A REVIEW OF THE PROCESS STEPS FOR PRODUCING ADVANCED BIOFUELS THROUGH THERMO-CHEMICAL CONVERSION OF BIOGAS

Report from a project within the collaborative research program *Renewable transportation fuels and systems*

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THE SWEDISH KNOWLEDGE CENTRE
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PREFACE

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f3 Swedish Knowledge Centre for Renewable Transportation Fuels is a networking organization which focuses on development of environmentally, economically and socially sustainable renewable fuels, and

- Provides a broad, scientifically based and trustworthy source of knowledge for industry, governments and public authorities
- Carries through system-oriented research related to the entire renewable fuels value chain
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EXECUTIVE SUMMARY

Research and development on using biomass as feedstock for production of different biofuels has been studied for a long time, however, experience at large scale is a challenge. Most of the technologies on the market have been developed for processing fossil fuels, like crude oil or coal.

Thermochemical conversion of biomass for production of synthetic transport fuels using gasification is a promising way to meet these goals. One of the key challenges in using gasification systems with biomass and waste as feedstock is the upgrading of the raw gas produced in the gasifier. These materials replacing oil and coal contain large amounts of demanding impurities, such as alkali, inorganic compounds, sulphur and chlorine compounds.

Ideally the upgraded syngas consists of H_2 and CO at a correct ratio with very low water and CO_2 content allowed. This means that the tars, particulates, alkali salts and inorganic compounds must be removed for most of the applications. By using oxygen as the gasifying agent, instead of air, the content of nitrogen may be minimised without expensive nitrogen separation.

This report focuses on on-going research and development to find new technology solutions and on the key critical technology challenges concerning the purification and upgrading of the raw gas to synthesis gas and the subsequent different fuel synthesis processes, such as hot gas filtration, that can lead to better heating solutions and a higher degree of process integration as well as catalysts more resistant towards deactivation. This means that the temperature should be as high as possible for any upgrading unit in the refining system. Nevertheless, the temperature and pressure of the cleaned synthesis gas must meet the requirements of the downstream application, i.e. Fischer-Tropsch diesel, methanol etc. This report does not focus on the gasification concepts, as this already been covered earlier [1].

The product gas from the gasification process contains impurities deriving from the biomass in form of tars, particulates, and inorganic compounds, such as HCl, NH_3, COS, H_2S, and alkali salts. These compounds need to be removed from the raw gas, to some extent, depending on the end application desired.

Depending on the gasification technology and process conditions used for a specific feedstock a relatively large quantity of tars may be produced. The problem with tars is that they can, even at very low concentrations, create troubles in further down-stream equipment by plugging filters, pipes and cause coking of catalysts in the upgrading processes of the syngas. This is also one of the key troubles stopping the commercialisation of the gasification technology.

There are several applications with respect to produced synthesis gas to be used as different biofuels or green chemicals. The major applications will be discussed, starting with the production of hydrogen and then followed by the synthesis of synthetic natural gas, methanol, dimethyl ether, Fischer-Tropsch diesel and higher alcohol synthesis, and describing alternatives combining these methods. The SNG and methanol synthesis are equilibrium constrained, while the synthesis of DME (one-step route), FT diesel and alcohols are not. All the reactions are exothermal (except for steam reforming of methane and tars) and therefore handling the temperature increase in the reactors is essential. In addition, the synthesis of methanol must be performed at high pressure (50-100 bar) to be industrially viable.

The aim of the report is to establish the state-of-the-art concerning the cleaning and upgrading of the raw gas to synthesis gas from biomass through thermo-chemical conversion and the subsequent different fuel synthesis processes.

SAMMANFATTNING

I flera decennier har man satsat mycket på forskning och utveckling för att kunna använda biomassa som råvara för produktion av olika biobränslen, idag är den stora utmaningen att få erfarenhet i stor skala och få lönsamhet i processerna. De flesta teknikerna som finns tillgänglig på marknaden har utvecklats för att processa fossila bränslen, som råolja eller kol.

Termokemisk omvandling av biomassa är ett lovande sätt för att producera olika sorters syntetiska drivmedel, då främst genom förgasningsteknik. En av de främsta utmaningarna i att använda termokemisk omvandling av biomassa och avfall är rening och uppgradering av rågasen som produceras i förgasaren. Dessa biobaserade material som är tänkta att ersätta olja och kol innehåller betydande mängder av alkaliska-, oorganiska-, svavel- och klor-föreningar.

Idealt består en syntesgas som har blivit uppgraderad av vätgas och kolmonoxid, i önskade förhållande, med mycket låga halter vatten och koldioxid. Detta innebär att tjäror, partiklar, alkalisalter och oorganiska föreningar, som nämnts tidigare, måste avlägsnas för de flesta tillämpningarna. Genom att använda syre som förgasningsmedel, i stället för luft, kan innehållet av kväve i gasen minimeras, så man undviker efterföljande dyrbar separation av kväve.

Denna rapport fokuserar på pågående forskning och utveckling för att hitta ny teknik och lösningar när det gäller rening och uppgradering av rågas till syntesgas, samt efterföljande bränslesyntesprocesser, såsom hetgas-filtrering, som skulle kunna ge smartare uppvärmnings lösningar och högre grad av integrering av processerna, samt utveckling av katalysatorer som är mer tåliga mot deaktivering. Detta innebär att temperaturen bör vara så hög som möjligt för varje enskild renings- och en uppgraderingsenhet, likväl måste temperaturen och trycket hos den renade syntesgasen uppfylla kraven för nedströms bränslesyntes, d.v.s. Fischer-Tropsch-diesel, metanol etc. Denna rapport fokuserar inte på de olika förgasningskoncepten vilka redan behandlats i en tidigare rapport [1].

Produktgasen från förgasningsprocessen innehåller orenheter som kommer ifrån biomassan i form av tjäror, partiklar och oorganiska föreningar, såsom HCl, NH_3, COS, H_2S och alkalisalter. Dessa föreningar behöver avlägsnas från produktgasen till olika koncentrationer beroende på den önskade slutanvändningen. Beroende på vilka processförhållanden och förgasningsteknik som används för ett specifikt råmaterial kan relativt stora mängder tjäror produceras. Problemet med tjära är att de även i mycket låga koncentrationer kan orsaka problem i efterföljande nedströmsprocesser genom att bland annat sätta igen filter och rördelar, samt även förgifta katalysatorer i de efterföljande uppgraderingsprocesserna för att framställa olika biobränslen. Tjärproblematiken är också en av de viktigaste utmaningarna som behöver lösas för att lyckas med kommersialiseringen av förgasningstekniken.

Det finns ett antal olika användningsområden för olika producerade syntesgaser beroende på vilka biobränslen eller gröna kemikalier man väljer att tillverka. De olika tillämpningarna diskuteras i rapporten med start av produktion av vätgas, följt av framställning av syntetisk naturgas (SNG), metanol, dimetyleter, Fischer Tropsch-diesel och syntes av högre alkoholer, samt beskrivningar av metoder som kombinerar dessa. Processystemen är olika för de olika slutprodukterna, där syntes av SNG och metanol begränsas av exempelvis dess jämvikt, medan syntes av dimetyleter, (DME), FT-diesel och alkoholer inte är jämviktsberoende. Samtliga reaktioner är exoterma, med undantag för

ångreformering av metan och tjäror, vilket medför att det är extremt viktigt att kontrollera temperaturökningen i reaktorerna. Dessutom måste syntes av metanol utföras vid höga tryck (50–100 bar) för att vara industriellt gångbar.

Syftet med rapporten är att redogöra för den senaste tekniken inom rening och uppgradering av rågas till syntesgas från biomassa för processer som använder termokemisk omvandling och även för de efterföljande processerna för att syntetisera de olika biobränslena.

CONTENTS

1 INTRODUCTION

Gasification of biomass to produce synthetic fuels via syngas is a demanding technology with many problems to solve. For example, high temperature filtration, reforming or partial oxidation of hydrocarbons (tars and other hydrocarbons), poisoning and deactivation of the catalyst, ammonia cracking, sulphur purification, etc. In addition to established synthetic processes, such as methanol, Fischer-Tropsch methane there is on-going research and development of new processes such as for ethanol, mixed alcohols and fermentation of synthesis gas. There is intensive research and development in the area, and it is important to follow the research frontier.

Production of synthetic fuels via synthesis gas also typically generates large amounts of excess heat and energy-rich waste gases. This means that it is also interesting to follow the development of these synthesis processes from an energy perspective.

In Sweden, biomass stands for a significant share of the energy demand. About a third was produced from biomass in 2015, however this included the bulk fuel in the pulp and paper industry as well as heat for heating. In the transport sector fossil fuels dominate, of a total of about 90 TWh is only 10 % is produced from biofuels (ethanol, RME and biogas). A major source of biomass is logging residues from forestry. Different studies give different results, but 10-50 TWh of forest by-products seem to be available in total. Biomass gasification is a key process to produce renewable transport fuels and a range of different kinds of biomass and waste resources may be converted.

Production of synthetic fuels from synthesis gas, such as Fischer-Tropsch diesel, has been known since the 1920s, from fossil fuels such as coal, and today most of the methanol used in the world is produced from reformed natural gas. There are several different gasification techniques for biomass and waste conversion to produce fuels for transportation as well as chemicals. In Figure 1 the different applicable processes, depending on fuel selected, gasification technology as well as down-stream application are illustrated. For production of high calorific syngas from waste or biomass, there are typically two gasification technologies suitable, one is operating at a high temperature, 1100-1300ºC, using an entrained flow gasifier, the other operating a fluidised bed gasifier coupled with a down-stream catalytic reformer, both working close to 900ºC [2].

Gasifying using entrained flow gasifiers is an established technology especially using coal as fuel, however solid waste and biomass cannot directly be introduced into the entrained flow gasifier and therefore pre-treatments of the inlet biomass, such as pyrolysis and torrefaction techniques are necessary or by modifying the feeding system.

Gasification of biomass using fluidised bed techniques is a less mature method, however the fluidised bed technology has already been demonstrated using waste and biomass for heat and/or electricity production.

In any case, to succeed economically in producing transportation fuels as well as green chemicals by using either gasification technique, compact pressurised systems are necessary together with an overall efficient conversion system for large-scale production.

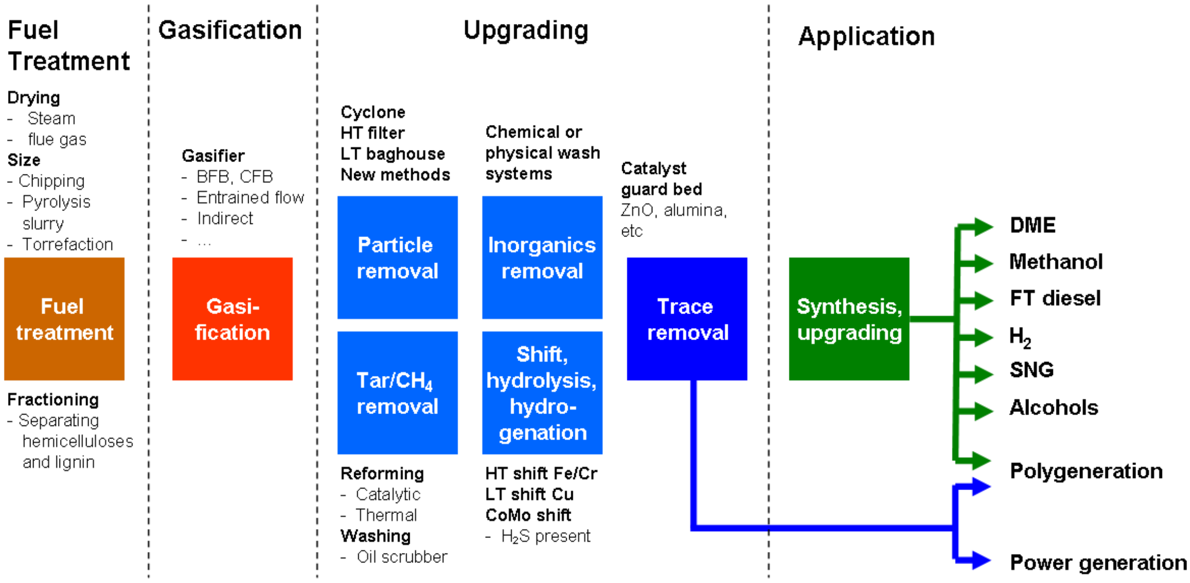

Figure 1. Overview of different processes that may be included in a biomass gasification system [3].

Gasification of biomass to produce synthesis gas, however, makes quite different demands on the purification and upgrading of product gas than the gasification of fossil fuels does. The product gas contains large amounts of dust, ash, alkali and charcoal, tars and other hydrocarbons, sulphur compounds (H_2S, COS) and ammonia [4]. Tars and hydrocarbons must be converted into synthesis gas (CO_2, CO, H_2) or be utilised otherwise to achieve good energy efficiency and economy [5]. This upgrading is made difficult by the presence of impurities in the gas and this must be solved in some way. When the gas is upgraded and purified, the composition may be adjusted so that it fits the selected synthesis step. If the synthesis gas is clean enough, the source (renewable or fossil) has no role in the synthesis step. The usual syntheses are commercial and facilities available from engineering companies. New processes are, however, being developed and it is important to monitor developments [6].

In the gasification process a carbonaceous fuel, e.g. coal or biomass, is reacted with air or oxygen (and in some cases steam) to yield a gas. This is normally performed at temperatures between 500ºC and 1400ºC, with pressures ranging from atmospheric to 35 bar. This is performed for many reasons:

- Improved efficiency for electricity production, via combined cycle
- Gas that may be distributed/used in a more efficient manor than biomass/coal
- The gas may be used as basis for fuel and/or chemical production

The first useful gasifier was constructed during the 1840s in France and the technology has been in development ever since. The intensity of the development, especially for fuel and chemical production, has to a large extent been dependent on the crude-oil price. Something that became very evident after the oil crisis during the 1970s, when intense development was commenced in Austria, Sweden, Finland and the US, aiming at producing substitutes for oil. During the 1990s the development focussed on the production of electricity and demonstration plants were built in Värnamo in Sweden and in the UK.

1.1 GASIFICATION CHEMISTRY

The gasification process is divided into four stages, depending on what is happening to the biomass in the gasifier. Firstly, the moisture in the biomass is removed until it is completely dry. Secondly, pyrolysis occurs which is a process that removes non-condensable gases and tar from the biomass. The biomass, in turn is, transformed into charcoal. Thirdly, some of the charcoal as well as the flammable part of the permanent gases react with the oxygen in the gasifier. This exothermal reaction of charcoal and flammable gases with oxygen provides the heat to the other three stages of gasification. The oxygen supplied to the system is enough to make the system self-sustaining in heat. The needed quantity of oxygen depends on several factors such as:

- moisture content of the biomass
- the amount of steam introduced
- the heat losses associated with the gasification

Finally, the last stage is reduction where charcoal and hydrocarbons react with gaseous carbon dioxide and water to form carbon monoxide and hydrogen; the different stages are summarised in Figure 2.

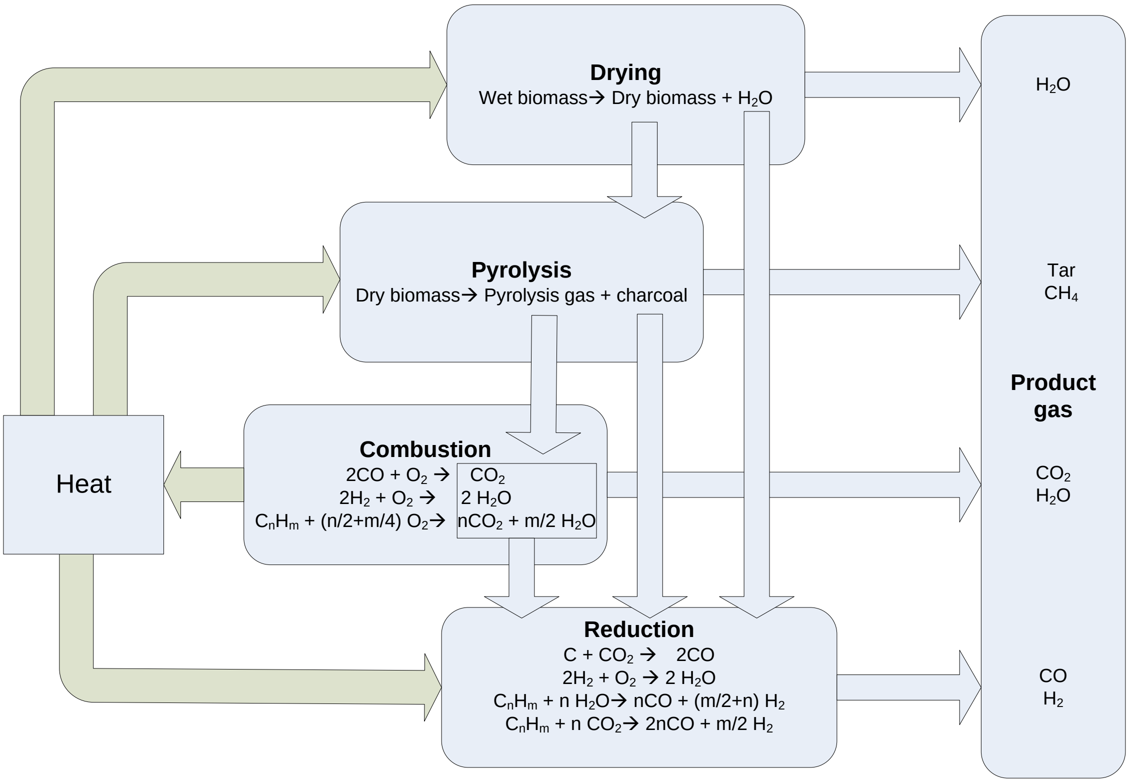

Figure 2. Schematic overview of the four gasification stages [7], reproduced with permission.

The exit gas from the gasifier will contain CO, CO_2, H_2O, H_2, CH_4, other gaseous, higher hydrocarbons and N_2 (the N_2 content is strongly correlated to the oxidant used). The gases aside, tar, charcoal and ash are obtained as liquids/solids, and the gas will also contain traces of HCN, NH_3, HCl, H_2S and, in addition, there will be traces of other nitrogen and sulphur-containing compounds.

The exit levels of the main products for some gasifier types are reported in Table 1. In the table some other factors that are important for results or controlling parameters when operating these systems are also reported.

Table 1. The gasifier exit levels for some fluidised bed gasifier types, Atmospheric Circulating Fluidised Bed (ACFB), Pressurised Circulating Fluidised Bed (PCFB) and Indirectly heated gasifier.

	Unit	ACFB	PCFB	Indirect
CO	Vol-%	26.9	16.1	42.5
H_2	Vol-%	33.1	18.3	23.1
CO_2	Vol-%	29.9	35.4	12.3
CH_4	Vol-%	7	13.5	16.6
N_2	Vol-%	0.7	12.3	0
C_2	Vol-%	2.4	4.4	5.5
H_2/CO-ratio	-	1.2	1.1	0.5
Energy in CH_4+C_2	%	36.2	65.1	54
Energy in H_2	%	32.7	17.2	14.5

In addition to the main components formed and reported in Table 1, there is also the formation of significant amounts of tar. The structure, measurement and conversion of these species is a field of intensive research and several definitions of tar compounds have arisen. In the following, one will be given:

> *very complex heterogeneous aqueous mixtures of organic molecules (aromatics, phenols, bases, asphaltenes, preasphaltenes, and particulate matter) in a broad range of concentrations related to the formation conditions (temperature, residence time pressure, feedstock, reactor design)* [8].

The amount of tar in the exit gas of the gasifier is very dependent on the design and operation of the gasifier. The tar functional groups and temperatures of formation may be schematically depicted as:

Mixed oxygenates (400ºC) → Phenol ethers (500ºC) → Alkylphenols (600ºC) → Heterocyclic phenols (700ºC) → Polyaromatic species (800ºC) → Larger polyaromatic species (900ºC)

Another way to distinguish the different tars from each other is to divide them into three classes. The formation temperature of the tars determines these classes and the classes are described in Figure 3.

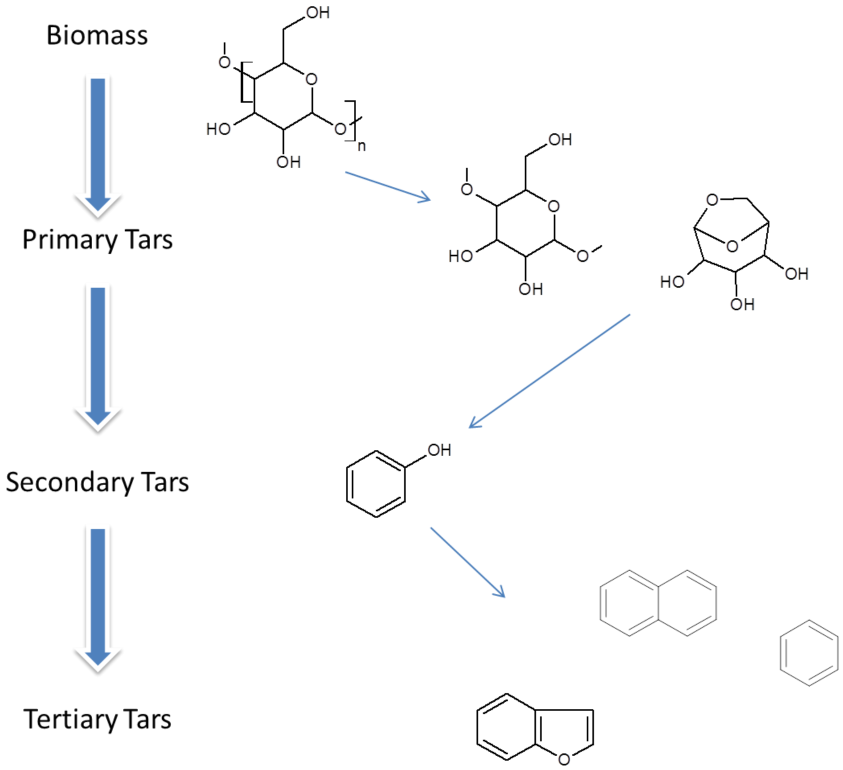

Figure 3. The first classes of tars and their origin [9], reproduced with permission.

These tar classes form at various temperatures. There will also be transitions from one class to another with increasing temperature. The primary tar class is present at 500ºC to 800ºC, the secondary tar class between 500ºC and 1000ºC, the alkylated tertiary products (class 3) are present between 650ºC and 1000ºC while the condensable tars (class 4) exist above 750ºC. The tar formation and the change from one class of tar to another is dependent on residence time as well as temperature.

1.2 GASIFICATION AGENTS

The high temperature in the gasifier decomposes the organic material in the biomass into volatile components and char by pyrolysis. To gasify the char a gasification agent is needed. The char may be gasified by oxygen:

$$C(s) + O_2 \rightarrow CO_2(g) + Heat \qquad (A)$$

$$C(s) + 1/2O_2 \rightarrow CO(g) + Heat \qquad (B)$$

The heat produced contributes to driving the pyrolysis of the solid material and to reactions that occur in the gas phase.

The char may also be gasified by steam and carbon dioxide:

$$C(s) + H_2O(g) + Heat \rightarrow CO(g) + H_2(g) \qquad (C)$$

$$C(s) + CO_2(g) + Heat \rightarrow 2\ CO(g) \qquad (D)$$

In those cases, heat is consumed. If oxygen is present, those reactions (C and D) occur in parallel with (A and B) and consume a part of the released heat. Without oxygen, for instance in a pure steam gasification process, the necessary heat must be provided by an external source, i.e. indirect gasification. This is the case for the Güssing type of gasifiers, for instance the ones used in the GOBIGAS project.

If oxygen is the gasification agent, either air or oxygen may be chosen. If air is chosen, the gas produced, in the gasifier will be diluted by a large amount of nitrogen (N_2), normally air-blown gasifiers are not used for biofuel production. This results in a larger amount of produced gas with a lower heating value, and the nitrogen needs to be separated. An air-blown gasifier produces a gas with a Low Heating Value (LHV) of 3.5-6 MJ/Nm^3 while oxygen blown gives a gas with a LHV of 10-15 MJ/Nm^3 [10].

2 UPGRADING

2.1 PARTICLE REMOVAL

Particulates in the syngas may also cause problems by blocking and erosion downstream in the upgrading equipment. Particulates deriving from the gasification consist of a mix of ash from the biomass, formed char and bed material from the fluidised bed [6]. For circulating fluidised bed gasification systems, cyclone separators are normally used to remove larger particulates, and recycle bed material and char back to the gasifier. Different baghouse and barrier filters are used for smaller particulates at temperatures below 350ºC such as, woven polymeric and ceramic materials or natural fibres. Candle filters, both ceramic and metallic, are used for higher temperatures up to 700ºC [11]. Fine dust particles follow the gas stream and clog the equipment downstream. To treat the gas, it must be free from particulate matter and it is desirable to remove the dust as close to the gasifier as possible. This means that the dust must be removed at high temperature.

2.1.1 Cyclones and multicyclones

Cyclones are mechanical separators, by centrifugal forces, of solid material. A multicyclone consists of an array of smaller cyclones in parallel with common inlet and outlet. By dividing the total flow on several small cyclones, the radius of each individual cyclone becomes smaller and the particles in the gas will experiences a larger centrifugal force. This leads to a higher degree of separation of the solid matter than in a single large cyclone. However, even in a multicyclone, the lower limit for efficient particle separation is in the range of 1-2 µm [12]. Depending on the construction material, for instance lining with refractory oxides, cyclones may be used at high temperature.

2.1.2 High-temperature filters

Filters are good for removing dust from streaming gases, such as flue gases from combustion. Baghouse filters consists of a bundle, of long tube shaped, filter bags made of fabric. The dirty gas is introduced into the baghouse, and particulate material, like dust and ash, is separated on the outside of the filter bags. This deposition builds up a filter cake, and the pressure drop over the filter bag increases. When the pressure drop becomes high enough, the filter is regenerated, or cleaned, by back-blowing. The solid material that falls off is collected in the bottom of the bag house and then removed. Bag filters may be used up 200-250ºC with temperature-resistant fabric.

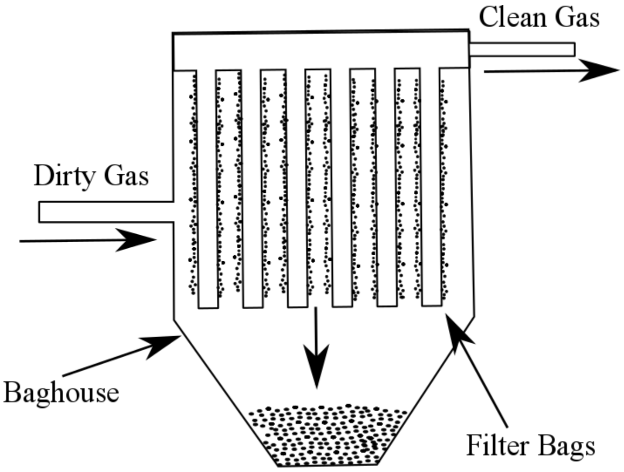

Figure 4. Schematics of a baghouse filter.

However, in biomass gasification there is a need to remove the dust at much higher temperature and it is typically performed at 350-500ºC [13]. This is done using the sintered metal or ceramic equivalent to the bag filter, the candle filter. Fabric and ceramic filters have been used both in demonstration and commercial plants, such as the Värnamo gasification plant in Sweden [14] and the Güssing Biokraftwerk [15] in Austria. In both plants the fabric filters were run at 160-180ºC and the ceramic filters at 340-370ºC.

However, cooling the gas to enable filtration and then re-heating the gas for further processing, deceases the efficiency of the gasification plant. Still, running the filters at high temperature (>500ºC) has caused problems by clogging. Tars and soot are suggested to cause the clogging by formation of a sticky cake [13]. Not only the temperature affects the performance but also the fuel and bed material. Simone et al [15] claim that with a correct choice, for instance with magnesite as bed material and clean wood it was possible to run the filter at 800ºC, while miscanthus clogged the filter at similar conditions.

Dia-Schumalith candle filters [13] were used in a 100 kWt atmospheric circulating fluidised bed gasifier between 600 and 800ºC for more than 50 h. The filter cake formation was studied with gas face velocities between 3 and 5 cm/s. Stabile filtrations were achieved in some tests.

Combined filters for dust removal and catalytic tar removal have been developed for a long time. The filters typically work at 800-850ºC and in the presence of 100 vppm H_2S. An evaluation using real gas reports a tar conversion of 81 % at 790ºC and 40 vppm of H_2S. The active material is usually traditional Ni supported on a thermostable carrier [16], [17]. The gasification plant in Lahti uses ceramic high temperature filters [18].

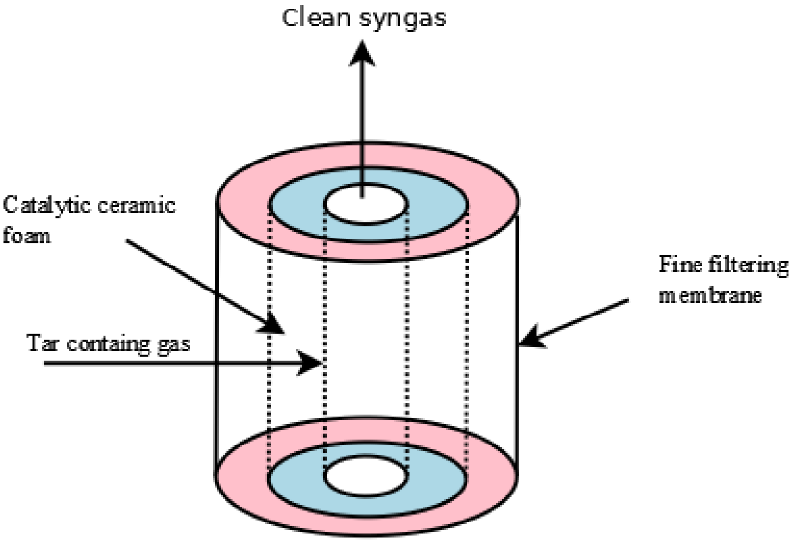

Figure 5. Catalytic candle filter [19].

2.2 TAR REMOVAL

Tars produced in the gasifier may be removed by different techniques from using wet scrubbing and condensation to simultaneously removing water from the raw gasification gas. The latter is not optimal since carbon and hydrogen are stored in the tars, and it also produces a large amount of wastewater with high organic content that later must be further cleaned.

The tars may also be divided into nonwater-soluble compounds, i.e. aromatics, and so-called water-soluble compounds, i.e. phenols. Tars will cause enormous problems in the process if not taken care of, this since different gasifiers produce different amounts of tars.

Table 2. Operating conditions for fluidized bed and entrained-flow gasifiers [20].

	BFB	**CFB**	**EF**
Temperature (ºC)	< 900	< 900	~ 1450
Tars	Moderate	Moderate	Very low
Control	Moderate	Moderate	Complex
Scale (MW_{th})	10-100	20- 500	>100
Feedstock	Less critical	Less critical	Only fines

To eliminate the tars from the producer gas, one could either remove the tars from the gas or convert the tars in the gas.

2.2.1 Tar scrubbing

Tars could be removed from the gas by scrubbing with a liquid medium, such as water or FAME (Fatty Methyl Esters). However, the gas must be sufficiently cool for the medium, hot gas will evaporate part of the water added and FAME will coke if the temperature is too high. An interesting example is the OLGA scrubbing technique [21], that uses oil as scrubbing medium, the oil taking up the tars is then recirculated to the gasifier where the energy content in the tar is recovered to the process.

The disadvantage of scrubbing using a liquid medium is the need for cooling the gas before the cleaning step; this decreases the total efficiency of the process.

This means that scrubbing the gas will be suitable for some plant operations, e.g. for use in gas engines for electric power production, since cool gas has higher energy density than hot gas. However, for synthesis gas production to perform synthesis of liquid fuels, a cooler gas is not wanted. Removal of the tars will reduce the chemically bound heat content of the gas, decreasing the yield of fuels that may be produced. In Table 3 the composition of the gas produced in the gasifier in Värnamo is shown, approximately 10 % of the heat content (LHV) in the gas is in the form of tars.

Table 3. Gas composition from the Värnamo gasifier [22].

Component	**After Gasifier**	**LHV wet**	**LHV wet**
	Vol %	MJ/Nm^3	MJ/kg
C_2-C_4	1.6	0.9	0.9
CH_4	8.2	3.1	2.8
CO	11.9	1.5	1.4
CO_2	27.9		
H_2	11.8	1.3	1.2
H_2O	37.7		
NH_3	0.3		
H2S	0.01		
Tars	0.3	0.7	0.6
LHV (total)		7.5	6.8

After removal, the tarry liquid also must be taken care of. Usually, tars are burnt in the process to generate heat for the gasification. This is done in Güssing [21] where the spent scrubber liquid (FAME+ tar) is burnt to heat the bed material in an external riser. In Harboøre the separated heavy tar is stored in tanks and burnt during the peak loads in winter to produce district heating.

2.2.2 Tar Cracking

The difference between tar cracking and tar reformation is that during the tar cracking, only large molecules are broken down while during reforming all hydrocarbons (including tars) are broken down into synthesis gas components (CO, CO_2 and H_2). The catalytic cracking should be carried out at or near the gasification unit, to improve the yield of the syngas and to minimise the organic compounds (tars) ending up in the produced waste water when the raw gas is cooled to remove the water content in the syngas.

Dolomite is a commonly used tar cracking catalyst. It consists of CaMg $(CO_3)_2$. This is a naturally occurring mineral and, depending on its original, it can contain varying amounts of impurities; it has been shown that iron can improve the activity. To activate the catalyst, it has to be calcined into CaO-MgO [19].

$$CaCO_3 \leftrightarrow CaO + CO_2$$

$$MgCO_3 \leftrightarrow MgO + CO_2$$

However, this reaction is reversible, this means that the dolomite catalyst is sensitive to the CO_2 partial pressure and can only be used at low pressure (< 10 bar). The dolomite may be used as in-bed catalyst, but it is soft and erodes quickly, for instance in fluidised beds. However, dolomites have low activity for methane reforming in the product gas and are consequently not the best choice for production of syngas alone, but could be used when methane is the desired product [23], [24].

2.2.3 Tar reforming

Steam reforming

Using metal catalysts supported on thermostable carriers, hydrocarbons may be converted into synthesis gas, CO, CO_2 and H_2, by steam reforming.

$$C_nH_m + nH_2O \leftrightarrow nCO + (m/2 + n)\ H_2$$

$$C_nH_m + 2n\ H_2O \rightarrow nCO_2 + (m+4n)/2\ H_2$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

For instance, for methane:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H_r = 205\ \text{kJ/mol}$$

$$CH_4 + 2\ H_2O \leftrightarrow CO_2 + 4H_2 \qquad \Delta H_r = 163\ \text{kJ/mol}$$

The steam reforming reactions are endothermal, i.e. they bind heat. This means that heat must be supplied or the temperature in the reactor will drop. For tar cracking Ni-based catalysts are substantially more efficient compared to dolomites, and are also active for methane reforming [24]. These Ni-based catalysts may also be used in fluidised bed applications. Below in Figure 6, a schematic drawing of a gasification-steam reforming unit is shown.

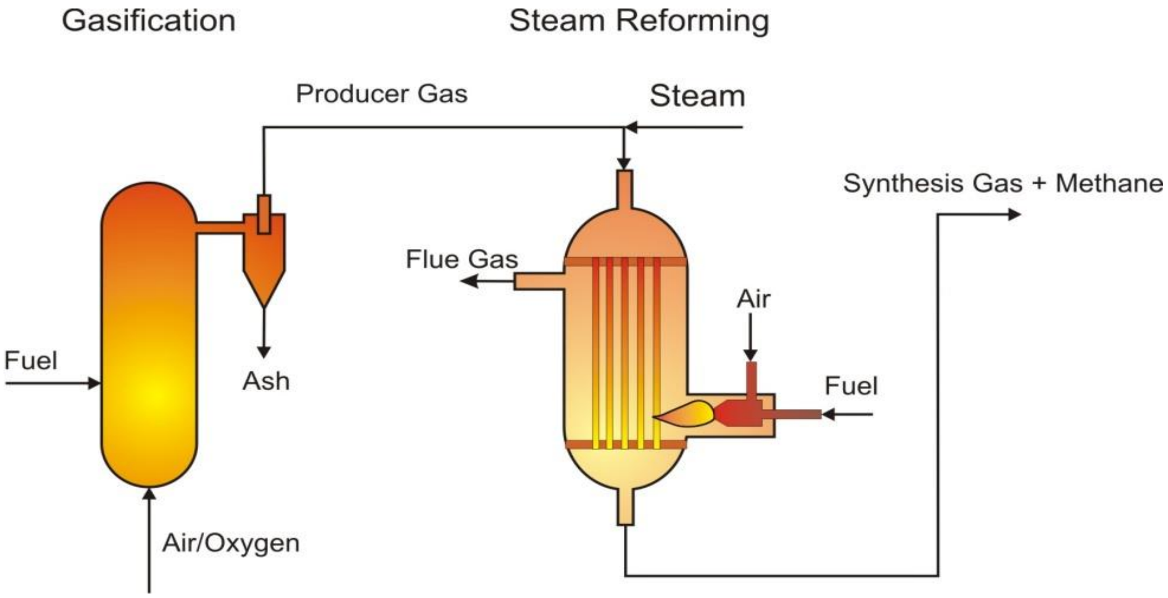

Figure 6. Schematic drawing of a gasification-steam reforming unit.

Since heat must be transferred to the reaction, the reactor consists of a bundle of narrow tubes, containing the catalyst. Heat is provided by a burner that heats the tubes from the outside.

The hydrocarbons will react and form synthesis gas. There is, however, an equilibrium between the formed synthesis gas and methane. The equilibrium may be shifted by addition of steam as can be seen in Figure 7.

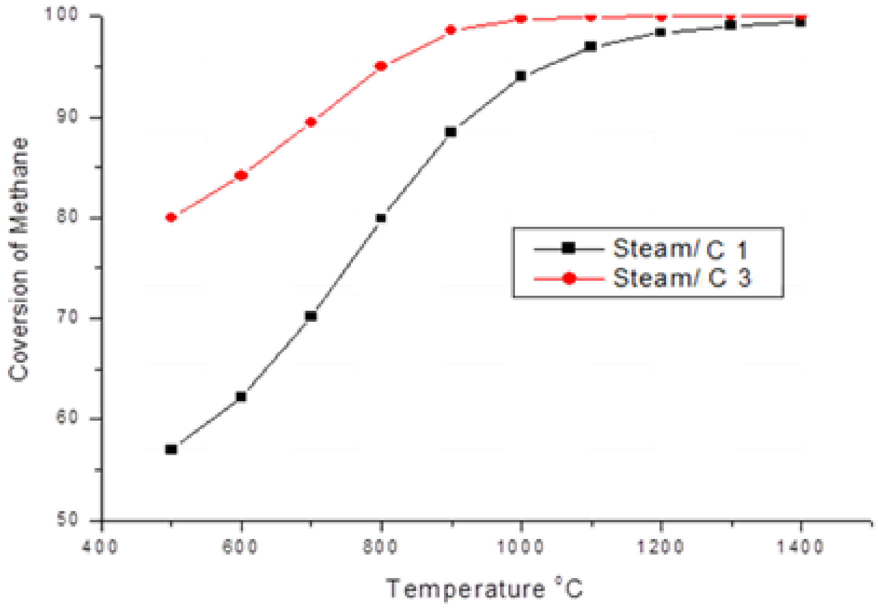

Figure 7. Steam reforming of methane at steam to carbon ratios 1 and 3, 101 kPa.

In the steam reforming reaction, the total number of moles in the gas increases. A consequence of this is that the reaction is pressure dependent, see Figure 8.

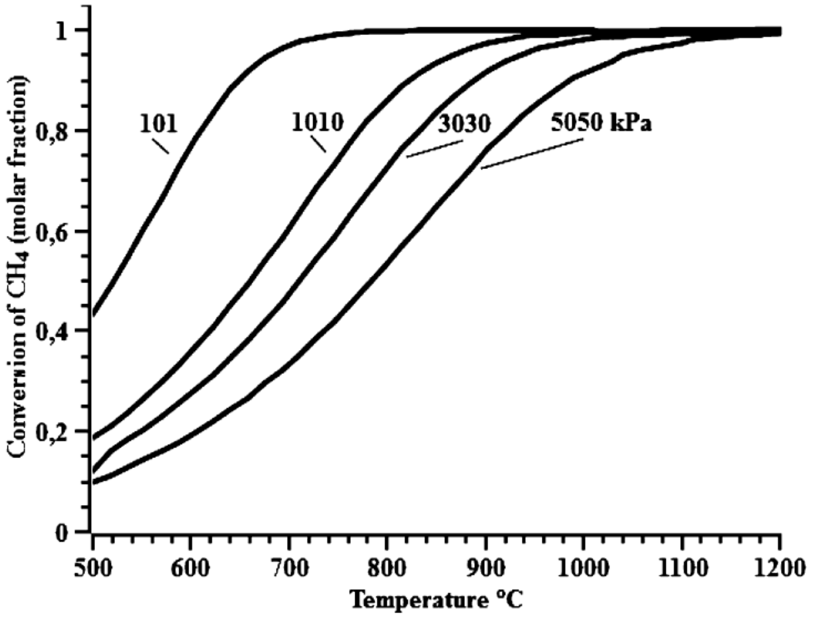

Figure 8. Steam reforming of methane at steam/C=3, pressure dependency of conversion.

Despite the negative impact of high pressure, steam reforming is usually performed at elevated pressure. The reason for this is that the production capacity of the unit becomes much higher.

The catalyst normally used is metallic nickel supported on α-alumina or spinel. Also, precious metals are active for the reforming reaction but are not commonly used in industrial applications. Depending on the amount of dust in the producer gas, either a packed (clean gas 1-10 mg/Nm^3) or a monolithic bed (dusty gas 10-30 mg/Nm^3) may be used [25]. This is a parallel to Selective Catalytic Reduction (SCR) of nitrogen oxides from combustion plants. To obtain a sufficiently high reactor temperature for the reaction, the catalytic bed must be placed before the dust removal. If the monolithic bed is correctly designed, the dust will pass through, in the channels, and will not clog the bed.

Ni catalysts are sensitive to sulphur and the activity drops significantly, if present. However, the activity may be restored by increasing the operating temperature. The activity loss due to sulphur poisoning is also increased at elevated pressures. This is due the adsorption of hydrogen sulphide (H_2S) on the surface of the Ni crystallites, see Figure 9. An increase in temperature decreases the surface coverage of hydrogen sulphide, freeing surface for the reforming reaction and an increased pressure increases the surface coverage by sulphur, decreasing the accessible surface for the reforming reaction.

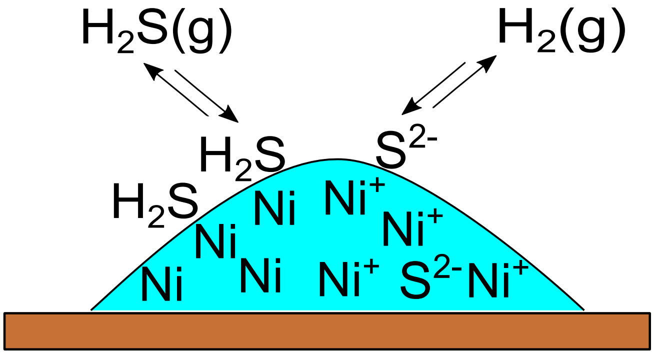

Figure 9. Adsorption of hydrogen sulphide on supported nickel.

The adsorbed hydrogen sulphide also oxidises the metallic Ni, in the bulk of the crystallite, into Ni^+ under formation of hydrogen H_2. This leads to a gradual conversion of the metallic crystallite into NiS by incorporation of S^{2-} ions into the bulk of the crystallite. This conversion, or partial conversion, of metallic Ni into NiS gives rise to an accumulation of sulphur in the catalyst. The formation of NiS is reversible but the reformation of metallic nickel goes slowly and even if the sulphur is removed from the inlet gas stream the catalyst reforming activity is hampered for a long time. This effect may be seen in Figure 10.

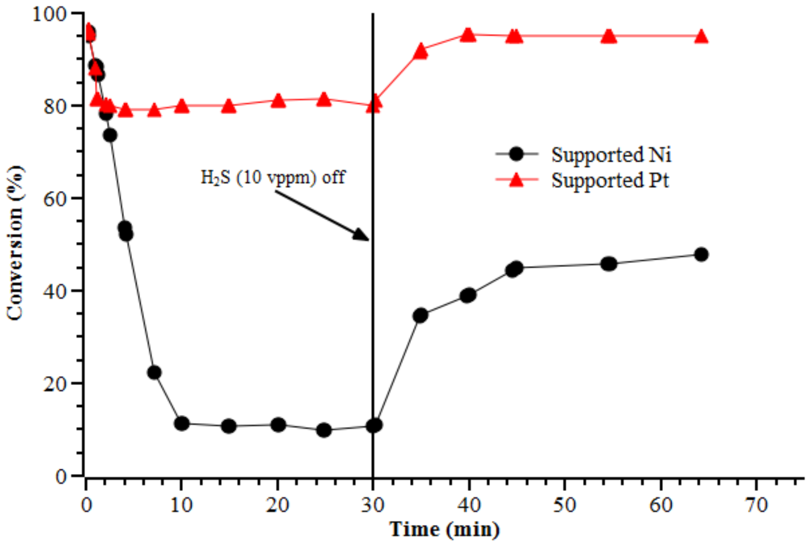

Figure 10. The hydrogen sulphide sensitivity of Ni and Pt supported catalyst. T=800°C, GHSV 450 000 h^{-1}, gas composition: 64 dm^3 methane/h, 188 dm^3/h steam, 150 dm^3/h N_2 and 150 dm^3/h H_2 [26].

The Pt catalyst is more resistant towards sulphur poisoning than the Ni catalyst. The spot market price for Pt (August 2015) was in the range of 200 000 SEK/kg while the nickel price is in the range of 10 SEK/kg. This means that the active material in a kg of Pt catalyst (1 w%) costs 2000 SEK compared to a nickel catalyst (10 w%) for which it costs 1 SEK. Thus, it is difficult to justify the use of Pt catalyst in large-scale industrial applications. It is more economic to use a large quantity of Ni catalyst instead. If the catalytic bed is designed in a proper way it should work even if the hydrogen sulphide level is about 100 vppm.

Topsoe is developing tar reforming catalysts for industrial use [27], see Figure 11. In dusty gas (10-30 g/Nm^3) cylindric megamonoliths, 1000 mm in height and 750 mm in diameter, are used. The megamonoliths are wash-coated metal monoliths. The open canals allow the ash to pass the catalytic bed without clogging.

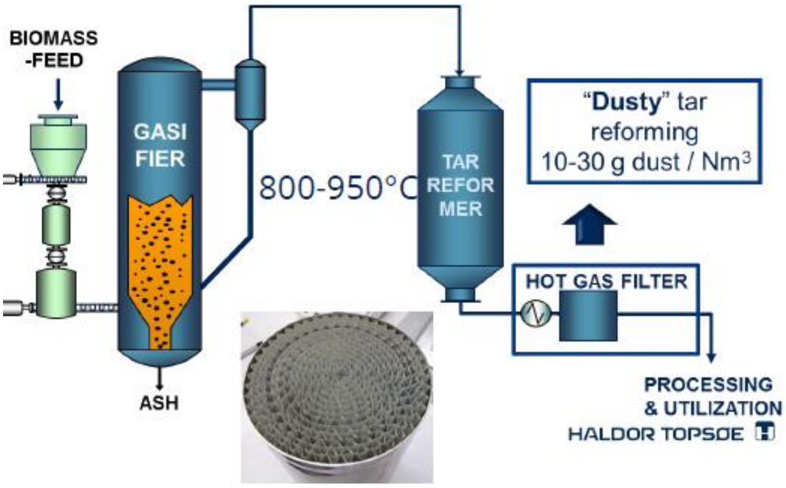

Figure 11. Tar reforming in dusty gas with Topsoe megamonoliths. Courtesy of Topsoe AS.

The megamonoliths are tested in the Skive plant in Denmark and at GTI/Chicago, USA. The research and development plant in Skive is run in cooperation between Skive Fjærvarme and Carbona/Andritz. The nominal thermal output is 19.5 MW with a maximum output of 28 MW and the plant is equipped with catalytic tar reforming. The tar reforming unit is being developed by Topsoe. The plants 3 Jenbacher gas engines produce 6 MW electric power and 11.5 MW heat in combined heat and power production. The electric efficiency is 31 % and the total efficiency is 90 %.

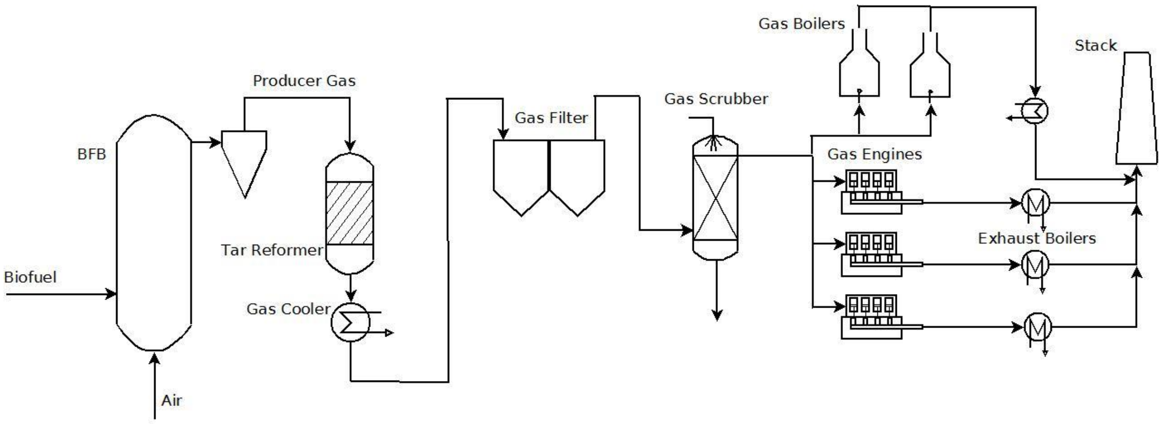

Figure 12. Schematic of the Skive plant (Carbona/Andritz) [28].

The operating temperature for the reformer is restricted by the stickiness of the ash, but in the range of 800-950ºC and 0-20 bar in pressure. Typical hydrocarbon composition of the producer gas is C1-C3, benzene and 1-20 g/Nm^3 tar (mainly naphthalene + 3-6-ring polyaromatics).

Other catalytic materials

As stated above, precious metals are active for the reforming of hydrocarbons, including tars, but are normally not used in industrial scale due to the costs. However, in smaller applications, for instance in hydrogen generators for PEM cells were the performance/size becomes an important factor, precious metal catalysts may be used [29].

A way of improving the sulphur tolerance for Ni catalysts would be to remove the Ni metal bulk that can be converted into NiS. A way to achieve this would be to use atomically dispersed Ni, i.e. to place the Ni as separate atoms on the catalyst surface. In this case there would be no Ni bulk that accumulates sulphur. This is the idea in the development of catalysts where the active material, for instance Ni, is substituted into the lattice of a crystalline material. Figure 13 shows results for a Ni-substituted β-hexaaluminate that is being developed. The hexaluminate is a high-temperature stable material that has been used, substituted by various active materials, in high-temperature catalytic combustion. In Parsland et al this catalyst was tested in a slip stream from a 100 kWt CFB [30]. In Figure 13, the result of two different substitution levels (Ni-1 and Ni-2) are shown at 850ºC and atmospheric pressure. The total amount of tars is in the range of 2-2.5 g/Nm^3 and is measured at three different points with SPA. CFBG is after the gasifier but before the high-temperature filter, bef Cat (before catalys) is at the inlet of the reactor and after Cat (after catalys) is at the outlet of the reactor. The result is distributed on the type of tars, 1-5 rings and above. No steam was added, so 50% steam content resulted from fuel moisture and combustion. The sulphur level was not measured during the tests but is estimated to lie between 50-100 vppm.

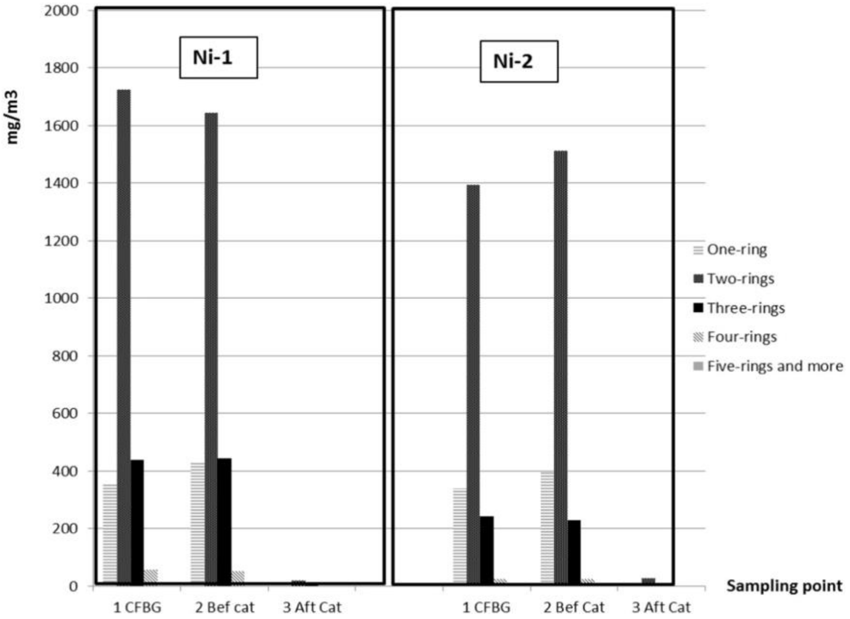

Figure 13. The diagram shows tar levels for a Ni-substituted hexaaluminate used for hydrocarbon reforming. The sampling point for CFBG is after the gasifier but before the high temperature filter, bef Cat (before catalys) is at the inlet of the reactor and after Cat (after catalys) is at the outlet of the reactor tested with two different substitution levels (Ni-1 and Ni-2) at 850ºC and atmospheric pressure.

The results show very large reduction of all tars, including benzene, toluene and xylenes.

Autothermal reforming and partial oxidation

To improve the reforming process both autothermal reforming and partial oxidation could be implemented. Due to the problems associated with obtaining high conversion of methane during steam reforming, the steam reforming unit was supplemented by a secondary reformer step, see Figure 14 [31].

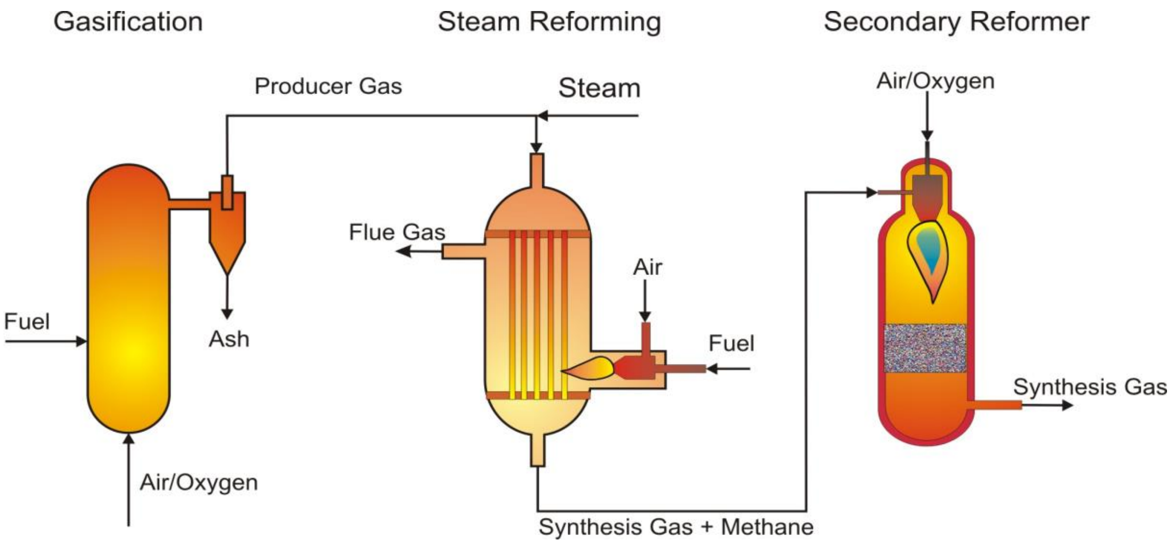

Figure 14. Gasification-steam reforming unit with a secondary reformer step.

The secondary reformer step could be of two different types, Auto Thermal Reformer (ATR) or Partial Oxidation (POX).

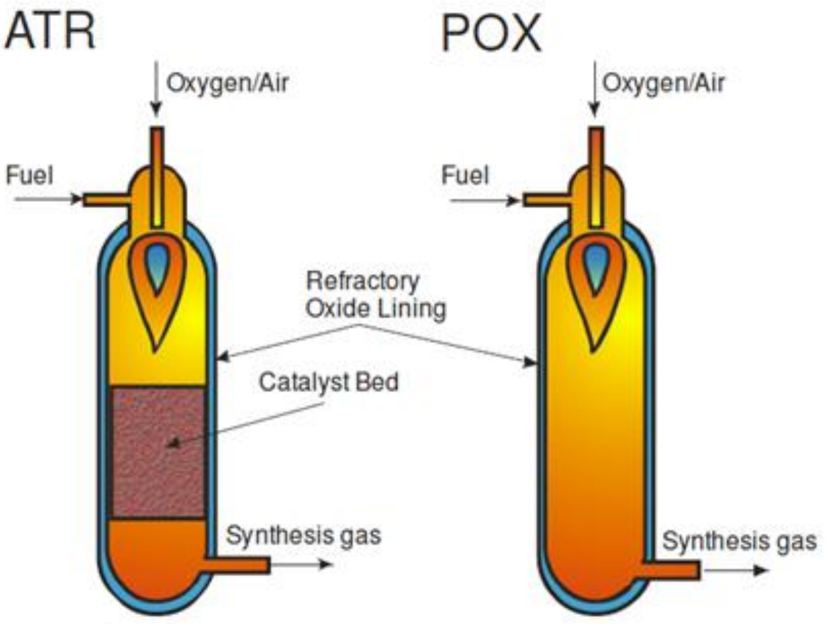

Figure 15. Comparison between ATR and POX reactors.

The two different processes are very similar, in the ATR unit a catalytic bed is fitted while the POX unit contains only empty space to give the gas sufficient residence time, see Figure 15. The two units are heated in the same way; a portion of the gas is burnt inside, in a special burner, to raise the temperature so the reaction can occur.

Since the ATR unit is equipped with a catalyst, a smaller portion of the gas must be burnt than in the case of POX. While the ATR requires a temperature of 800-1000ºC, the POX needs a temperature of 1200-1400ºC for the homogeneous gas phase reactions [32].

This means that the ATR process has higher efficiency, conserves more chemically bound heat in the gas, than does the POX process. However, the POX unit does not contain any catalyst that might be deactivated and needs to be replaced.

Inorganics removal

Except for the hydrocarbons and the tars, the gas also contains inorganic compounds such as Cl and S-containing compounds, e.g., hydrogen sulphide H_2S, carbonyl sulphide COS, HCN and ammonia.

These compounds may be removed by both chemical and physical washing methods. For instance, when using the Rectisol process to remove H_2S and COS, as methanol is used as solvent, CO_2 is simultaneously removed from the syngas [33].

Due to the reducing condition in the gasifier, ammonia is formed from organically bound nitrogen in the fuel. Rather high levels may be formed, in the Värnamo gasifier 3000 vppm of ammonia was formed (Table 3). If a reforming Ni catalyst is present, the ammonia is broken down in a process called ammonia cracking. This seems to be rather the reverse of the Haber-Bosch process used to produce ammonia [34].

$$2NH_3 \leftrightarrow N_2 + 3H_2$$

In Figure 16, the equilibrium for ammonia has been calculated for a stoichiometric amount of N_2 + H_2. To produce ammonia, high pressure and low temperature are required. In the catalytic bed in the reformer the temperature is usually in the range of 800-1000ºC. So even if the reformer is pressurised, the ammonia wants to decompose. This will, however, require a catalyst active for the decomposition, and Ni-based catalysts are normally used in sulphur-free environment. As stated before, the Ni catalysts are poisoned by sulphur.

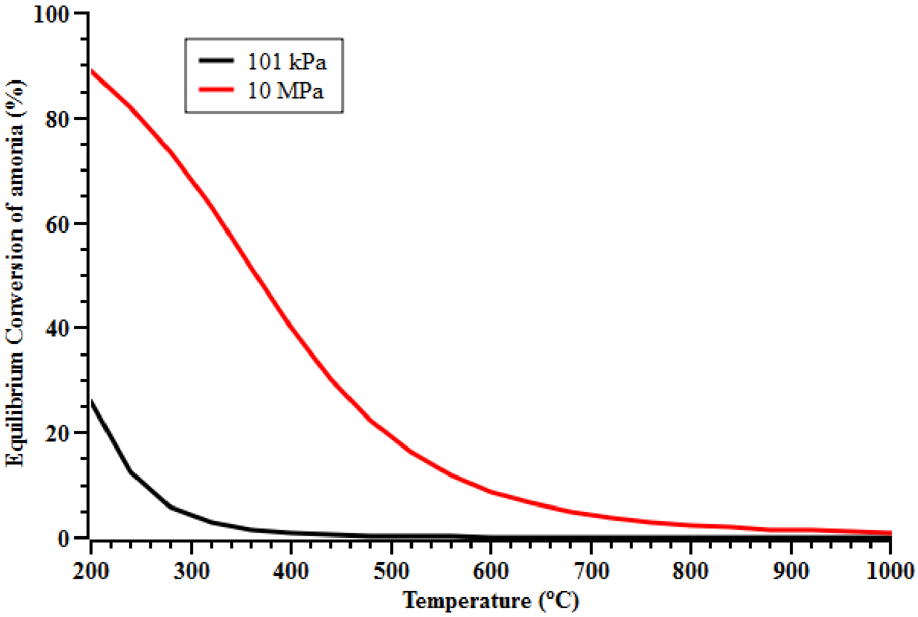

Figure 16. NH_3 equilibrium calculation of ammonia stability in a stoichiometric mixture of N_2 and H_2.

In the Skive plant the ammonia reduction has gradually been increased during the development work, for instance in 2010 70 % reduction was reported [35] and lately ammonia slip-free conditions have been reported [36].

2.3 WATER GAS SHIFT

The water gas shift reaction is an important tool for varying the H_2/CO factor, which directly affects the process design and is normally related to requirements of the back-end applications and other important needs.

WGS units are placed downstream the reformer to shift the H_2/CO ratio (Eq. 1) to the desired level. The reaction is moderately exothermic with favourable kinetics at higher temperatures. Under adiabatic conditions, conversion in a single bed is thermodynamically limited (as the reaction proceeds, the heat of reaction increases the operating temperature), but improvements in conversion may be achieved by using subsequent stages with cooling. Since the flow contains CO, CO_2, H_2O and H_2, additional reactions can occur, depending on the H_2O/CO ratio and favoured at high temperatures: methanation (Eq. 2), CO disproportionation or decomposition (Eq. 3).

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^0_{298} = -41 \text{ kJ/mol*} \qquad (1)$$

$$CO + 3\,H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H^0_{298} = -206 \text{ kJ/mol*} \qquad (2)$$

$$2\,CO \leftrightarrow CO_2 + C \qquad \Delta H^0_{298} = -172 \text{ kJ/mol*} \qquad (3)$$

**reaction to the right*

An increase of the H_2O/CO ratio lowers the risk of carbon formation. At ratios higher than H_2O/CO = 2, carbon will not exist in the equilibrium mixture when the reaction temperature is higher than 230ºC. At ratio 1, the formation of carbon becomes thermodynamically favourable over the entire reaction temperature range. Methane formation is favoured between 200 and 450ºC and at low H_2O/CO ratios [37]. Methane formation can be reduced by selectively removing the H_2 from the reaction stream (by means of a separation membrane) [38].

A catalyst that is active at low temperatures is sought. In industrial applications under continuous operation, the classical catalyst formulations employed are FeCr oxide for the high temperature shift, HTS, typically in the range 360-400ºC, and Cu/ZnO–Al_2O_3 for low temperature shift, LTS, operating just above the dew point, the lowest possible inlet temperature is about 200ºC for good performance under steady state conditions. Figure 17 shows a combined HT and LT shift steps, for production of gas containing high concentration of hydrogen, with cooling in between the two steps.

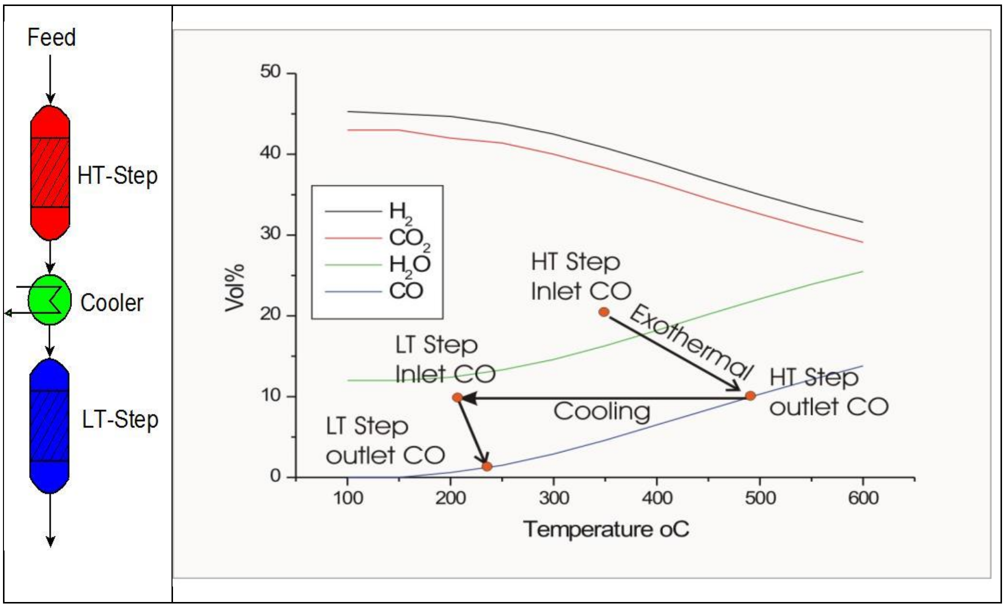

Figure 17. Two-step unit for production of gas containing high concentration of hydrogen [32].

At 500ºC, the gas reaches equilibrium. To reach lower CO levels (higher H_2), the gas is cooled down, in this case to 200ºC, and then enters the LT step. Since the amount of CO to convert is lower, this conversion increases the temperature in the reactor to a lesser extent than in the HT step. This means that the CO level now reaches low values, i.e. the yield of H_2 becomes high.

For liquid fuel synthesis the required H_2/CO ratio is between 2 (Fisher-Tropsch, methanol) and 3 (methane), so shifting the gas far to hydrogen is not necessary. This means that a LT-shift step normally is not necessary.

2.3.1 HT shift

The high temperature, HT-catalyst was introduced by BASF in 1915 and essentially the same catalyst is used today. The active phase is magnetite (Fe_3O_4) and Cr, in the form of Cr_2O_3, acts as a structural promoter stabilising the magnetite crystals [39]. These catalysts demonstrate WGS activity only at inlet temperatures above 300ºC.

The average life is about 3-5 years. These catalysts are supplied in the oxidised condition (Fe_2O_3, CrO_3) and must be reduced to activate them. The reduction step is normally carried out in situ, Figure 18 [40], with a large dilution (H_2O or N_2) to avoid the exothermic reduction to FeO or metallic Fe which will promote the reactions of methanation (reaction 2) and the CO disproportionation (reaction 3) [41].

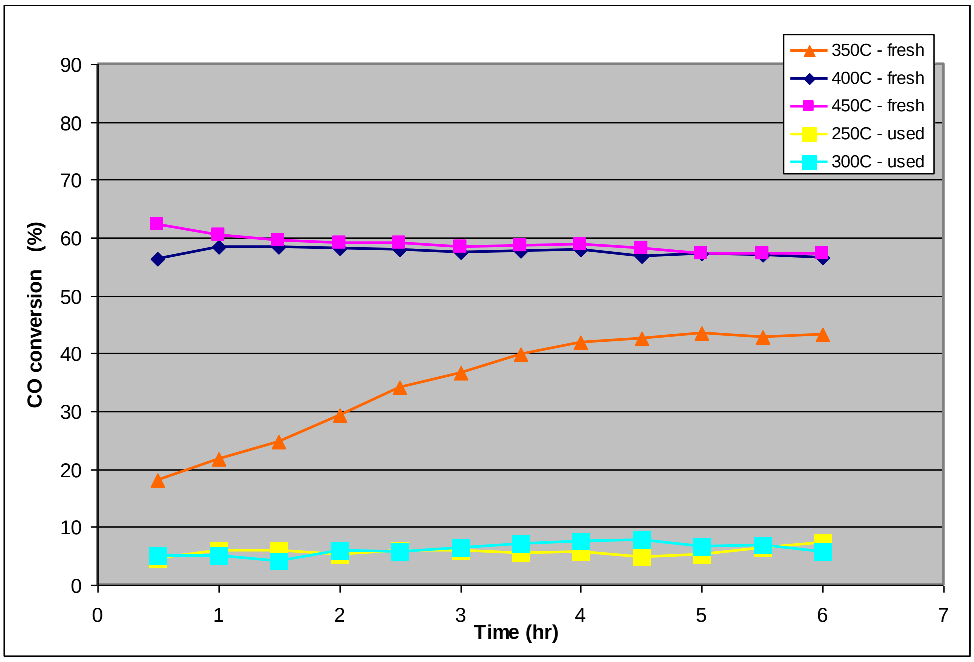

Figure 18. In situ activation of fresh and used FeCr catalysts in microreactor [40].

Sometimes, alkaline compounds (such as MgO) are present, to reduce the acidity, responsible for promoting coke formation. Since the catalyst is pyroforic and cannot stand liquid water, the catalytic bed must be isolated from air and purged with inert gas when the unit is shut down.

2.3.2 LT shift Cu/ZnO

Usually Cu/ZnO catalysts are used in the LT shift step (210-270ºC). Although their activity increases with temperature, sintering proceeds so rapidly above 260ºC (because of copper's low Hüttig temperature [42]), that a satisfactory catalyst life cannot be achieved. Moreover, high gas purity is required because these catalysts are very susceptible to sulphur poisoning (< 0.1 ppm H_2S), since the conversion of Cu and ZnO to Cu_2S and ZnS, respectively is very favoured. Indeed, ZnO is commonly used in plants as a trap for sulphur. These catalysts are supplied as oxides and must be reduced to metallic copper, which is the active species, before they are used. The reduction must be carried out in the presence of an inert gas to limit the temperature to which the catalyst is exposed.

2.4 LT SHIFT COMO

WGS of gases containing appreciable amounts of sulphur or heavy hydrocarbons such as tar requires catalysts consisting mainly of cobalt and molybdenum instead of the iron oxide type [43] [44] [45]. They exhibit a wide range of applications between ca 230 and 500ºC. Their activity increases significantly between 40 and 80 bar, and full activity only occurs when the CoMo catalyst is sulphided. Further, once sulphided there is a much smaller risk of methanation taking place. These catalysts must therefore be pre-sulphided or sulphided during start up (with a $H_2/N_2/H_2S$ stream). A minimum of ca. 3-5 ppm of hydrogen sulphide in the dry raw gas, depending on the operating conditions (P, T, H_2O/CO ratio) is required to maintain the catalyst activity. The sulphur content has no upper limit. Co is a multiple-function promoter [46], usually used commercially with Mo in catalytic hydrotreating. It causes molybdenum oxide to be better dispersed on the support, thus facilitating the easy reduction and sulphidation of the oxide. Co also promotes the dissociation of adsorbed CO and activation of H_2 for hydrogenation. The effect of higher Co/Mo ratio, providing higher activity may be accounted for by the dispersing ability of Co on Mo by the formation of $CoMoO_4$. After reduction and sulfidation $CoMoO_4$ is transformed into the active phase Co-Mo-S, with Co on the corner or edges of MoS_2 slabs. However, an excess of Co will result in its isolated form. The CoMo sulphides are mainly supported on alumina, zirconia and titania and show [47] good performances (titania>alumina>zirconia) with highly sulphided feeds. No loss of activity or major deterioration of physical properties takes place during normal operation, and lives of up to ten years may be expected. More recently, alkaline compounds (potassium [48]) have been used as promoters. However, these formulations are less active than copper-based LT shift catalysts operating with pure feed gas and they only reach full activity when they are properly sulphided. Moreover, in processes using sulphided catalysts and handling sulphur-containing streams, there are many drawbacks such as corrosion of equipment and instrumentation, difficulties in characterisation of catalysts and analysis of sulphur contents in the system as well as the danger of poisoning.

2.5 PRECIOUS METAL CATALYST

Catalysts based on Pt/CeO_2 are reported [49] as active and non-pyrophoric, with activity higher than that of conventional WGS catalysts in the medium-temperature range (300–400ºC). Work performed at Johnson Matthey on Pt/CeO_2 catalysts indicated that despite the high initial activity obtained in the medium–high temperature range (325–400ºC), the catalyst loses activity under synthetic and real reformate tests. The deactivation may be explained by several mechanisms, including surface coverage with in-situ formed carbonate-like species, and partial loss of the re-oxidising ability in the highly reducing CO/H_2 environment. In addition, methanation takes place on Pt/CeO_2, also seen at temperatures higher than 375ºC, therefore, a Pt catalyst was developed by Johnson Matthey. This formulation is non-pyrophoric, has no methanation activity over a large range of temperatures (200-500ºC) and has a much higher WGS activity and durability than a reference $Pt–CeO_2$ catalyst.

Non-pyrophoric, precious metal–HTS catalysts further promoted to suppress methanation were also reported by Engelhard [50]. Ruthenium deposited on $\alpha\text{-}Fe_2O_3$ has been mentioned in the literature [49] as giving promising WGS conversions with no methanation activity.

2.6 HYDROLYSIS AND HYDROGENATION

The WGS catalyst is also responsible for some more reaction, as mentioned above the WGS catalyst can hydrogenate CO to methane. However, also olefins are hydrogenated over the WGS catalyst. Carbonyl sulphide (COS) is found in synthesis gas due to the equilibrium between CO_2 and H_2S at high temperature, reaction (4) [32]. In the form of COS the sulphur cannot be removed by absorption, by ZnO for instance.

$$H_2S + CO_2 \leftarrow\rightarrow COS + H_2O \qquad (4)$$

At lower temperature the carbonyl sulphide may be decomposed by hydrolysis (the reverse reaction) over a catalyst.

Also HCN may be present in the synthesis gas due to equilibrium between CO and NH_3.

$$CO + NH_3 \leftarrow\rightarrow HCN + H_2O \qquad (5)$$

In a similar way to COS, the HCN may be decomposed over a catalyst at an appropriate temperature.

The WGS catalysts (Cu/ZnO is not used in presence of sulphur) are active for those reactions. In plants where a part of the flow is bypassed the WGS step, for instance if the H_2/CO-ratio should be tunable a separate hydrolysis step then becomes necessary as seen in Figure 19.

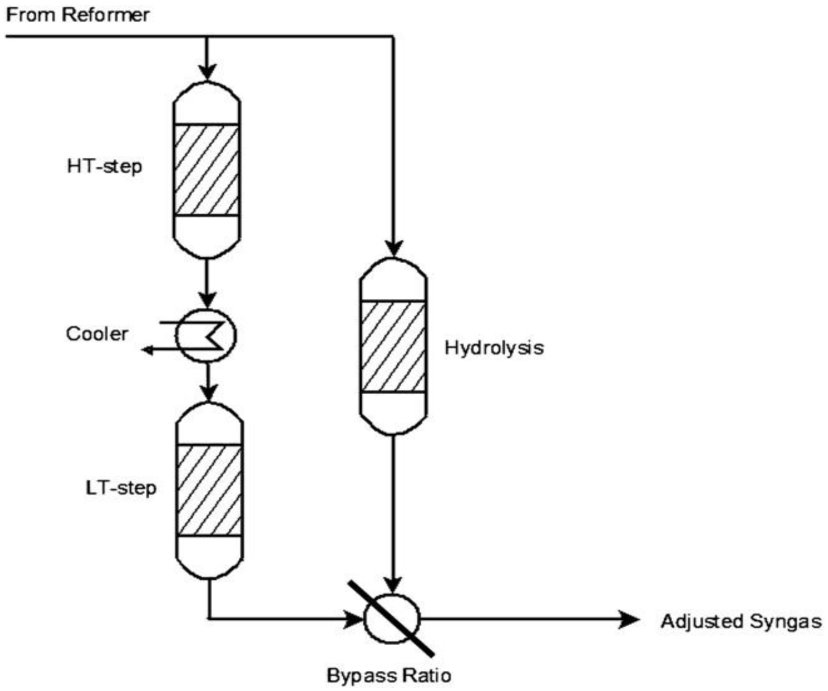

Figure 19. Combined HT-LT shift steps with tuneable H_2/CO ratio [32].

Hydrolysis, decomposition by reaction with water, is normally catalysed by acidic catalysts, such as γ-alumina, acidic zeolites or mounted mineral acids. Important factors are the amount of acidity and the strength of acidity.

2.7 CO_2 REMOVAL TECHNOLOGIES

The removal of carbon dioxide may be performed in several ways in this context. It may be removed in scrubbing using a number of different solvents:

- Physical absorption
  - Water
  - Polyethylene glycol (Selexol process)
  - Methanol (Rectisol process)
  - N-methyl-2-pyrrolidone (Purisol process)
  - Propylene carbonate (Fluor process)

- Chemical
  - MDEA
  - MEA
  - DEA
  - aMDEA
  - Chilled ammonia

Or the carbon dioxide may be removed using other physical processes such as pressure swing adsorption or membrane separation.

2.7.1 Absorption

The solubility of different components in the physical solvents, or the ability of the chemical solvents to react with different gas molecules influences the selectivity and activity of the various solvents. The most commonly used physical solvent is methanol, followed by polyethylene glycol: the Rectisol and Selexol processes. The first of these processes is often considered for the gasification context as it is not only selective to CO_2, but also COS, CS_2, mercaptans, HCN and higher hydrocarbons. The low operating temperature is, however, a significant cost driver [50]. The Selexol solvent has a high capacity for absorption of impurities such as sulphur as well as ammonia, HCN and other higher hydrocarbons. H_2S is up to nine times more soluble in the Selexol solvent than CO_2, which makes it suitable for selective removal of H_2S. Hydrocarbons are also very soluble in the solvent and the solubility increases with increasing molecular weight. Water is also highly soluble in the Selexol solvent. Due to this quality the Selexol process is often used for simultaneous hydrocarbon and water dew point control [50].

Analogous to the purification of anaerobic digestion, the use of water as a scrubbing agent is also possible. H_2S is also soluble in a water stream and may be removed in the desorption column. Water scrubbing has advantages in no heat use, no use of chemicals and desulphurisation being carried out simultaneously. The drawbacks are the relatively high electricity costs for compression of the gas and fairly high use of water [51] [52]; if the gasifier operates at pressure the first drawback may be ignored.

In chemical absorption the absorption heat is higher than for physical absorption since the carbon dioxide not only dissolves in the solvent, but reacts with a reagent as well. Monoethanolamine, MEA, is the most common scrubbing agent. The main problem associated with MEA is corrosion of the absorption equipment in the presence of impurities, e.g. oxygen. Unfortunately, MEA has the disadvantage of forming irreversible reaction products with COS and CS_2, which deteriorates the solvent. If SO_2 and NO_2 are present in the gas this also causes solvent degradation due to reaction with the amine [53] [54].

As mentioned above, anaerobic digestion is a good analogue to removal of CO_2 in the gasification context. The most widely used solvents are aqueous alkanolamines, such as N-methyldiethanolamine (MDEA). However, MDEA has a low reaction rate for the reaction with CO_2, compared to other alkanolamines and is therefore often activated by adding piperazine (PZ) as a promoter [55] [56]. Absorption of H_2S in MDEA solutions is a common technique for selective removal of H_2S from CO_2-rich gases. However, other impurities, such as higher hydrocarbons absorbed in the solvent, may cause foaming, which significantly reduces the absorption capacity of the process. MDEA itself is only moderately miscible with hydrocarbons.

The ammonia process is similar to that of the alkanolamines. The reaction of ammonia with CO_2, however, has a much lower heat of reaction than that of conventional amine solutions which leads to considerable energy savings [57]. The absorption is run at a low temperature, below 20ºC, to reduce ammonia losses. Most impurities in the gas are removed prior to the absorption step as the gas is passed through a desulphurisation unit and cooling towers [58].

2.7.2 Physical separation techniques

The physical separation techniques utilise other means of separation than absorption into liquids, pressure swing adsorption and membranes should be mentioned. Pressure swing adsorption (PSA) is a dry method used to separate gases via physical properties. Membrane separation uses a membrane with different permeabilities for the different gas components and thus achieves separation [59]. A more thorough description of the PSA technology for biomethane enrichment may be found in SGC report 270 [60] where a thorough description of membrane systems used for gas separation is also available. Another area of research is the use of Ionic Liquids for CO2 separation, that will be interesting to follow, mostly the research has been dedicated to designing novel materials for CO2 capture with specific attention for so called MOFs (metal organic frameworks) [61].

3 APPLICATIONS

There are a number of uses with respect to produced synthesis gas. The major applications will be discussed in the following sections, starting with the production of hydrogen. This is followed by the synthesis of substitute or synthetic natural gas, methanol, dimethyl ether, Fischer-Tropsch diesel and higher alcohol synthesis.

3.1 HYDROGEN

Hydrogen may be produced from a wide array of carbonaceous fuels and biomass is only one of them. Most of the hydrogen produced in the world is derived from natural gas and the major use is for ammonia synthesis. Hydrogen, however, receives significant interest as a suggested new energy carrier for vehicles. The process leading up to pure hydrogen depends to a large degree on the starting material. After leaving the gasifier, the gas is a mixture of H_2, CO, CO_2, CH_4, higher hydrocarbons and H_2O as well as dust (ash and/or bed material). As previously described the particles need to be removed as well as the higher hydrocarbons. Thereafter, to maximise the hydrogen yield, the water-gas shift reaction is performed. As mentioned above, this is likely done in two steps with a high-temperature and a low-temperature step with intercooling. Finally, the CO_2 is removed using one of the techniques described above. The most common technique used in industry is PSA, however in this case there is a good use of the PSA off-gas as a furnace fuel; this is not the case in the gasification context.

3.2 SNG

The first step in synthesising methane or SNG is the generation of synthesis gas. To further increase the CH_4 content of the produced biomass-based gas, methanation is necessary. The methane synthesis process has a very high total efficiency. The methanation reaction is strongly exothermal and because of this, heat removal from the reactors employed is crucial [62]; a more extensive summary may be found in reference [63]. Methane from the methanation reactor is upgraded, by CO_2 separation. Usually large-scale separation processes are used, such as PSA, and physical absorption by Selexol and the emerging membrane technology separation. Methanation follows reactions (1) and (2). The methanation reactions are favoured by high pressures and low temperatures. Due to the high heat release and to the high reactant concentrations, measures must be employed to avoid hot spots and to limit the temperature. The temperature should also be kept low due to the equilibrium [64].

$$CO + 3\,H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H^0_{298} = -206\ \text{kJ/mol} \qquad (1)$$

$$CO_2 + 4\,H_2 \leftrightarrow CH_4 + 2\,H_2O \qquad \Delta H^0_{298} = -165\ \text{kJ/mol} \qquad (2)$$

$$2\,CO \leftrightarrow CO_2 + C \qquad \Delta H^0_{298} = -172\ \text{kJ/mol} \qquad (3)$$

$$CH_4 \leftrightarrow C + 2\,H_2 \qquad (4)$$

The catalyst used in methanation reactors is normally nickel-based and supported on alumina, kaolin or calcium aluminate. Sulphur and arsenic are severe catalyst poisons and must be removed upstream the catalyst. The catalyst contains < 15 wt % nickel and safety measure must be taken to prevent the formation of the highly toxic nickel carbonyl $Ni(CO)_4$. The formation of the carbonyl is preferential at low temperatures, < 200ºC, and high partial pressures of CO. It is therefore important to have proper procedures for start-up and shutdown [62].

CO also reacts with iron to form iron carbonyl, which is poisonous and causes corrosion problems. Iron carbonyl decomposes on the catalyst as well when the temperature is increased. Thus, CO must be heated in stainless steel heat exchangers. Years of plant operations have shown that with the right precautions, carbonyl formation may be suppressed successfully [62].

CO_2, in reaction (2), is first converted to CO with the reverse shift reaction. This formed CO is then reacted to CH_4 according to reaction (1) [64]. The Boudouard reaction (3) will be thermodynamically favoured at elevated temperatures, e.g., at the outlet of the reactor. However if temperatures are kept moderately low and small residual hydrogen exists in the gas outlet, it can be avoided [62]. Typically, the reaction is operated at inlet temperatures of 250-300ºC and at pressures more than 30 bar. The high pressure favours the equilibrium and improves the kinetics. After upgrading the produced CH_4, the concentrations are normally greater than 90 mol% and the heating value is typically higher than 33 MJ/m^3 [65]. For upgrading to motor fuel standards, SNG for vehicles, the gas is additionally cleaned to nearly pure methane.

3.2.1 H_2/CO-ratio

Synthesis gas for methane production is usually classified by its stoichiometric number (SN), i.e. the relationship between the hydrogen and the carbon oxides and higher hydrocarbons according to equation (A) [66].

$$SN = \frac{V_{H2}}{3V_{CO} + 4V_{CO2} + 2V_{C2H4}} \qquad \text{(A)}$$

During stoichiometric methanation, there is a small or no risk of carbon formation according to the Boudouard reaction (3), even at elevated temperatures as high as 700ºC. This, however, does become a problem at lower SN. Lower SN also requires carbon dioxide removal to a greater extent upstream the methanation reactor.

3.2.2 Reactor designs

To control the heat of reaction in methanation there are a few variations in reactor designs that have been proven to be successful. There are several commercially available methanation systems in use. Most of them are designed for methanation of syngas produced from coal gasification at high pressures. Thus, the methanation reactors are designed for pressures of 40-60 bar [63] [67].

Recycle-Gas Processes

The recycle-gas process uses adiabatic reactors with product-gas recycling. The recycled gas increases the mass-throughput in the first reactor and increases the amount of heat that may be absorbed without over-heating. The recycled gas is cooled and compressed to the reactor operating pressure before it is mixed with fresh syngas.

Haldor Topsoe A/S has developed a methanation process that is called TREMP™, see Figure 20, i.e. Topsoe’s Recycle Energy-efficient Methanation Process. The system uses three adiabatic reactors with product recycle and intermediate cooling. The temperatures of the reactors are controlled by the recycle ratio and are held below the maximum allowed for the catalyst. The catalyst used has been developed by Haldor Topsoe A/S and has good temperature resistance allowing temperatures of 250-700ºC. The catalyst is called MCR-2X and according to Topsoe has excellent durability [63] [68].

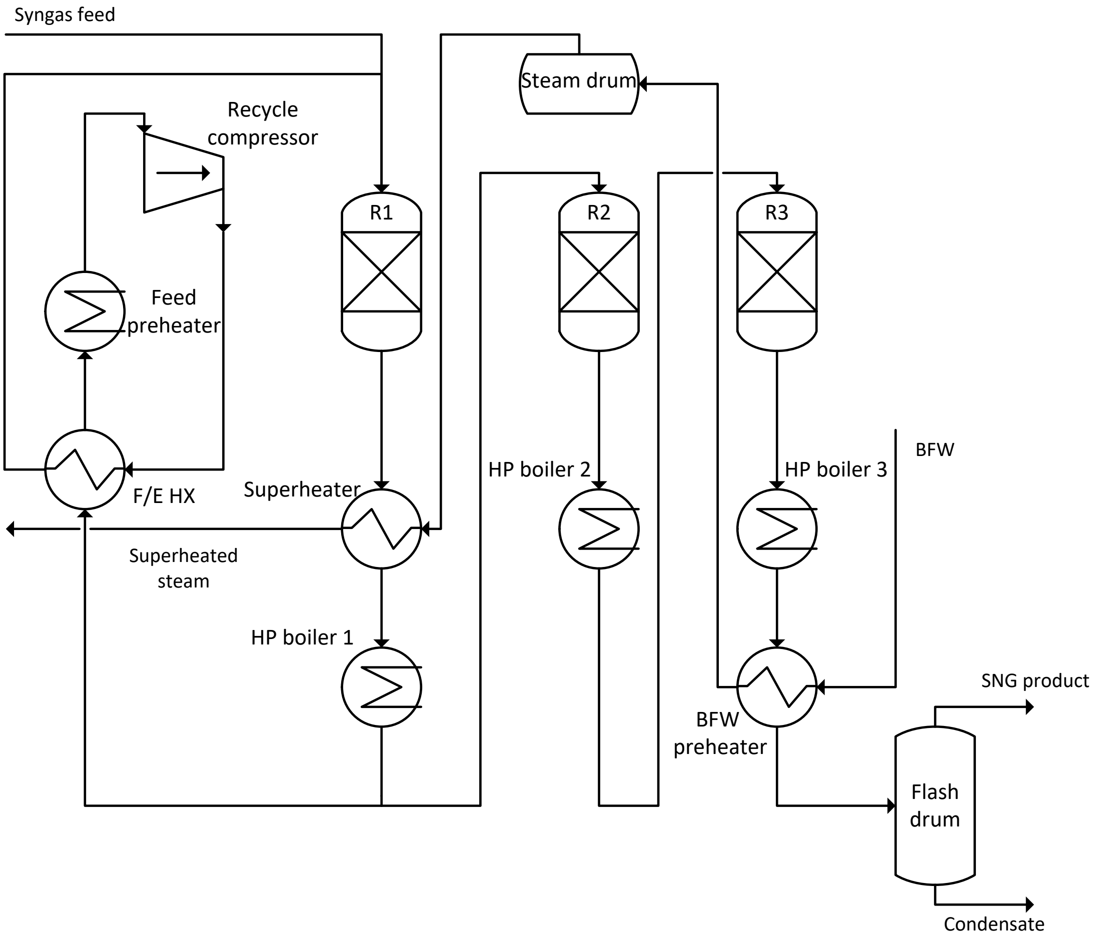

Figure 20. Haldor Topsoe's methanation process TREMP.

The disadvantage with recycling the product gas is the higher volume of gas that needs to be processed and the dilution of the reactant gases. It also increases the cost and energy loss due to the need to compress the recycled gas.

TWR – Through-wall-Cooled Reactor

Through-wall-cooled reactors are usually employed as reactors in chemical processes that utilise heterogeneous gas reactions. The reactor design is relatively simple and may be compared to a shell-and-tube heat exchanger. The tubes are filled with catalyst and are cooled either by boiling water or a high temperature oil. Figure 21 shows a TWR system [62].

The cooling method used in these types of reactors increases the difficulties of controlling the heat of reaction. As the methanation reaction is highly exothermal, the temperature control becomes increasingly difficult and thus hot spots may become a severe problem in TWR reactors.

The main advantage with the plug-flow reactor is that only a single reactor is required because the reactor can contain any number of tubes, making it rather easy to scale the process to various sizes.

This results in lower investment and operating cost. The largest disadvantage of the reactor is the problems involved in replacing depleted catalyst [62].

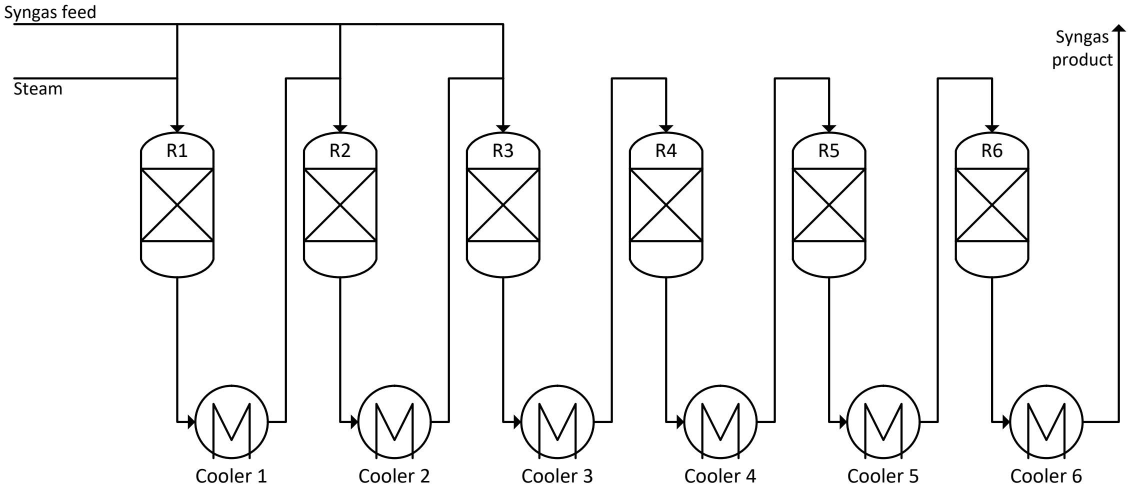

Figure 21. Single-pass through wall-cooled methanation process [62].

Fluidised-bed reactor

Methanation as well as other highly exothermal processes may favourably be carried out in a fluidised reactor. The main advantages with fluidised bed reactors are:

- Evenly dispersed catalyst and reactant gases
- Low thermal gradients and thus better temperature control
- Easy catalyst replacement

Two processes were found in the literature that use a fluidised bed, the technologies developed at Thyssen and Paul Scherrer Institute. The *Comflux* methanation, developed by Thyssengas, was operated 1980-1985 for about 8,000 h. The process was run at 60 bar and with a H_2/CO of 2.7-4. This has several advantages such as minimising the carbon dioxide formation from the water-gas shift reaction [69]. In addition to this, further work has been performed in recent years at the Paul Scherrer Institute [70] [71] [72]. Disadvantages with the technology are the lower reaction rate due to appearance of the fluidised bed behaving as a constantly stirred tank reactor and that attrition of the catalyst is unavoidable. Catalyst particles will end up in filters downstream and may react further with unreacted gas, creating a potential safety hazard.

3.2.3 Gas quality

There are significant differences in required gas quality within Europe. Describing the differences in the various gas qualities is outside the scope of this report. In this report the Swedish standard for vehicle gas has been used as target quality [73], more specifically the type A quality. The motor octane number is determined using calculations according to ISO 15403 [74]. The problem with using this definition in the present case is the hydrogen content. The standard does not consider any hydrogen content in the gas. An alternative method is to use the definition in SAE 922359 [75]. However, also this expression has been developed without hydrogen in the gas and even though it may be used for determining the motor octane number in the present case, its validity may be questioned for the gas mixture at hand. Therefore, the motor octane number has not been reported for the case study although it is within range of that specified in ISO 15403.

3.3 METHANOL

Methanol as alternative fuel has great potential and is an excellent fuel for spark-ignition engines and may easily be blended with gasoline. However, the use has so far been limited. Today most of the methanol produced worldwide is directly used for formaldehyde production.

The methanol synthesis process has a relatively high total efficiency up to 56% [76], however for methanol production the economy is greatly dependent on how the large heat fluxes produced by the exothermic process are being utilised.

Methanol (CH_3OH) may be produced from synthesis gas according to:

$$CO_2(g) + 3H_2(g) \leftrightarrow CH_3OH(g) + H_2O(g) \qquad \Delta H_r = -50 \text{ kJ/mol}$$

$$CO_2(g) + H_2(g) \leftrightarrow CO(g) + H_2O(g) \qquad \Delta H_r = +41 \text{ kJ/mol}$$

$$CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g) \qquad \Delta H_r = -91 \text{ kJ/mol}$$

All the reactions are equilibrium reactions and the equilibrium is not particularly favourable at low pressures.

Normally the gas contains both CO and CO_2, so the ideal stoichiometry is not $H_2/CO = 2$. Instead it is the stoichiometric number $(H_2\text{-}CO_2)/(CO+CO_2)$ that should be 2 for ideal conversion [77]. However, a high CO_2 level limits the heat released by the exothermic reaction but produces more water, resulting in a diluted product.

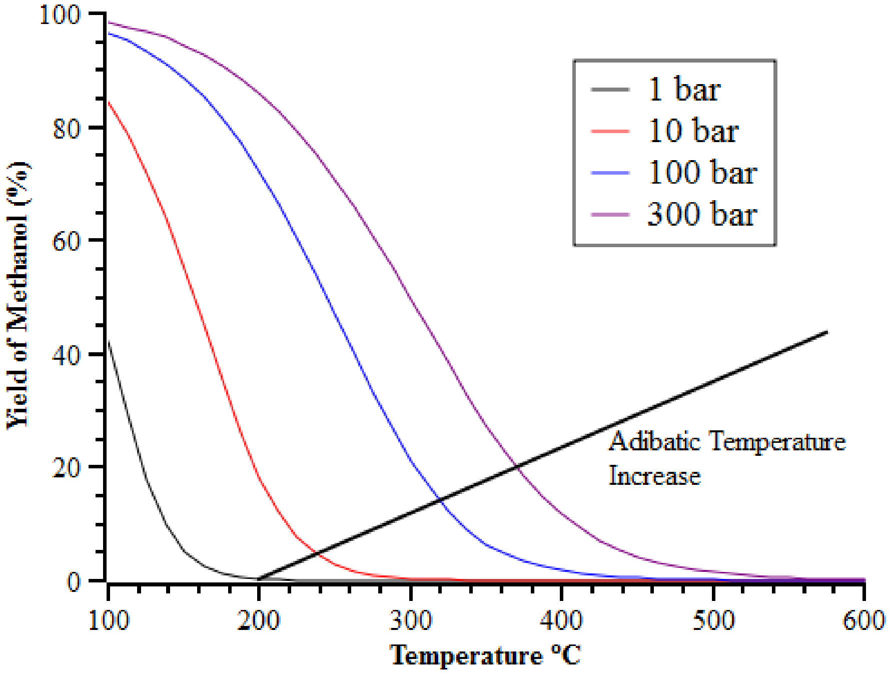

Figure 22. Equilibrium calculation of a $CO:H_2$ mixture with ratio 1:2 and the adiabatic temperature increase as function of conversion (assumed inlet temperature 200°C).

The reaction is limited by thermodynamic equilibrium and the process requires high pressure and low temperature to obtain high conversion. However, the catalysts, required for the reaction, have a minimum operation temperature. To ignite the reaction, the temperature must be at least around 200ºC.

According to Table 4, a typical feed for the synthesis is:

Table 4. Feed composition [77].

Component	Vol %
H_2	59-79
CO	15-27
CO_2	8
CH_4	3

If a composition within this span is chosen, for instance H_2 67, CO 22, CO_2 8 and CH_4 3 vol % and calculating the adiabatic temperature increase, then a full conversion (100 %) would correspond to a temperature increase of 880ºC. This temperature increase is of course fictitious, the conversion is limited by the equilibrium, described above, and thereby also the obtainable temperature. In Figure 23 the adiabatic temperature increase as function of the conversion is plotted together with the equilibrium conversion versus temperature and different pressures. The maximum obtainable conversion, at adiabatic conditions, is found at the intersection between the temperature line and the equilibrium line. The single pass conversion at adiabatic conditions is low to moderate depending on pressure.

To increase the conversion, several reactors may be used or a single reactor with divided beds with cooling in between as in Figure 24. By doing so, it is possible to climb on the equilibrium curve, see Figure 23.

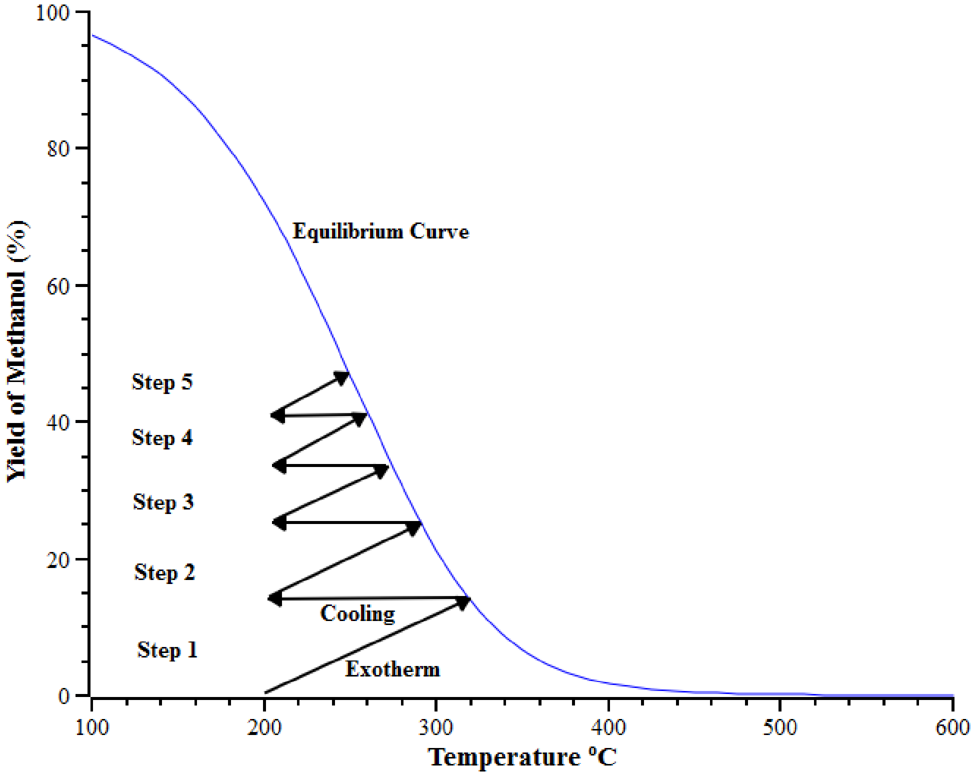

Figure 23. Improving methanol yield by multi-bed reactor with in-between cooling.

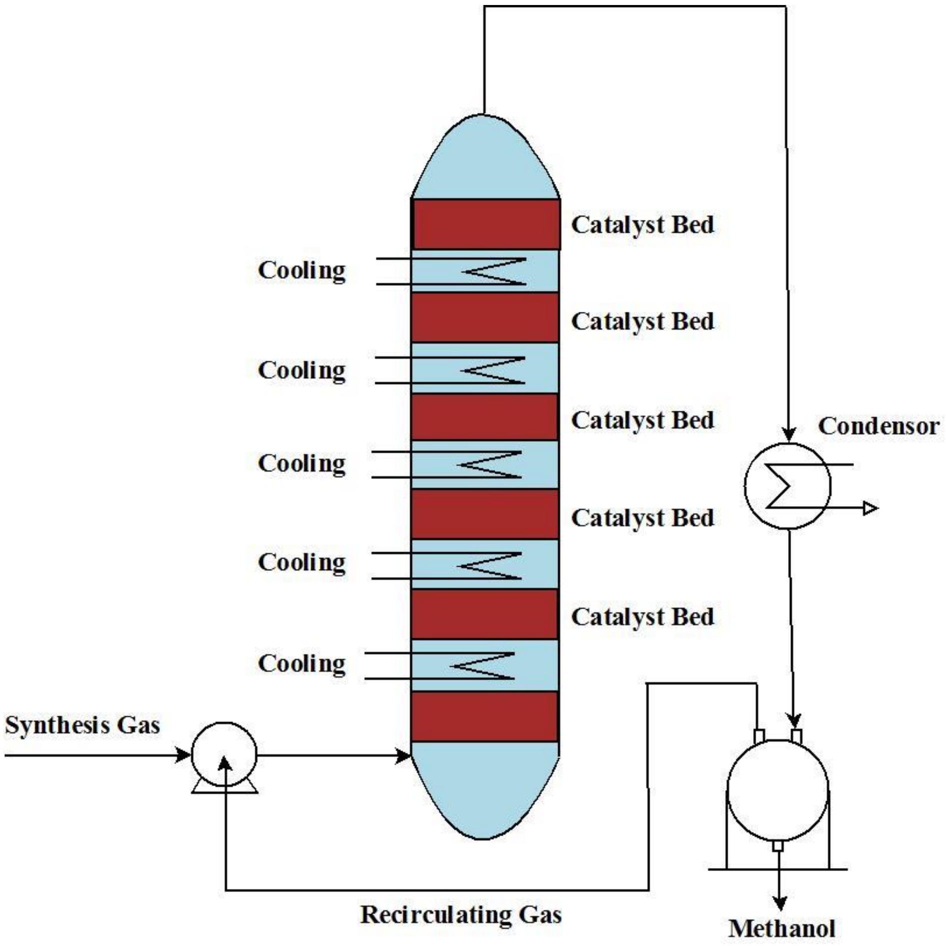

Figure 24. Multi-bed methanol reactor with in between bed cooling and gas recirculation.

However, full conversion of the synthesis gas will not be obtained, unless the produced methanol is separated from the gas and the gas is recirculated.

Another strategy is to run the process isothermally. To obtain isothermal conditions for this highly exothermal process efficient cooling must be applied. Lurgi has solved this by using a boiling water reactor as shown in Figure 25. The catalyst is located inside a bundle of tubes, similar to a tube heat exchanger. The tubes are placed in an outer shell filled with water. By controlling the pressure of the boiling water, a very precise temperature control may be obtained in the catalyst filled tubes. The generated steam may be used as process steam or could be used in a steam turbine for power generation. The reactor operates in a temperature range of 240-260ºC and the yield of methanol, depending on operating pressure, may reach 30-40 % in a single pass.

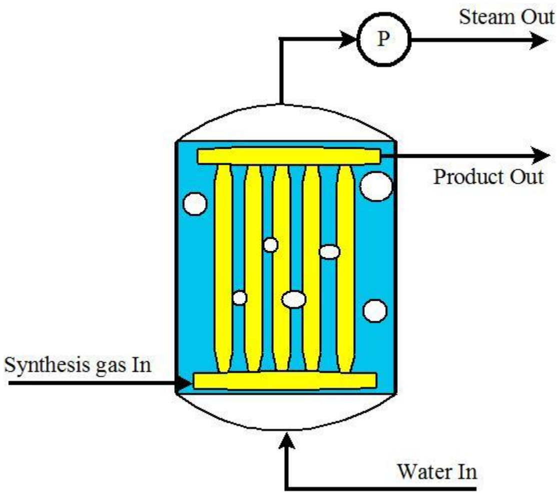

Figure 25. Lurgi boiling water reactor.

Other suppliers may have used different methods to obtain adiabatically or isothermally operating reactors, however, the main issue with the methanol synthesis is the unfavourable equilibrium and the highly exothermal reactions.

3.3.1 Catalysts for the methanol process

$Cu/ZnO/Al_2O_3$

Catalysts used for methanol production are usually based on copper, a very active component. Copper sinters, however, very easily and the metal is normally stabilized by ZnO and Al_2O_3. The catalyst is very sensitive towards sulphur and requires sulphur levels below 1 ppm. The H_2S content of the gas will be reduced in water scrubbing and/or a flue gas condensing step, but there will remain at least an amount of H_2S in the gas corresponding to the liquid-gas phase equilibrium. The active component copper, first forms surface sulphides that block the surface and then it will form bulk CuS. The ZnO component is industrially used for desulphurisation by absorption and gives the catalyst a bit of self-protection [78].

Chlorine is a sever poison for the catalyst, however, not commonly present in the gas. Volatile metallic carbonyls such as $Fe(CO)_5$ and $Ni(CO)_4$ may be generated in the gas upgrading equipment itself, for instance from the steel in the reforming reactor. Deposed on the catalyst they may act as Fisher-Tropsch catalysts, deactivating the catalyst by covering its surface with high-boiling waxes. In units using coal gasification for production of synthesis gas, arsenic has been found in deactivated methanol catalysts. Nitrogen-containing compounds such as, NH_3, HCN and CH_3CN seems not to affect the activity of the methanol catalyst.

MoS_2

In contrast to the Cu/ZnO catalyst, molybdenum disulphide (MoS_2) catalysts require sulphur to be present in the gas. It is therefore an attractive type of catalyst to use for synthesis in synthesis gas with high sulphur content. However, the selectivity for methanol is only 50 %, compared to 99 % for Cu/ZnO. The other products are methane and other alcohols, such as ethanol.

3.4 DME

DME, Dimethyl ether, is a gas with properties similar to those of Liquid Petroleum Gas (LPG). At Standard Temperature and Pressure (STP, 0 ºC,101 kPa) it is a gas, but condenses into a liquid at 506 kPa at 20ºC (270 kPa at 0 ºC). The liquid density is about 0.67 kg/dm^3 at 20ºC with a heat of combustion ΔHc= 28 MJ/kg. Compared to diesel (35 MJ/dm^3), DME has about half the energy density, 19 MJ/dm^3, at 20ºC [79].

DME can be produced by dehydration of methanol over an acidic catalyst such as zeolites or modified γ-alumina. [80]

$$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H_r = -23\ \text{kJ/mol} \qquad \text{(A)}$$

This means that DME may be produced in a two-step process where methanol is synthesised in the first step and DME in the second. However, it is also possible to directly produce DME from synthesis gas, for instance by performing both the methanol synthesis and DME synthesis as consecutive reactions in the same unit.

$$2\ CO + 4\ H_2 \rightarrow 2\ CH_3OH$$

$$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

+--------------------------------------

$$2\ CO + 4\ H_2 \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H_r = -205\ \text{kJ/mol} \qquad \text{(B)}$$

or: $$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2 \qquad \Delta H_r = -246\ \text{kJ/mol} \qquad \text{(C)}$$

Both reactions decrease the number of moles in the gas, this means that an increased pressure will increase the conversion of synthesis gas. Reaction conditions for the direct DME synthesis process according to (C), 240-280ºC and 3-7 MPa [81].

The direct DME synthesis is very exothermal; it combines the exothermal methanol synthesis with the exothermal DME dehydration reaction. It is crucial to keep the temperature below 300ºC to avoid deactivation of the catalyst. This is because the direct DME catalyst is a combined Cu/acidic-catalyst. As stated earlier, Cu-catalysts sinter at temperatures above 300ºC. To keep the temperature under control, a slurry reactor is used where the catalyst is suspended as a fine powder in a high boiling-point oil. The production of DME has also been studied in a polygeneration process for heat, power and DME production by integrating gasification with a CHP plant that was modelled and simulated by Salman et.al [82] to improve the efficiency of the total process.

3.5 FT DIESEL

In this section a general background to the Fischer-Tropsch (FT) reaction will be given. The chemistry involved in the FT synthesis has been described [83] as "a surprising phenomenon in heterogeneous catalysis that attracts the interest of world experts: the gases CO and H_2 enter the reactor and a hydrocarbon liquid exits." The thermodynamically preferred hydrocarbon product is methane, so it is surprising that higher hydrocarbons are the predominant products.

3.5.1 History

The FT process was developed in Germany in the first half of the 20th century [84]. In 1938 nine plants were operating using cobalt-based catalysts at atmospheric conditions with a total capacity of 0.66 million tons per annum. After World War II, all plants in Germany were shut down since they were uneconomic. Today the world's largest FT units based on solid fuel (coal) conversion to diesel and gasoline are located in South Africa [85]. A FT process based on gasified biomass would probably have a total mass yield of up to or above 50% [76].

The reaction may be performed either in a fixed bed reactor or a slurry reactor. Since the reaction is very exothermic, it is very difficult to transfer data obtained in a laboratory reactor to larger scale.

The length and the distribution between the various hydrocarbons depend on the catalyst, but also on the operating condition. The distribution is normally expressed using an Anderson-Schultz-Flory-expression (ASF) for the chain growth, see Figure 26. This may be expressed mathematically and the results are to be found in Figure 27.

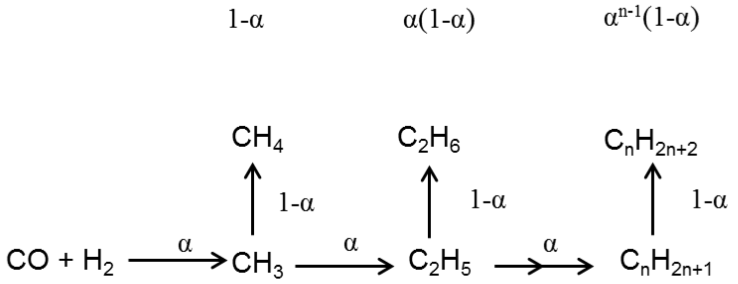

Figure 26. Logic behind ASF (reproduced with permission [86]).

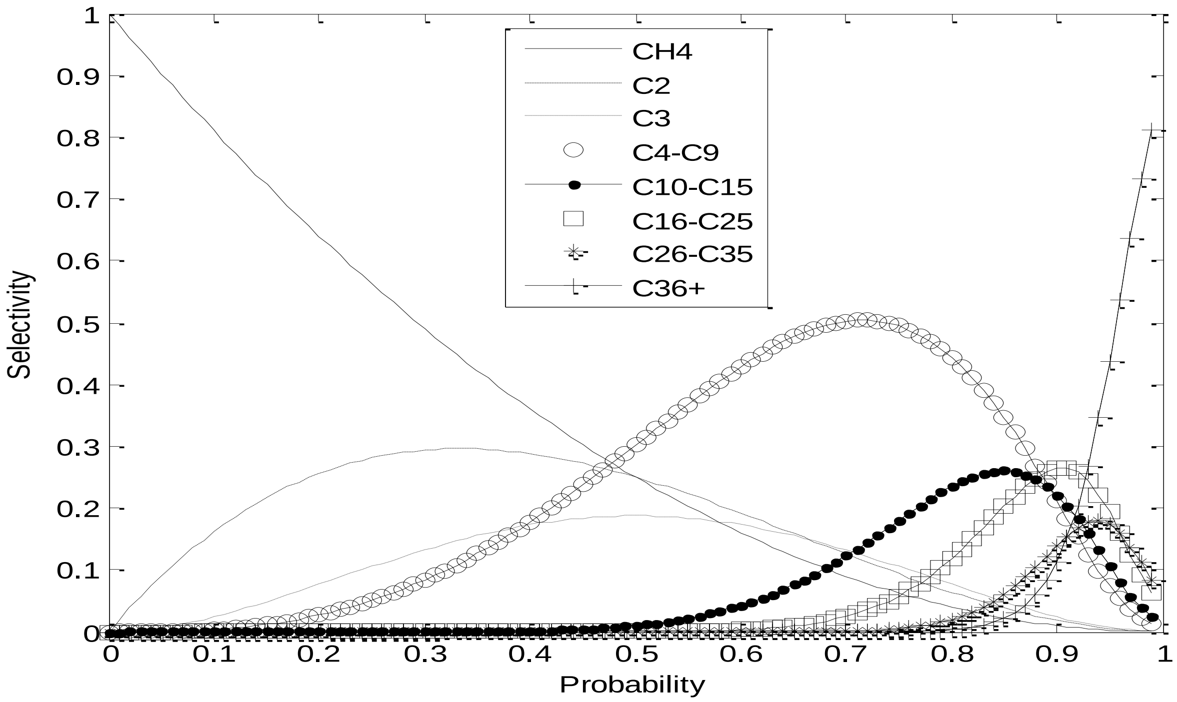

Figure 27. Distribution of hydrocarbons given different probability numbers (alfa number), (reproduced with permission [86]).

The emphasis for a modern FT wax process is to produce more long-chain straight hydrocarbons [87]. The produced waxes are thereafter cracked into desired products such as diesel fuel with low aromatics content and no sulphur.

Only Ni, Fe, Co and Ru have sufficient activity for commercial FT catalysts [88]. Ruthenium is the most active but is the most rare and expensive, see Table 5. Nickel is also very active, however it is very active for hydrogenation, the selectivity to methane is high while low for alkanes. It also forms volatile nickel carbonyls at low temperature and high pressure and the catalyst is slowly lost from the reactor.

Table 5. Approximate relative cost of metals active for the FT synthesis.

Metal	Fe	Ni	Co	Ru
Relative cost	1	250	1000	48000

This leaves only Fe and Co as useful materials for the FT process and these catalysts will be dealt with individually later on in the text. Co has higher activity than Fe and is used in plants for diesel fuel production. Good activity and selectivity are not sufficient factors for the catalyst, also particle size, porosity and particle strength are important. Under reaction conditions, the pore diffusion becomes a limiting factor for large particles. To cope with this, the particle size must be decreased or/and the average pore size increased. Decreasing particle size in fixed beds increases the pressure drop over the reactor and increases the cost-of-compression. If the particle strength is too low, fragmentation of the particles may occur during operation, leading to unexpected increase in the pressure drop. The catalysts are sensitive to sulphur and deactivate if sulphur components are present in the inlet stream. The poisoning starts at the reactor inlet and moves downstream. Even as low a concentration as 0.03 mg/m^3 will yield a significant catalyst deactivation [89].

3.5.2 Reactor types

The reactors employed for the synthesis of FT diesel are the same as in the case of methanation with respect to fixed bed reactors (through-wall cooled) and fluidised beds. However, there is also slurry bed, or ebullating bed reactors in service. The use of an ebullating bed is made possible by the high boiling-point waxes that are formed in the process and that may be used as “solvent” for the catalyst. The problems posed in the production of FT products are the same as in the other processes using synthesis gas and mainly stem from the exothermal heat-of-reaction that needs to be taken care of so as not to overheat the catalyst or reactor.

3.5.3 Catalysts

Historically FT catalysts were alkali-doped iron catalysts, however more up-to-date catalysts are based on Co promoted with Re. Rhenium helps improve the reducibility of cobalt, and also increases the Co dispersion, that enhances the activity of the FT catalyst [90].

Iron-based catalysts

The catalyst used by Sasol is prepared by dissolving scrap iron together with copper metal in nitric acid and co-precipitating oxides-hydroxides by addition of sodium carbonate solution [91]. Several parameters, such as temperature of precipitation, concentration of solution and the final pH affect the properties of the catalyst, like porosity and specific surface. The precipitate is washed, re-slurried with water and potassium water glass is added. The filter cake may either be extruded to yield fixed bed catalyst or re-slurried and spray-dried to yield slurry reactor catalyst.

Table 6. Influence of silica on precipitated hematite [88].

	Unreduced			**Reduced in H_2**			
g SiO2/ 100 g Fe	Pore volume /cm³ g⁻¹	Specific surface area/m² g⁻¹	Area in pores > 4.5 nm/m² g⁻¹	Pore volume/ cm³ g⁻¹	Specific surface area/m² g⁻¹	Area in pores > 4.5 nm/m² g⁻¹	Reduction/%[a]
0	0.37	275	41	0.22	35	35	100
8	0.47	345	59	0.43	190	68	80
19	0.74	375	90	0.48	250	80	46
25	0.71	390	94	0.61	270	84	58
29	0.75	370	96	0.65	265	85	57
50	NA[b]	405	NA	NA	280	NA	NA

[a] % of total Fe present in metallic state after a fixed time at a fixed temperature.

[b] NA not available.

The surface area and porosity increase as the silica content increases, see Table 6. The use of carbonates for precipitation gives higher porosity than the use of hydroxides for the precipitation. As the Fe/Si ratio is typically >4, the silica does not act as a support but as a binder, improving the strength and acting as a spacer to minimise the sintering. A typical catalyst contains 25g SiO_2, 5 g Cu and 5 g K_2O per 100 g Fe.

The catalyst is reduced by hydrogen at as low a temperature as 220 °C. The role of Cu in the catalyst is, allegedly, to decrease the reduction temperature. Full reduction is not necessary since the complete conversion to Fe_3C_2 is performed in the FT reactor.

Iron catalysts for production of gasoline and chemicals

These catalysts are used in fast fluidised bed/circulating fluidised bed reactors and need to be robust. The catalysts are produced by fusing iron oxide together with promoters, such as K_2O, MgO and Al_2O_3, at about 1500°C. The melt is poured into ingots and are rapidly cooled. After cooling, the ingots are crushed, and the desired particle size fraction is separated. Since the surface area of the fused catalyst is almost zero it requires pre-reduction to develop the surface area necessary for the reaction. The reduction is carried out with H_2 at 350-450°C [92].

Carbon deposition during FT synthesis

Due to the Boudouard reaction, elementary carbon is deposited on the catalyst surface above 300°C. The activation energy of the reaction is higher than for the FT reaction: therefore the rate of carbon deposition increases faster than the FT reaction at increased temperature. If the reactor operates at around or below 240 °C, no carbon deposits occur. Promoters may increase the rate of deposition, for instance alkali.

Cobalt-based catalysts

The original German Co-catalyst was prepared by co-precipitating nitrates of cobalt and thorium in the presence of kieselguhr [92]. The mass ratio was typically 100 Co: 18 ThO_2: 100 kiselguhr. Addition of 2 % Cu increased the rate of reduction, however, it also increased the rate of deactivation. The large amount of Co in the catalyst would make this catalyst expensive today. Because of the high costs of Co, it is important to minimise the amount of cobalt used, but still have a high metal surface area. This is done by supporting the active phase on a stable, high surface-area carrier. Usually this is done by impregnating the carrier with a dissolved Co salt, drying the calcinating the catalyst to form Co oxide. The final step is the reduction with hydrogen to obtain well dispersed Co metal.

With TiO_2 as support it was found that catalysts prepared from cobalt oxalate by speeding (heating mechanical mixtures) produced the most active catalyst. Incipient wetness impregnation with cobalt (III) acetylacetonate produced a more active catalyst than the commonly used nitrate. When loading 2.5 % Co using ammonium-Co citrate very small Co-oxide particles were formed that reacted with the alumina carrier and formed inactive aluminates. Catalysts prepared from nitrate formed larger particles that could be reduced and were active for the FT reaction. Goodwin et al. [93] compared a series of catalysts supported on TiO_2, SiO_2 and Al_2O_3 and the effect of Ru, Re, La and Zr. They concluded that alumina supported ruthenium promoted catalyst had the best performance, while the TiO_2 catalyst had inferior surface area.

Ruthenium increased the activity for alumina and titania supported Co catalyst while ZrO_2 did the same for Co/SiO_2 catalyst.

Deactivation of FT catalysts

Sulphur compounds in the feed gas rapidly deactivate the FT catalyst. The sulphur reacts with catalyst from the inlet and moves slowly downstream. Even at as low concentrations as 0.03 mg/m^3 poisoning is observed. The surface area of a fresh iron FT catalyst is approximately 200 m^2/g. In a catalyst that has lost 50 % of its initial activity the remaining surface area is 50 m^2/g. These changes indicate that a crystal growth has occurred on stream. Carbon deposition on the catalyst causes fouling.

Co vs. Fe

There are significant differences between the two types of catalyst. In the iron case, oxygen is removed from the reactor as CO_2 and in the cobalt case as H_2O. There is also a significant difference with respect to how inlet CO_2 is handled. Fe is indifferent to CO_2 or CO as it is shift active, while Co requires all inlet carbon to be in the monoxide form. An iron catalyst may be promoted with Zn to promote stability and Cu for easier reducibility; if Mn is added to the catalyst, shorter unsaturated carbon chains are favoured. In both the Co and Fe cases, meso and macro porous supports are preferred over micro porous ones.

3.6 ALCOHOLS

The synthesis of higher alcohol could be produced by a series of exothermic reactions, where syngas, i.e. CO and H_2, is converted into shorter alcohols over some specific catalyst:

1. Methanol: $CO + 2\ H_2 \rightleftharpoons CH_3OH$
2. Ethanol: $CO + 4\ H_2 \rightleftharpoons C_2H_5OH + H_2O$
3. Propanol: $CO + 6\ H_2 \rightleftharpoons C_3H_7OH + 2\ H_2O$
4. Butanol: $CO + 8\ H_2 \rightleftharpoons C_4H_9OH+ 3\ H_2O$
5. Any alcohol $n\ CO + 2n\ H_2 \rightleftharpoons C_nH_{2n+1}OH + (n-1)\ H_2O$

Depending on the catalyst and operation used different side reaction normally occurs with the formation of methane and hydrocarbon chains both olefins and paraffins. Also oxygenates as aldehydes, ethers and esters might be formed. Historically the production of higher alcohols has had an interest during the Second World War, and the interest has been renewed during high oil prices in the 1970s and 1980s

Currently, the synthesis of higher alcohols is not applied commercially anywhere in the world. The main reason for this is the lower selectivity for a specific alcohol, hence further separation steps are then needed. However, many interesting different conceptual processes do exist and are based on patented catalytic technologies [94]. Higher alcohol synthesis has been tested both in industrial plants and pilot plants or extensively tested in lab-scale reactors.

4 CONCLUSIONS AND CHALLENGES

As can be concluded there are many choices to be made before investing in a larger scale demonstration plant producing an alternative fuel derived from biomass, depending on the biomass available, gasification technology, and the biofuel to be produced, different kind of upgrading and cleaning processes are needed. The total efficiency of the plant depends on the heat management in every step included in the process, as in all multi-step systems. Gas filtering and clean-up units operate at different optimum temperatures that are lower than in the gasifier, often the operating temperature is limited by material issues and cooling is needed, which implies a lower efficiency and involving cooling equipment for the gas.

For biomass and waste gasification in pressurised fluidised bed systems the operating temperatures lie around 900 ºC, and it would be very valuable for the total efficiency if the removal of particulates could be carried out near the same operating temperature. However, at these high temperatures with the syngas comprising compounds with alkali, chlorine and sulphur, possible corrosion and other material problems are the main challenge. These gas contaminants must therefore be removed prior to the removal of particulates in high-temperature filters, or by introducing unconventional innovative methods for dust cake removal [95], [96]. In addition to sulphur poisoning and coking, when using waste and biomass as natural resources, not only ammonia, chlorine, alkali and other inorganic molecules will be present, also trace impurities and other poisons need to be studied carefully. Special consideration needs to be taken when using waste fractions that might contain PVC, since HCl will be formed in the gasifier. This all results in complex gas cleaning systems with high capital costs and expensive maintenance.

In Sweden different approaches for producing alternative motor fuels have been taken during the years, the best examples are the fluidised bed gasification demonstration plant in Värnamo and the Chemrec demonstration plant in Piteå using black liquor as input and more recently the GOBIGAS project in Gothenburg for the production of methane.

Before using the gas produced in the gasifier a number of impurities needs to be removed. These include particles, tars, sulphur and ammonia. Particles are formed in gasification, irrespective of the type of gasifier design used. A first, coarse separation is performed in one or several cyclone filters at high temperature. Thereafter bag-house filters (e.g. ceramic or textile) maybe used to separate the finer particles. A problem is, however, tar condensation in the filters and there is much work performed on trying to achieve filtration at as high a temperature as possible.

The far most stressed technical barriers regarding cleaning of the gases are tars. To remove the tar from the product gas there is a number of alternatives, but most important is that the gasifier is operated at optimal conditions for minimising initial tar formation. In fluid bed and entrained flow gasification a first step may be catalytic tar cracking after particle removal. In fluid bed gasification a catalyst, active in tar cracking, may be added to the fluidising bed to further remove any tar formed in the bed. In this kind of tar removal, natural minerals such as dolomite and olivine, are normally used, or catalysts normally used in hydrocarbon reforming or cracking. The tar can be reformed to CO and hydrogen by thermal reforming as well, when the temperature is increased to 1300ºC and the tar decomposes. Another method for removing tar from the gas is to scrub it by using hot oil (200-300ºC). The tar dissolves in the hot oil, which can be partly regenerated and the remaining tar-containing part is either burned or sent back to the gasifier for regasification.

Other important aspects are that the sulphur content of the gas depends on the type of biomass used, the gasification agent used etc., but a level at or above 100 ppm is not unusual. Sulphur levels this high are not acceptable if there are catalytic processes down-stream, or if the emissions of e.g. SO_2 are to be kept down. The sulphur may be separated by adsorbing it in ZnO, an irreversible process, or a commercially available reversible adsorbent can be used. There is also the possibility of scrubbing the gas with an amine solution. If a reversible alternative is chosen, elementary sulphur may be produced using the Claus process.

Furthermore, the levels of ammonia formed in gasification (3,000 ppm is not uncommon) are normally not considered a problem. When combusting the gas, nitrogen or in the worst-case NO_x (so-called fuel NO_x) is formed; there are, however, indications that there could be problems. Especially when the gasification is followed by down-stream catalytic processes, steam reforming in particular, where the catalyst might suffer from deactivation by long-term exposure to ammonia.

Not to forget the composition of the product gas depends very much on the gasification technology, the gasifying agent and the biomass feedstock. Of particular significance is the choice of gasifying agent, i.e. air, oxygen, water, since it has a huge impact on the composition and quality of the gas, The gasifying agent also affects the choice of cleaning and upgrading processes to syngas and its suitability for different end-use applications as fuels or green chemicals.

There will be a compromise between the capital cost of the whole cleaning unit and the system efficiency, since solid waste, e.g. ash, sorbents, bed material and wastewater all involve handling costs. Consequently, installing very effective catalysts, results in unnecessary costs because of expensive gas cleaning; however the synthesis units further down-stream, especially for Fischer-Tropsch diesel, and DME/methanol will profit from an effective gas cleaning which extends the catalysts lifetime. The catalyst materials in the upgrading processes essentially need to be more stable and resistant to different kinds of deactivation.

Finally, as for all multi-step processes, the heat management and hence the total efficiency depend on the different clean-up units. Unfortunately, the available conventional gas filtering units for removing particulates and impurities, and also subsequent catalytic conversion steps have lower optimum working temperatures than the operating temperature in the gasification units. Therefore, process intensification is an important development throughout chemical industries, which includes simultaneous integration of both synthesis steps and separation, other examples are advanced heat exchangers with heat integration in order to increase the heat transfer rates. For cost-effective solutions and efficient application, new solutions for cleaning and up-grading of the gases are necessary.

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