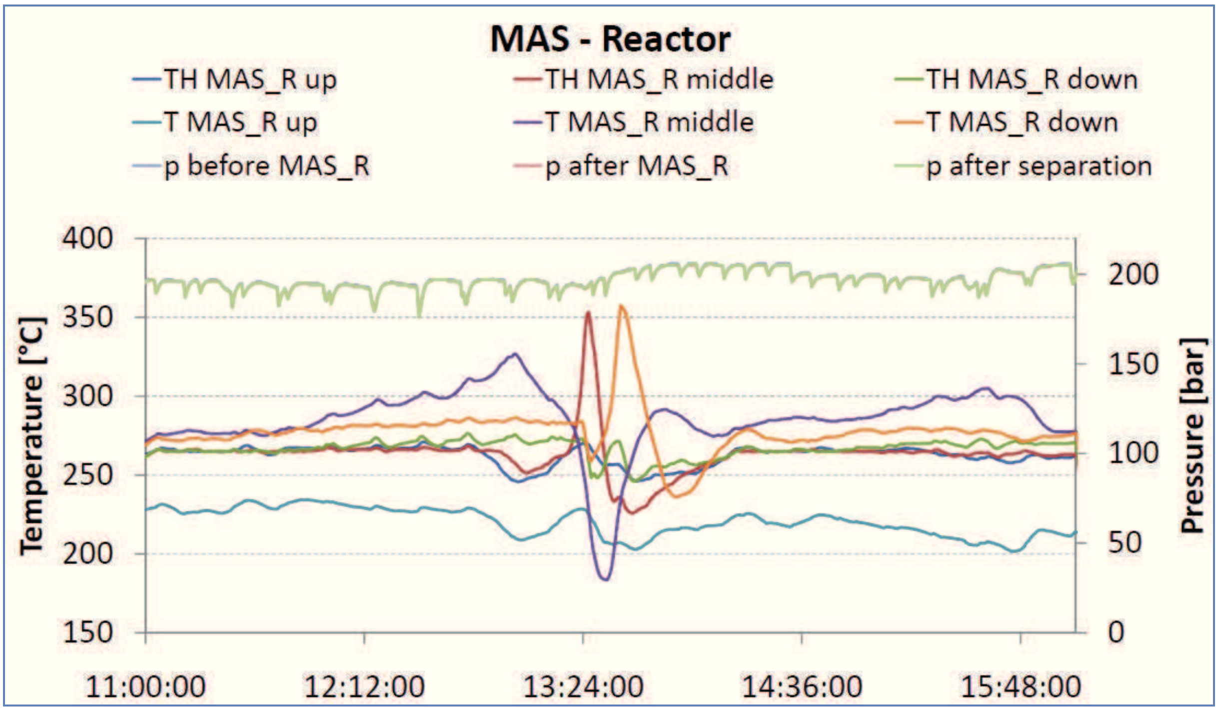
Experiment no. 8 (100 bar, 320 ℃, 4,8 m $_n$³/h)



Experiment no. 9 (150 bar, 300 ℃, 3,5 m $_n$³/h)



Experiment no. 10 (200 bar, 280 ℃, 2,5 m$_n$³/h)

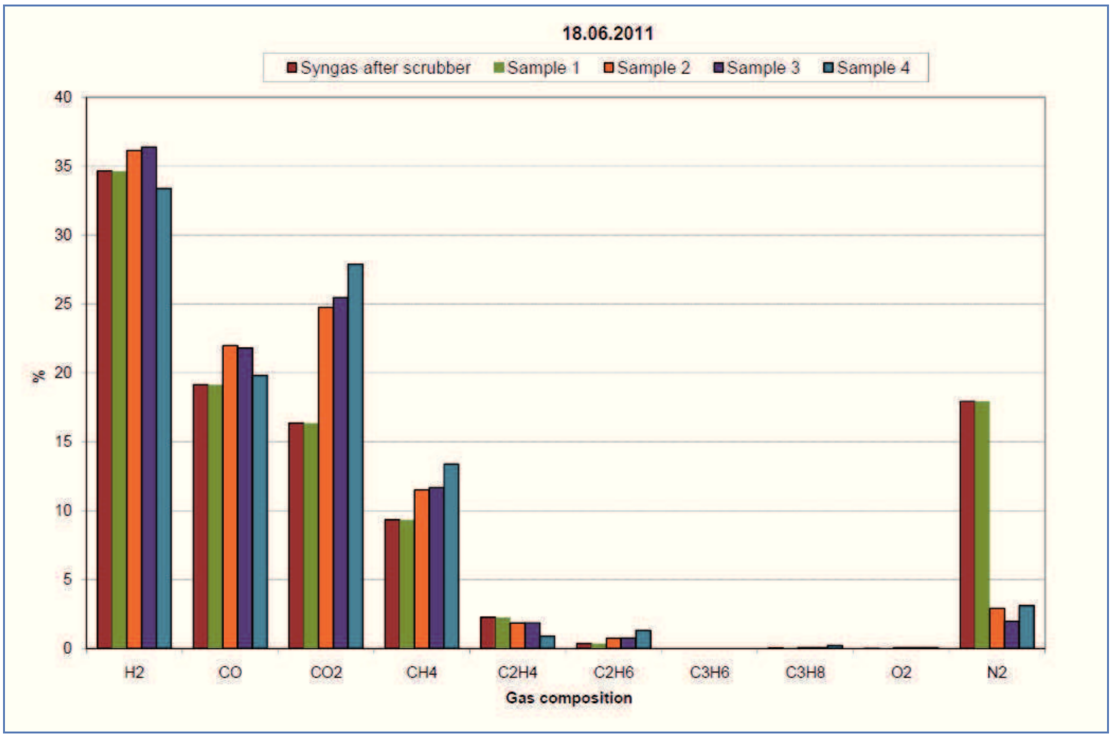


8.6 Gas analysis

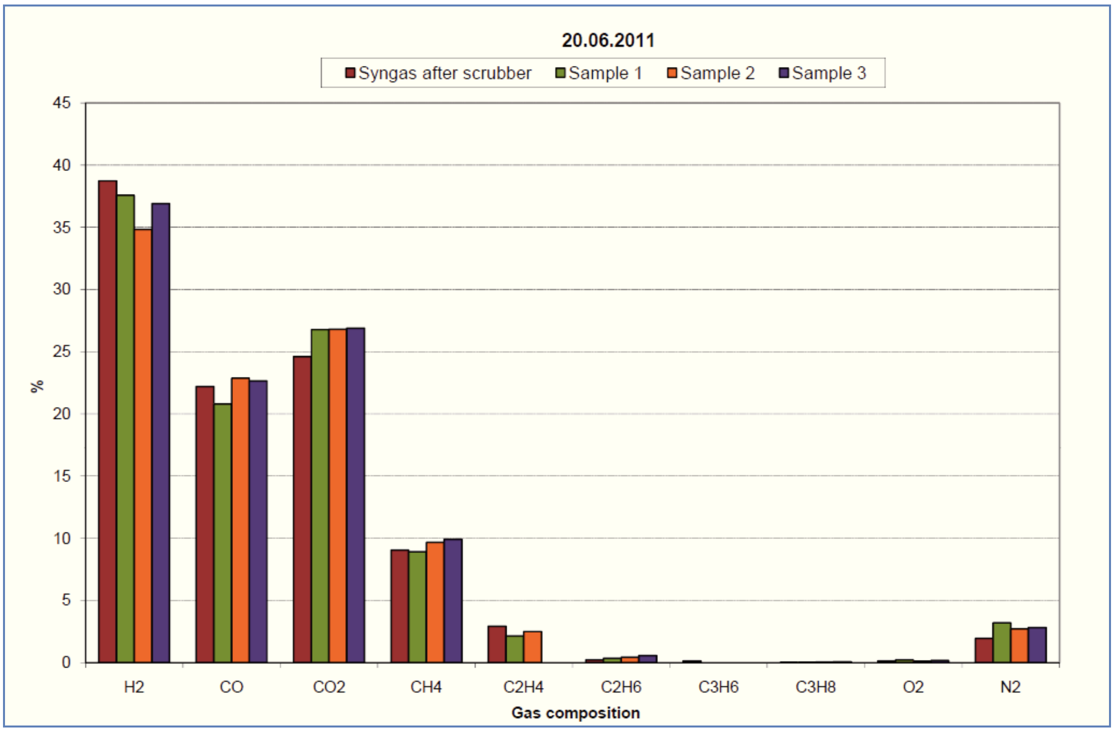
Overview of gas composition

Sample	Gas composition [vol%]									
	H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	O_2	N_2
Experiments 2011-05-18										
SG after scrubber	37.1697	23.6492	22.3297	10.8351	3.5989	0.2655	0.2392	0.0336	0.2671	1.6120
Sample 1	34.6338	19.1240	16.3415	9.3324	2.2490	0.3533	0.0000	0.0300	0.0034	17.9326
Sample 2	36.1351	21.9814	24.7574	11.5031	1.8439	0.7398	0.0000	0.0747	0.0657	2.8989
Sample 3	36.3854	21.7896	25.4543	11.6763	1.8636	0.7549	0.0000	0.0710	0.0521	1.9528
Sample 4	33.3771	19.8039	27.8658	13.3717	0.8931	1.3088	0.0000	0.2108	0.0641	3.1047
Experiments 2011-06-20										
SG after scrubber	38.7221	22.2022	24.5958	9.0552	2.9320	0.2296	0.1458	0.0268	0.1390	1.9515
Sample 1	37.5751	20.7901	26.7722	8.9092	2.1515	0.3531	0.0000	0.0331	0.2151	3.2006
Sample 2	34.8264	22.8662	26.7957	9.6779	2.5067	0.4474	0.0000	0.0467	0.1149	2.7181
Sample 3	36.9004	22.6546	26.9029	9.9182	0.0000	0.5727	0.0000	0.0619	0.1695	2.8198
Experiments 2011-06-21										
SG after scrubber 1	36.9988	21.9420	24.3334	8.7560	2.8608	0.2521	0.1471	0.0288	0.2622	4.4188
SG after scrubber 2	38.8307	21.6114	24.6597	8.6264	2.8498	0.2482	0.1499	0.0279	0.2611	2.7349
Sample 1	36.4581	22.2956	25.4880	9.2399	2.3883	0.4602	0.0000	0.0001	0.2397	3.4301
Sample 2	37.2352	22.2219	25.4596	9.2828	2.4233	0.4593	0.0000	0.0431	0.0980	2.7768
Sample 3	36.6982	22.2555	25.2329	9.5990	2.3804	0.5062	0.0000	0.0475	0.2704	3.0099
Experiments 2011-06-22										
SG after scrubber	41.0458	21.9295	23.8049	8.2770	2.7194	0.2437	0.1387	0.0230	0.1557	1.6623
Sample 1	38.4931	21.7225	24.8087	8.4270	2.3563	0.4050	0.0000	0.0370	0.3602	3.3902
Sample 2	39.1881	20.8769	24.7203	8.2084	2.2726	0.4034	0.0000	0.0347	0.0782	4.2174
Experiments 2011-06-28										
SG after scrubber	41.7285	20.5879	22.6574	7.4334	2.3567	0.2399	0.0977	0.0240	0.5769	4.2976
Sample 1	41.1809	21.1133	23.7630	7.7023	1.9856	0.3612	0.0000	0.0296	0.4480	3.4161
Sample 2	41.3903	21.1075	24.3711	8.1067	2.0889	0.3838	0.0000	0.0316	0.1525	2.3676
Experiments 2011-06-29										
SG after scrubber	40.2920	20.7769	23.5580	8.3327	2.6829	0.2562	0.1231	0.0287	0.4845	3.4650

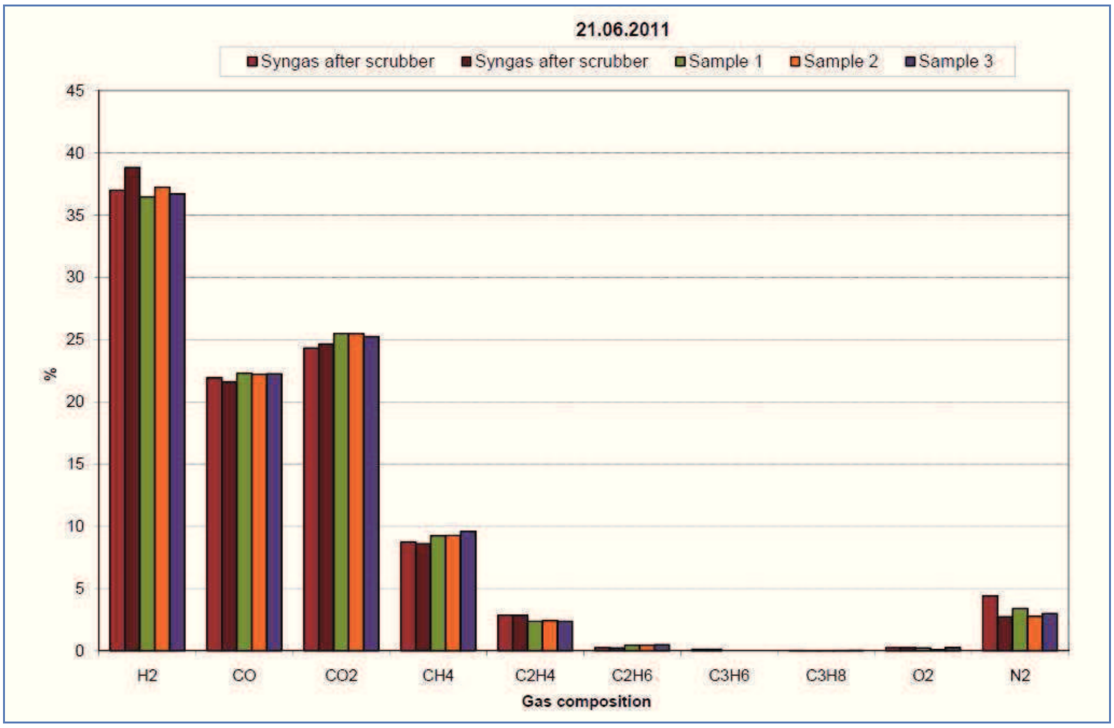
Gas composition 2011-05-18



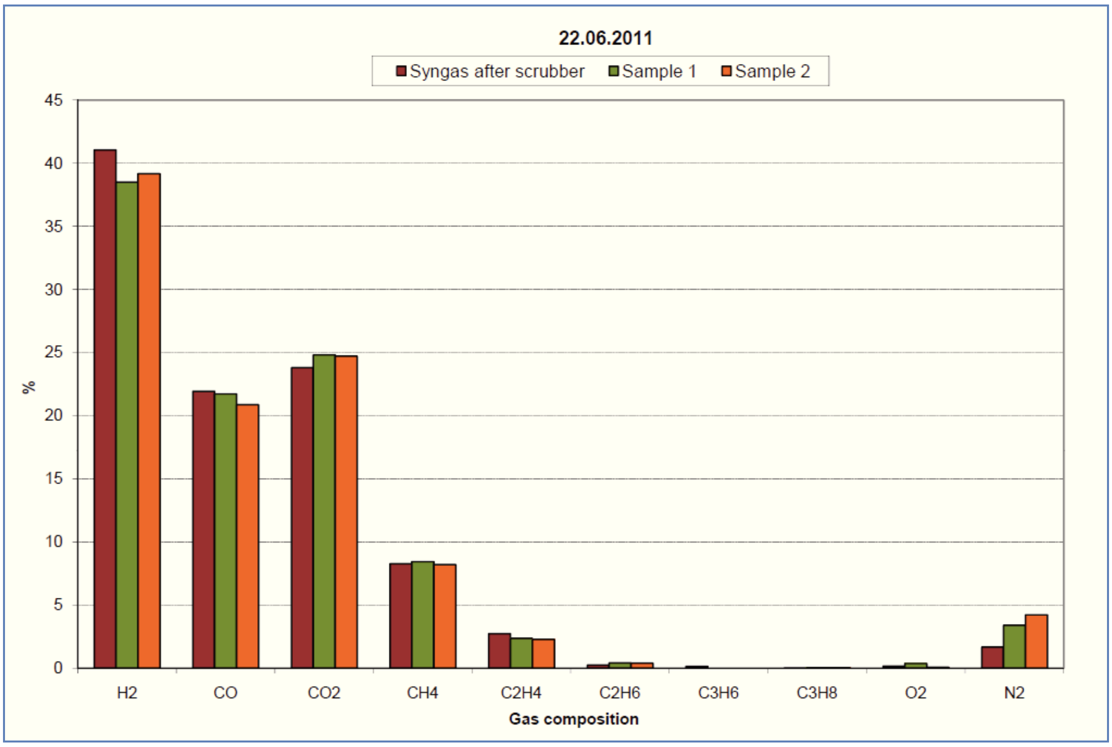
Gas composition 2011-06-20



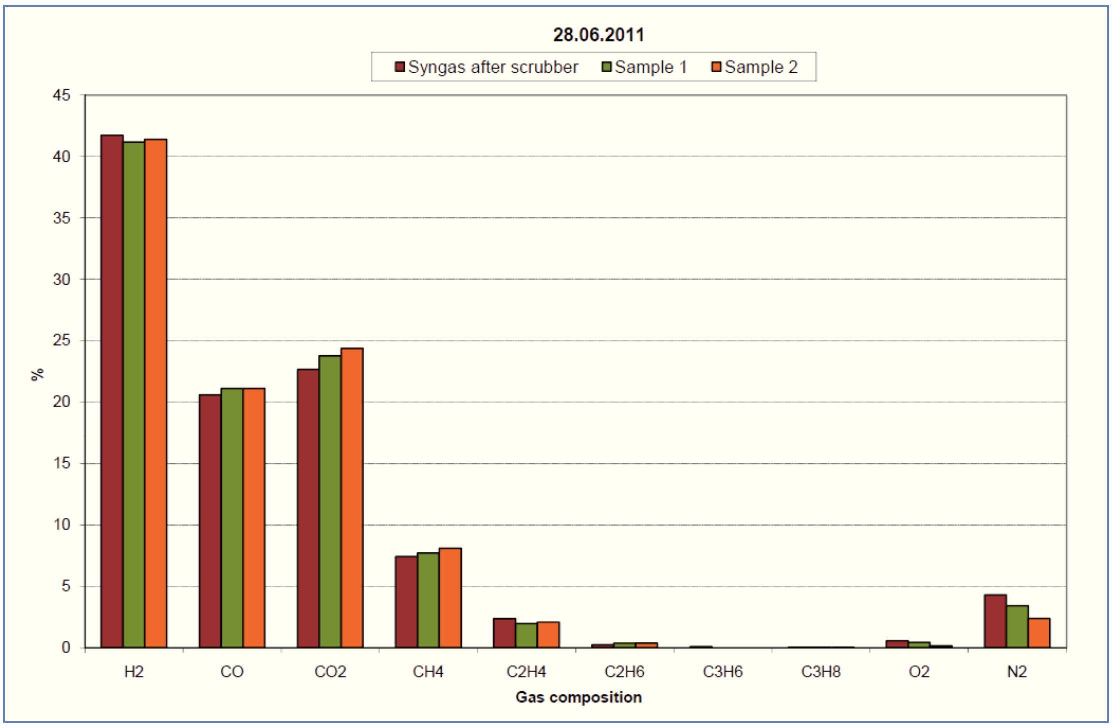
Gas composition 2011-06-21



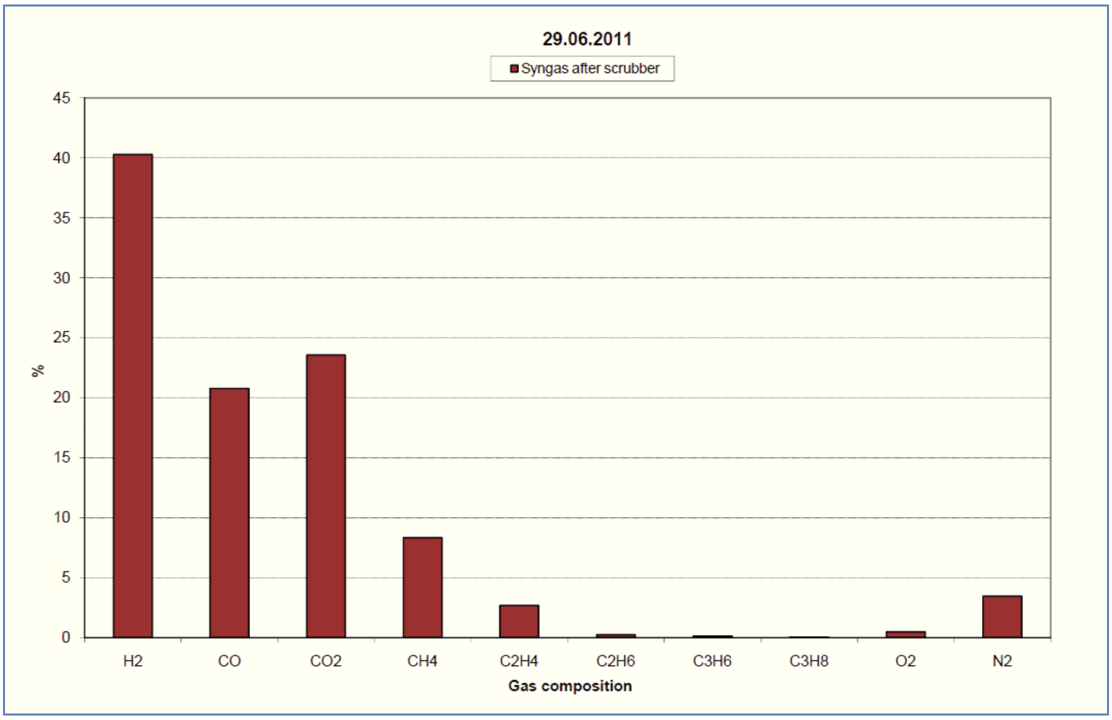
Gas composition 2011-06-22



Gas composition 2011-06-28



Gas composition 2011-06-29

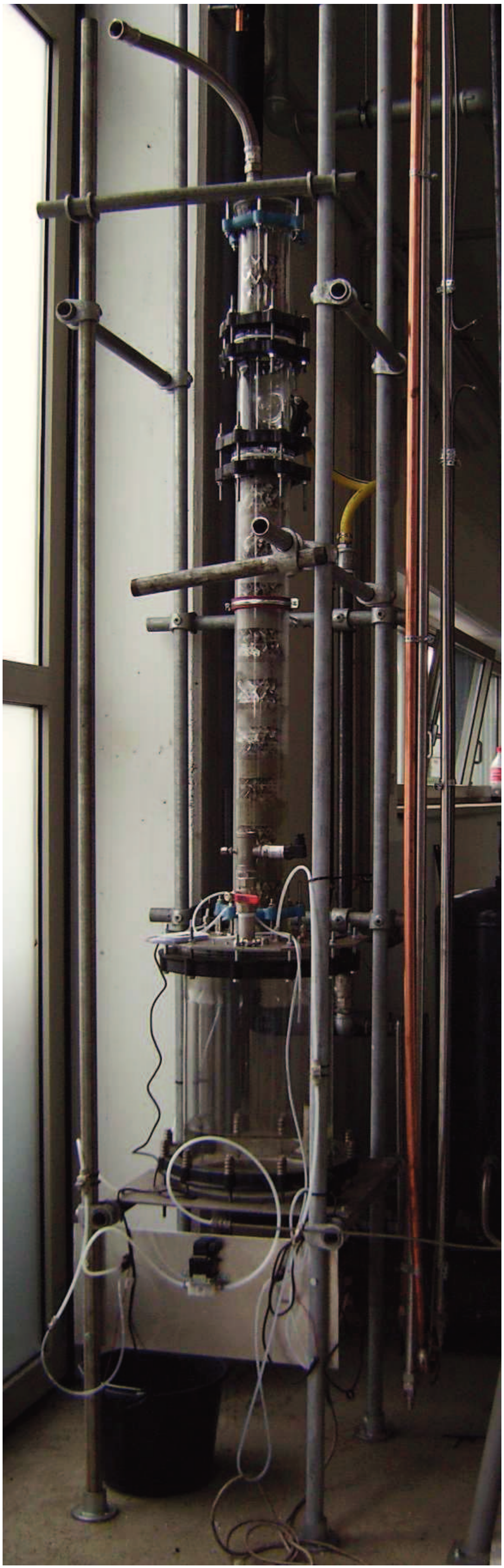


8.7 Pictures of the plant

MAS pilot plant

Steam Reformer

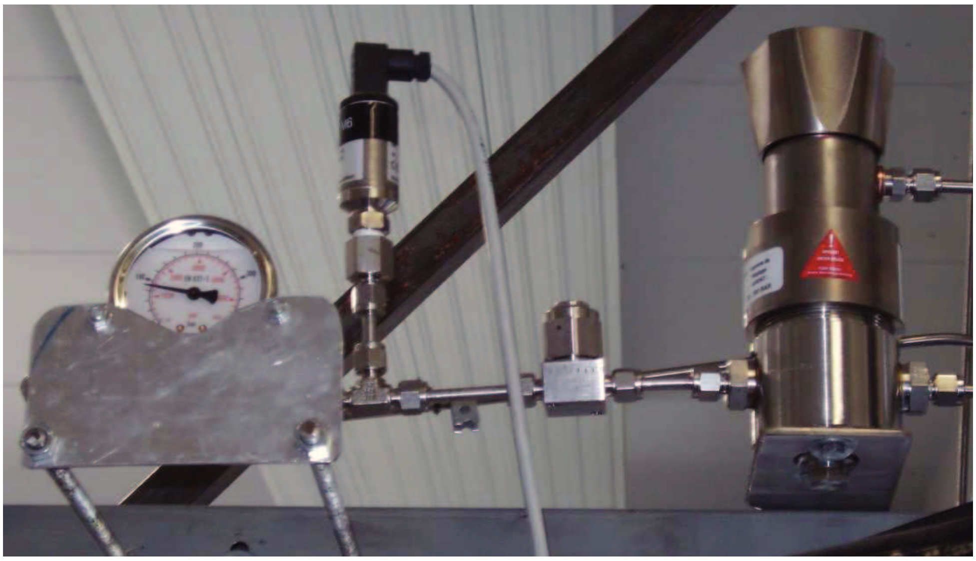
Scrubber



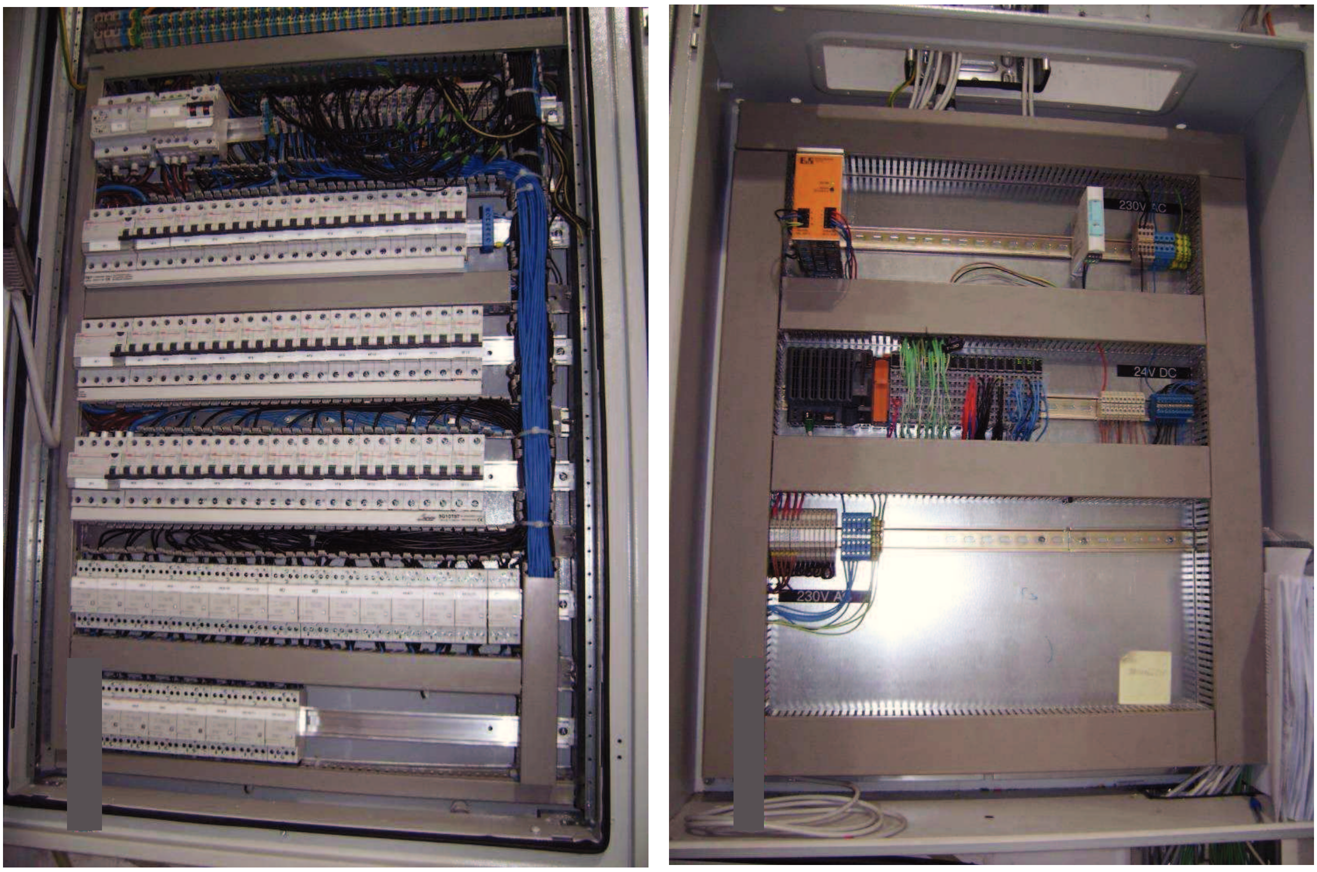
Gas meter

Compressor

Expansion valve including pressure measurement



Enclosures for electric installation and control system



Measuring station

Three-way valve to tail gas/blow off line

Scrubber, reactor, condenser and steam reformer