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A review of thermo-chemical conversion of biomass into biofuels-focusing on gas cleaning and up-grading process steps

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Executive summary

It is not easy to replace fossil-based fuels in the transport sector, however, an appealing solution is to use biomass and waste for the production of renewable alternatives. Thermochemical conversion of biomass for production of synthetic transport fuels by the use of 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. Therefore, 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.

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, clever 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 particular 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 or methanol.

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 1300°C and the tar decomposes. Another method for removing tar from the gas is to scrub it by using hot oil (200-300°C). 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. SO₂ 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.

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.

The ideal upgraded syngas consists of H₂ and CO at a correct ratio with very low water and CO₂ content allowed. This means that the tars, particulates, alkali salts and inorganic compounds mentioned earlier have to 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.

In summary, there are a number of uses with respect to produced synthesis gas. 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 of the reactions are exothermal (with the exception of steam reforming of methane and tars) and therefore handling the temperature increase in the reactors is essential. In addition, the synthesis of methanol has to be performed at high pressure (50-100 bar) to be industrially viable.

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 waste water 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 life-time. The catalyst materials in the upgrading processes essentially need to be more stable and resistant to different kinds of deactivation.

Finally, 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. Another example is to combine exothermic and endothermic reactions to support reforming reactions by using the intrinsic energy content. For cost-effective solutions and efficient application, new solutions for cleaning and upgrading of the gases are necessary.

Sammanfattning

Det är en stor utmaning att ersätta fossila bränslen inom transportsektorn, en tilltalande lösning är att använda biomassa och avfall för produktion av förnyelsebara drivmedel. 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 en rening och uppgradering av rågasen som produceras i förgasaren. Dessa material som är tänkta att ersätta olja och kol innehåller betydande mängder av alkaliska-, oorganiska-, svavel- och klor-föreningar.

De olika renings- och uppgraderingsstegen påverkar den totala verkningsgraden på hela processen, därför blir hanteringen av värme i de olika process strömmarna viktiga, som för alla processer i flera steg. Dessvärre, har de tillgängliga konventionella gas filtreringsenheterna för att ta bort partiklar och orenheter, och även efterföljande katalytiska omvandlingssteg, lägre optimala arbetstemperaturer än drifttemperaturen hos förgasningsenheterna.

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, smarta uppvärmnings lösningar och högre grad av integrationsprocess, samt 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 eller metanol.

Ett antal orenheter behöver tas bort innan gasen som producerats i förgasaren kan användas, dessa inkluderar partiklar, tjärar, svavelföreningar och ammoniak. Partiklar bildas alltid vid förgasning, oberoende av vilken typ av förgasningsteknik som används, en första grovseparation utförs i en eller flera cyklonfilter vid höga temperaturer. För att separera de finare partiklarna används därefter olika keramiska- eller textilfilter, ett problem är dock kondensation av tjära i filtren, mycket arbete utförs på att försöka uppnå filtrering vid så hög temperatur som möjligt, så att man slipper tjärproblemen.

Det största hindret när det gäller rening och uppgradering av gaserna är tjära. För att bli av med tjäran från produktgasen finns ett antal olika alternativ, men det väsentligaste är att själva förgasaren drivs vid optimala förhållanden för att minimera att tjära bildas överhuvudtaget.

För förgasning med fluidiserad bädd och entrained flowförgasning skulle det första steget kunna vara katalytisk tjärkrackning efter att ha avlägsnat alla partiklar. Vid förgasning i fluidiserad bädd kan aktiva katalysatorer tillsättas till den fluidiserande bädden som kan kracka tjäran redan i bädden och hindra att ytterligare eventuell tjära bildas. Katalysatorer som används är främst naturliga mineraler, såsom dolomit och olivin, dessa användes normalt vid reformering eller krackning av kolväten.

Tjäran kan reformeras till vätgas och kolmonoxid genom termisk reformering såsom när temperaturen höjs till 1300°C och tjäran sönderfaller. En annan metod för att avlägsna tjära från gasen är att tvätta gasen med hjälp av het olja (200-300°C). Tjäran löser sig i den heta oljan, som delvis kan vara regenererad och den återstående tjärhaltiga delen kan antingen brännas eller återföras till förgasaren för förgasning.

Svavelföreningar är en annan viktig kontaminering som behöver tas bort ur gasen, svavelhalten i gasen beror främst på vilken typ av biomassa som används. Nivåer över 100 ppm inte är ovanligt och är inte acceptabelt för efterföljande nedströms katalytiska processer, eller om utsläppen av t.ex. SO₂ ska hållas nere.

Svavel kan separeras genom adsorption med ZnO som är en irreversibel process, eller genom kommersiellt tillgängliga reversibla adsorbenter som kan användas. Ytterligare alternativ är att tvätta/skrubba gasen med en aminlösning. Om ett reversibelt alternativ används kan elementärt svavel framställas med hjälp av Claus-processen.

Ammoniak bildas vid förgasning och nivåer runt 3000 ppm är inte ovanligt, men anses vanligtvis inte ett problem efterföljande nedströms processer. Om gasen förbränns, kan dock kväve eller i värsta fall NO_x (så kallad bränsle NO_x) bildas. Det finns dock indikationer på att problem kan uppstå, speciellt när förgasning följs av nedströms katalytiska processer, exempelvis vid ångreforming där katalysatorn kan deaktiveras vid långvarig exponering för ammoniak

Sammansättningen på produktgasen beror framförallt på valet av förgasningsteknik, vilket förgasningsmedel som används, samt viken sorts biomassa som används. Valet av förgasningsmedel, dvs. luft, syre, vatten, är extra viktigt eftersom det har en direkt inverkan på sammansättningen och kvaliteten hos gasen. Valet av förgasningsmedel påverkar också vilka renings- och uppgraderingsprocesser som kan användas och lämpar sig bäst för olika slutanvändningstillämpningar som t.ex. drivmedel eller för gröna kemikalier.

Idealt består en syntesgas som är uppgraderad av vätgas och kolmonoxid i korrekt förhållande, med mycket låga halter vatten och koldioxid. Detta innebär att tjäror, partiklar, alkalialter 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.

Sammanfattningsvis finns det ett antal olika användningsområden för olika producerade syntesgaser. De olika tillämpningarna kommer att diskuteras i rapporten med början med 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 där syntes av SNG och metanol begränsas 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 viktigt att kontrollera temperaturökningen i reaktorerna. Dessutom måste syntes av metanol utföras vid högt tryck (50-100 bar) för att vara industriellt gångbar.

För att hålla nere kapitalkostnaderna för hela reningssystemet och systemets effektivitet behöver man kompromissa, eftersom hanteringen av fast avfall, t.ex. aska, absorberande medel, bäddmaterial och avloppsvatten alla innebär kostnader.

Att installera väldigt effektiva katalysatorer resulterar i dyrare gasrening på grund av onödiga kostnader, men nedströms syntesprocesser kommer att dra nytta av effektiv gasrening som förlänger katalysatorernas livstid, särskilt för Fischer-Tropsch-diesel, och DME/metanol syntes. Generellt måste katalysatorerna i de olika uppgraderingsprocesserna vara mer stabila och motståndskraftiga mot olika typer av deaktivering.

Slutligen är process-intensifiering ett viktigt område för utveckling inom hela kemiindustrin som bland annat omfattar integration av både syntes och separationssteg, med olika former av avancerad värmeväxling med värmeintegration för att öka värmeöverföringshastigheten, och att kombinera exoterma och endoterma reaktioner. Därför är det nödvändigt med nya innovativa lösningar för rening och uppgradering av gaserna för att få fram kostnadseffektiva och effektiva tillämpningar.

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Introduction

Gasification of biomass for the production of 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.

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. The focus is on describing the technology, synthesis options, catalyst performances, thermodynamics and, efficiencies and yields for the different sub-systems/processes. This report does not focus on the gasification concepts, which has been covered in an earlier report from F3 [1].

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. Of a total of 384 TWh in 2013, just over a third (130 TWh) was produced from biofuels. 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 for the production of 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 downstream 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, 1100-1300°C, using an entrained flow gasifier, the other operating a fluidised bed gasifier coupled with a down-stream catalytic reformer, both working close to 900°C [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 pretreatments 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.

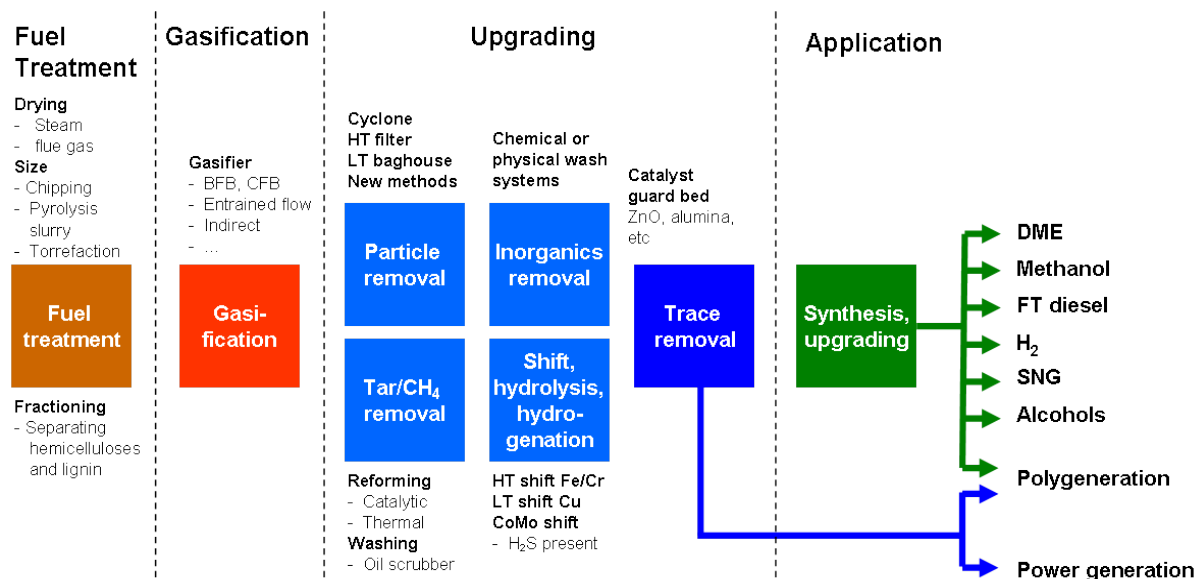


Figure 1. Overview of different processes that may be included in a biomass gasification system [3].

Gasification of biomass for the production of 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 (H₂S, COS) and ammonia. Tars and hydrocarbons must be converted into synthesis gas (CO₂, CO, H₂) or be utilised otherwise to achieve good energy efficiency and economy. 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.

Fuel pre-treatment and gasification

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 500°C and 1400°C, 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 manner 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 and in the UK.

This report mainly focusses on the steps after the production of the gas, the gas purification and upgrading stages, as described in Figure 1.

In the following chapter the process from biomass, via pre-treatment, gasification will be described. The most common types of gasifiers will be explained with respect to gas quality and operating conditions.

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.

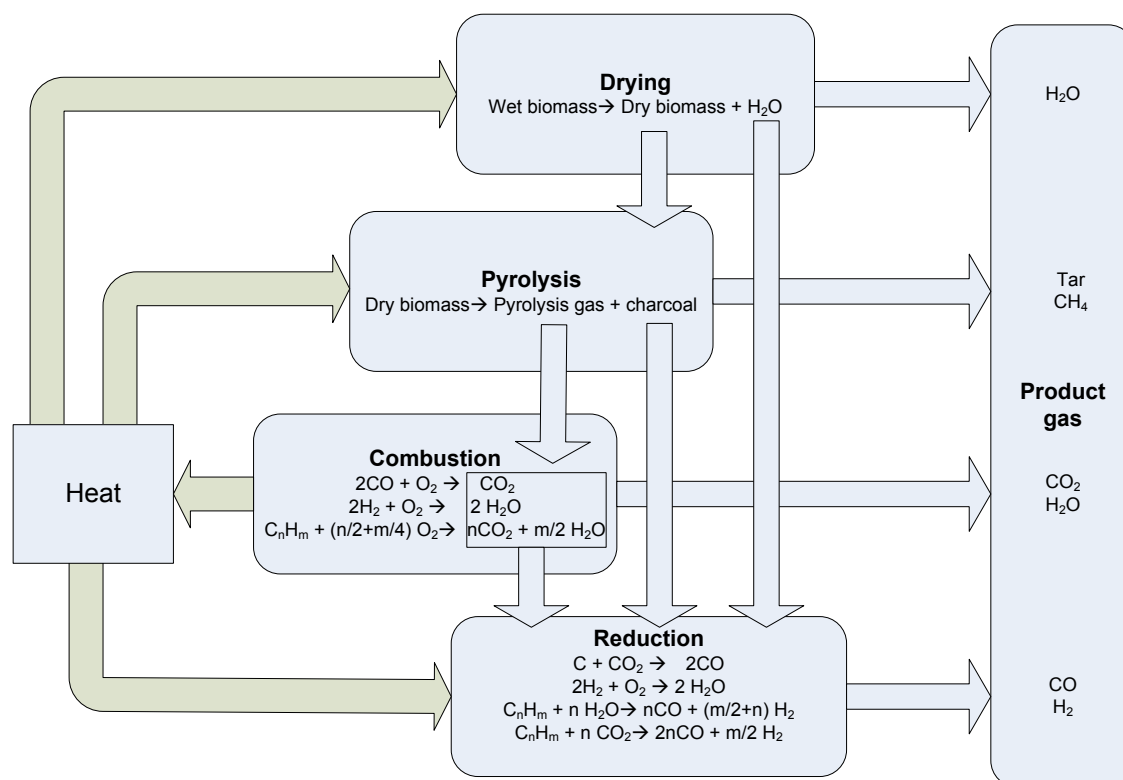


Figure 2. Schematic overview of the four gasification stages [4], reproduced with permission.

The exit gas from the gasifier will contain CO, CO₂, H₂O, H₂, CH₄, other gaseous, higher hydrocarbons and N₂ (the N₂ 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, NH₃, HCl, H₂S 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

C₂	Vol-%	2.4	4.4	5.5
H₂/CO-ratio	-	1.2	1.1	0.5
Energy in CH₄+C₂	%	36.2	65.1	54
Energy in H₂	%	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)" [5].

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 (400°C) → Phenol ethers (500°C) → Alkylphenols (600°C) → Heterocyclic phenols (700°C) → Polyaromatic species (800°C) → Larger polyaromatic species (900°C)

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.

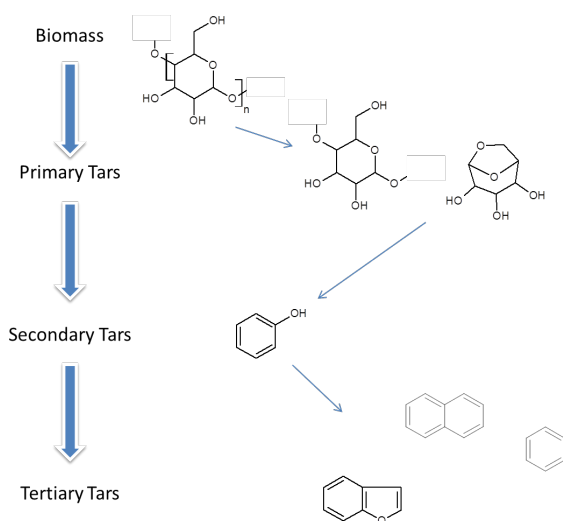


Figure 3. The first classes of tars and their origin [6], reproduced with permission.

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 500°C to 800°C, the secondary tar class between 500°C and 1000°C, the alkylated tertiary products (class 3) are present between 650°C and 1000°C while the condensable tars (class 4) exist above 750°C. The tar formation and the change from one class of tar to another is dependent on residence time as well as temperature.

Pre-treatment

Before the biomass feedstock is entered into the gasification system, it is handled in different ways to improve the operation of the gasification system. Parameters of importance are particle size and how much moisture the fuel contains.

Grinding

The requirement with respect to particle size depends to a large degree on the design of the gasifier. There are cases that require medium-size particles 10-20 mm (fixed bed) [7], and 5 mm (fluid bed), while other cases require sizes of 1 mm or less (entrained flow) [8]. To obtain these size ranges, a chipper may be used in the first and second instance while a hammer mill will have to be used in the third instance.

Drying

The overall system efficiency is dependent on the moisture level of the biomass. To further help the performance and operability of the gasification system the biomass is dried before it is entered into the gasifier. There is a correlation between moisture content and performance; however, the biomass is rarely dried below 10 % for economic reasons [9]. A typical biomass moisture level is 35 %, which is lowered to at least 15 % before the biomass is allowed to enter the gasification reactor. The traditional type of dryer is applicable to this application, e.g. rotary drum or steam driers. Normally, surplus heat from the process is used in the drying operation.

Gasifier feeding systems

The main factor in determining the feeding system into the gasifier is whether the operating pressure of the reactor is at or above ambient pressure. If the reactor operates at a pressure, above ambient a locked hopper system is normally used. This system is made up of three vessels in series where vessel one operates at ambient pressure, vessel two varies in pressure from ambient to the operating pressure and the third vessel operates at the reaction pressure of the gasifier. Using a screw, the biomass is transported into the first vessel, whereafter the biomass is let down into vessel two through a hatch. This second vessel is subsequently pressurised to the operating pressure of the gasifier (or slightly above) and a transportation screw moves the biomass into the third vessel, from which the biomass is fed into the reactor. As can be imagined, the gas used to pressurise the intermediate vessel will have to be inert for safety. At atmospheric pressure, the biomass may be screw-fed directly into the gasifier.

Gasification

When looking into the topic of gasification, there are several different designs of the actual reactor for converting biomass into producer gas, the carbon monoxide and hydrogen-rich gas desired. There are three different types of reactors used for biomass gasification and they are broadly differentiated by the type and structure of the biomass inside the reactor. The first type is fixed or moving bed reactors, where the biomass is situated inside the reactor and slowly moves through the reactor as it is consumed, this reactor type is generally considered suitable for the smaller scale or less than 5 MW_{th}. The second type of reactor considered is the fluidising, both bubbling and circulating, type of gasification reactors. This type of reactor is generally considered suitable from 5 MW_{th} to 200 MW_{th}. The final reactor type is the entrained flow type reactor, which is considered suitable for 100-700 MW_{th}. In addition, all of these types may be directly or indirectly heated.

Fixed bed gasification

The easiest way to convert biomass into an energy-rich gas is to use fixed bed gasification. This is the approach used for the wood-gas generators used for car propulsion during the 2nd world war. This type of gasifiers may be further divided into sub-groups such as updraft, downdraft and crossdraft flow, Figure 4.

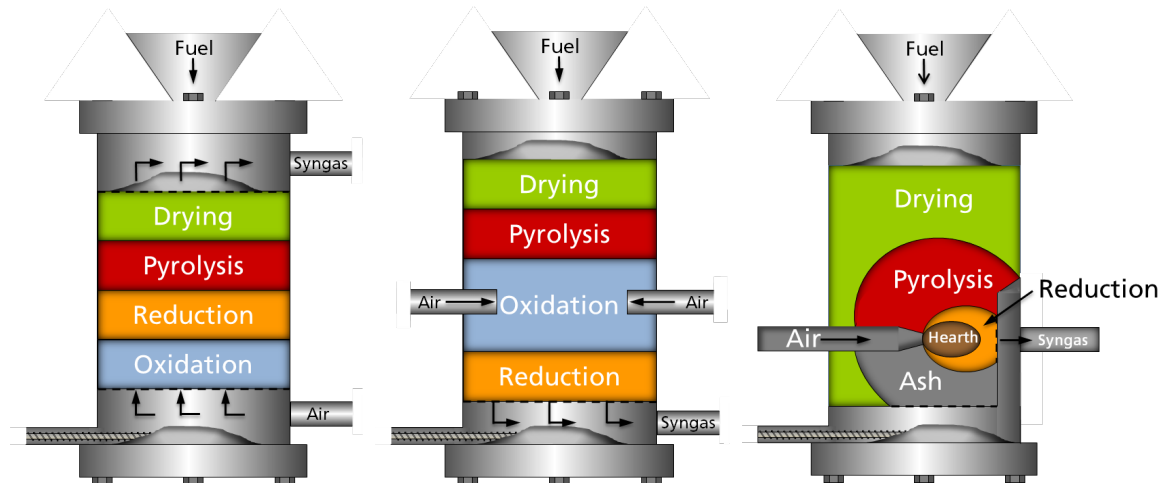


Figure 4. Different types of fixed bed gasifiers, from the left: updraft, downdraft and crossdraft [10], reproduced with permission.

Independently of the fixed bed gasifier type used, the fuel is always entered at the top. The operating temperature ranges from 300 to 1000°C depending on where in the bed it is measured. Which sub-category the gasifier ends up in is determined by the flow path of the oxidant (air, oxygen, steam) through the reactor and where it is introduced. The most prominent feature of the fixed bed gasifier type is that it is simple in construction and gives a relatively good gas quality despite the simplicity of the system [10].

Fluidised bed gasification

In this type of gasifier, a heat transfer medium, e.g. sand, olivine or dolomite, is used to enhance the biomass conversion. There are two subcategories in this gasifier classification, bubbling and circulating, and the categories follow the same definition as for combustion, see Figure 5.

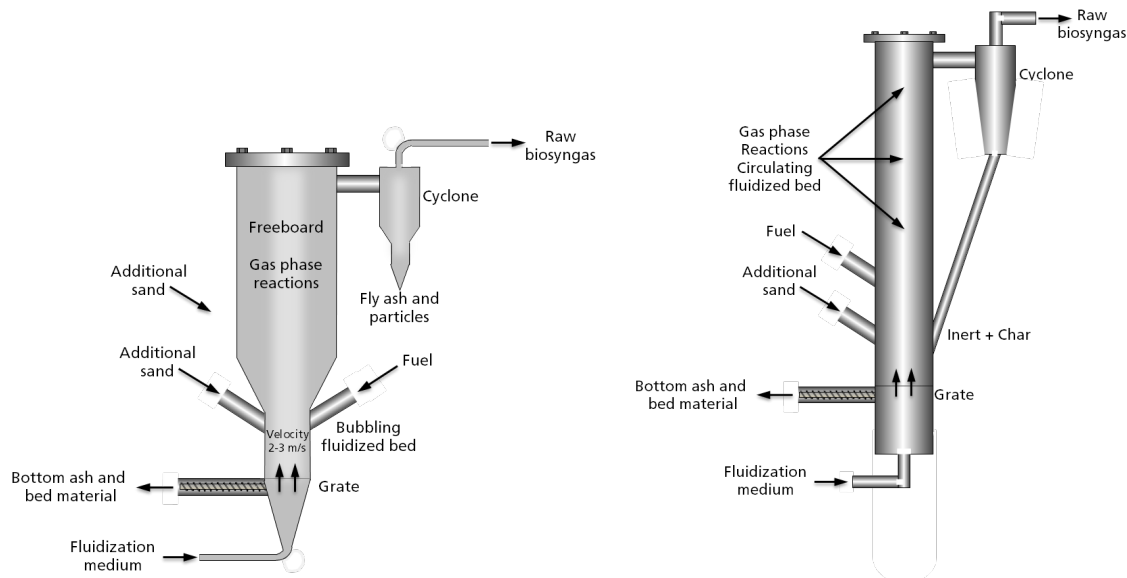


Figure 5. The different categories of fluidised bed gasification, bubbling bed and circulating fluidised bed [10], reproduced with permission.

In the bubbling type gasifier, the feedstock is introduced just above the sand bed and the oxidant is used to create the bubbles in the bed (entered in the bottom). The linear velocity is about 2-3 m/s through the bed and the operating temperature ranges from 650 to 900°C. In the circulating type gasifiers a higher velocity (5-10 m/s) makes the particle suspend in the gas and the feedstock, charcoal,

bed material and ash are separated in a cyclone filter. The temperature is usually in the 800-1000°C range. Both types are found operating at elevated and atmospheric pressure alike; this type has a higher throughput than the fixed bed gasifiers. However, the sand also increases the dust content in the gas [10].

Indirect gasification indicates that heat is added through some kind of heat exchange, avoiding dilution of the product gas. This type of gasification may be performed using any kind of gasification principle, but is mostly used in fluidised bed gasification, see Figure 6.

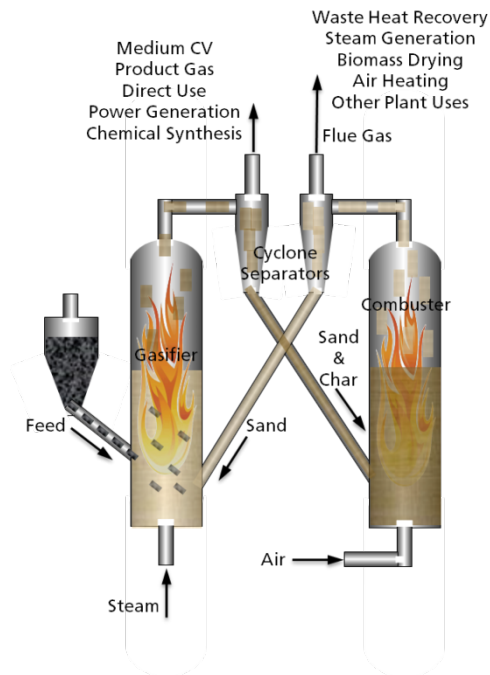


Figure 6. Example of indirect gasification [11].

Entrained Flow Gasification

This type of gasification is the most common worldwide, based on coal as feedstock and takes place at high temperature (>1200°C). Because the design assumes on entraining the feedstock particles in the gasification medium, the particles have to be small. This also influences the residence time, which is short. Two design examples are found in Figure 7.

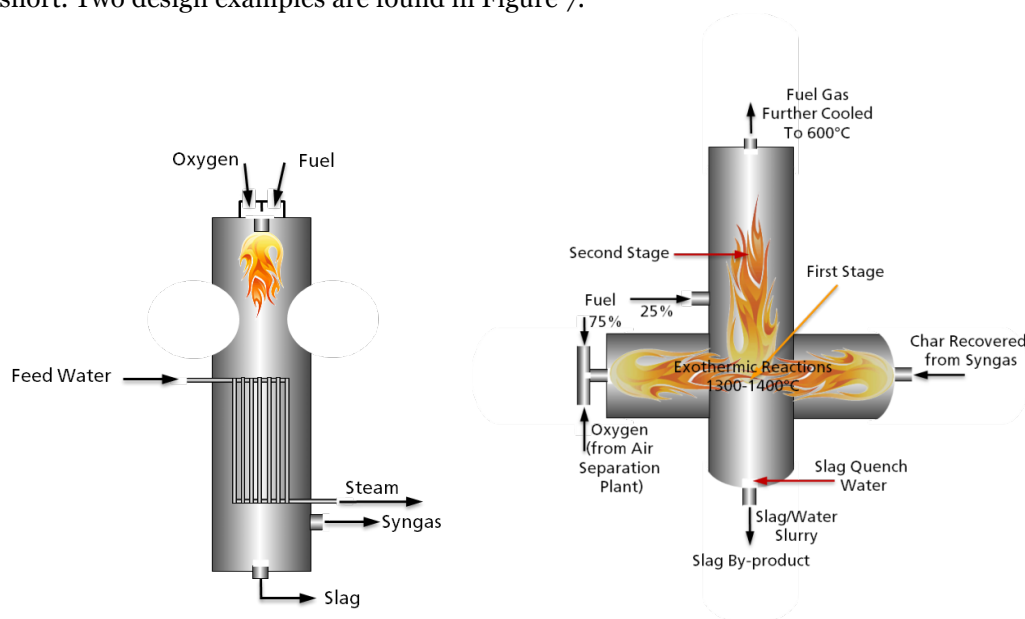
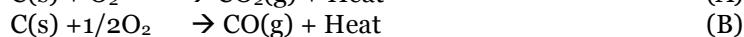


Figure 7. Different designs of entrained flow gasifiers, downstream and upstream gasifier [10].

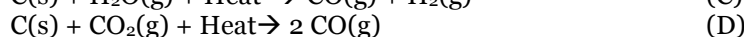
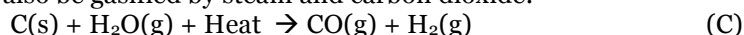
Gasification agents

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:



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:



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 has to 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). This results in a larger amount of produced gas with a lower heating value. An air-blown gasifier produces a gas with a Low Heating Value (LHV) of 3.5-6 MJ/Nm³ while oxygen blown gives a gas with a LHV of 10-15 MJ/Nm³ [12].

A synthesis gas containing a large volume of inert gas requires larger equipment, reactors, tubes, heat-exchangers and more, due to the higher volumetric flow. Hence, conversion of the synthesis gas becomes lower due to lower partial pressures of the reactants consequently lowering reaction rates, the dilution also leads to larger losses, heat and material losses.

For large industrial oxygen-blown gasification plants, cryogenic distillation of air for oxygen production seems to be the preferred technology. Figure 8 shows a schematic drawing of a cryogenic distillation plant.

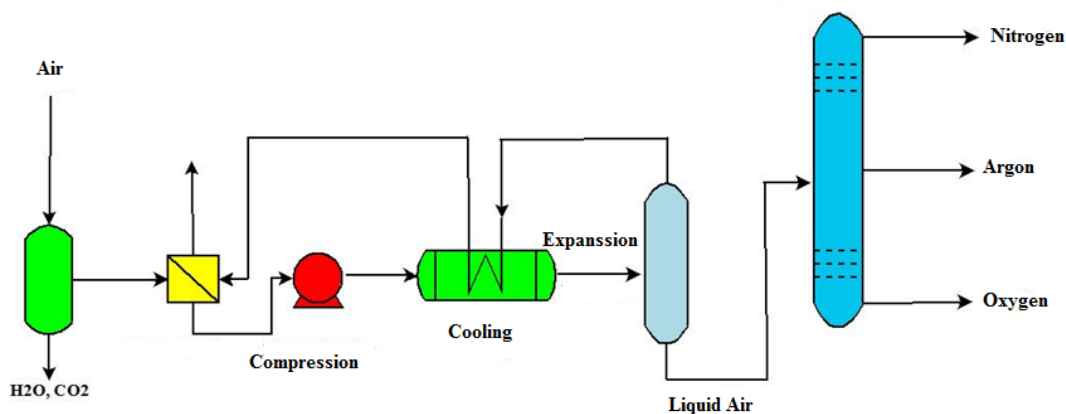


Figure 8. Production of liquid oxygen by cryogenic distillation.

Air from the atmosphere is dried and the carbon dioxide content is removed. The dried gas is then compressed into a pressure tank. When the air is compressed the temperature increases. If this heat is removed the temperature will fall below the inlet temperature when the gas is expanded. So the compressed air in the pressure tank is chilled by the outgoing cooler gas. This means that the temperature in the pressure tank, and in the expansion tank, continuously falls. When the temperature

becomes sufficiently low, liquid air will condense in the expansion tank. The liquid air is pumped to a fractionating column where nitrogen, argon and oxygen are separated.

Upgrading

The product gas from the gasification process contains impurities deriving from the biomass in form of tars, particulates, and inorganic compounds, such as HCl, NH₃, COS, H₂S, and alkali salts. These compounds need to be removed from the raw gas, to some extent, depending on the end application desired [13].

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 [14]. This is also one of the key troubles stopping the commercialisation of the gasification technology [15].

Particulates in the syngas may also cause problems by blocking and erosion downstream in the upgrading equipments. Particulates deriving from the gasification consist of a mix of ash from the biomass, formed char and bed material from the fluidised bed [15]. 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 350°C such as, woven polymeric and ceramic materials or natural fibres. Candle filters, both ceramic and metallic, are used for higher temperatures up to 700°C [16].

Particle removal

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.

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 experience 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 [17]. Depending on the construction material, for instance lining with refractory oxides, cyclones may be used at high temperature. MEVA ENERGY, for instance, has constructed a cyclone gasifier that runs at 900°C [18].

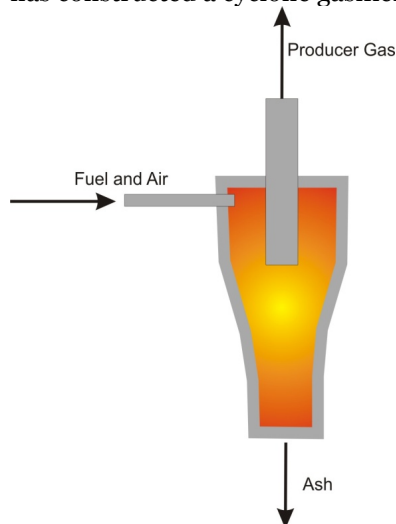


Figure 9. Schematics of Meva Energy's vortex intensive power process gasifier.

High-temperature filters

Filters are good for removing dust from streaming gases, such as flue gases from combustion. Baghouse filters consist 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 to 200-250°C with some kind of temperature-resistant fabric.

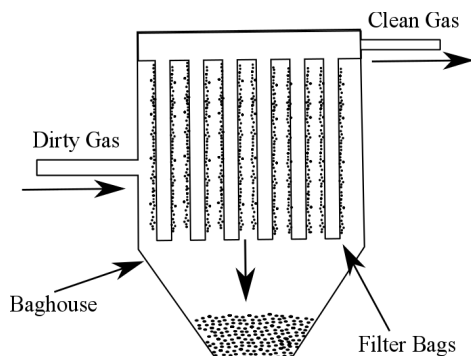


Figure 10. Schematics of a baghouse filter.

However, in biomass gasification there is a need to remove the dust at much higher temperature and it is typically performed at 350-500°C [19]. 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 [20] and the Güssing Biokraftwerk [21] in Austria. In both plants the fabric filters were run at 160-180°C and the ceramic filters at 340-370°C.

However, cooling the gas to enable filtration and then re-heating the gas for further processing, decreases the efficiency of the gasification plant. Still, running the filters at high temperature (>500°C) has caused problems by clogging. Tars and soot are suggested to cause the clogging by formation of a sticky cake [19]. Not only the temperature affects the performance but also the fuel and bed material. Simone [21] claims that with a correct choice, for instance with magnesite as bed material and clean wood it was possible to run the filter at 800°C, while miscanthus clogged the filter at similar conditions.

Dia-Schumalith candle filters [19] were used in a 100 kWt atmospheric circulating fluidised bed gasifier between 600 and 800°C for more than 50 h. The filter cake formation was studied with gas face velocities between 3 and 5 cm/s. Stable 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 800-850°C and in the presence of 100 vppm H₂S. An evaluation using real gas reports a tar conversion of 81 % at 790°C and 40 vppm of H₂S. The active material is usually traditional Ni supported on a thermostable carrier [22], [23].

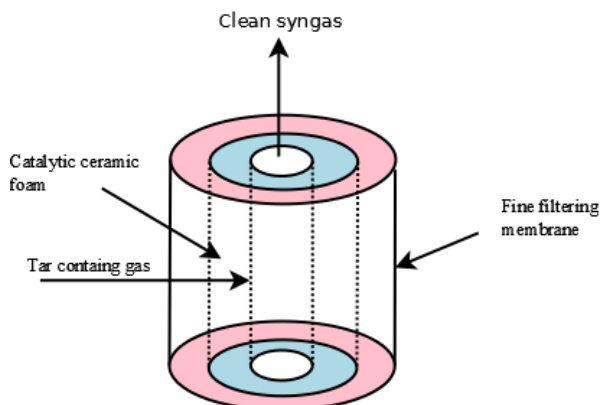


Figure 11. Catalytic candle filter [22].

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 has to 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 generally speaking since different gasifiers produce different amounts of tars.

Table 2. Operating conditions for fluidised-bed and entrained-flow gasifiers [24].

	BFB	CFB	EF
Temperature (°C)	< 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.

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 [25], 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.

Component	After Gasifier	LHV wet	LHV wet
	Vol %	MJ/Nm ³	MJ/kg
C₂-C₄	1.6	0.9	0.9
CH₄	8.2	3.1	2.8
CO	11.9	1.5	1.4
CO₂	27.9		
H₂	11.8	1.3	1.2
H₂O	37.7		
NH₃	0.3		
H₂S	0.01		

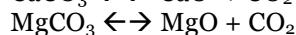
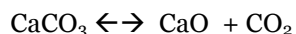
Tars	0.3	0.7	0.6
LHV (total)		7.5	6.8

After removal, the tarry liquid also has to be taken care of. Usually the tars are burnt in the process to generate heat for the gasification. This is done in Güssing [**Fel! Bokmärket är inte definierat.**] 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

Tar Cracking

The difference between tar cracking and tar reformation is that during the tar cracking only large molecules, such as the tars are broken down while during reforming all hydrocarbons (including tars) are broken down into synthesis gas components (CO, CO₂ and H₂). 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(CO₃)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 [26].

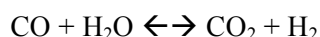
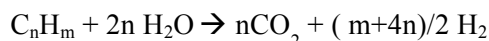
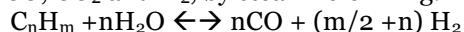


However, this reaction is reversible, this means that the dolomite catalyst is sensitive to the CO₂ partial pressure and can only be used at low pressure (< 10 bar). The dolomite may be used as in-bed catalyst, but it is soft and erodes quickly, for instance in fluidised beds. However, dolomites have low activity for methane reforming in the product gas and are consequently not the best choice for production of syngas alone [27, 28].

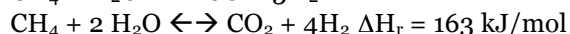
Tar reforming

Steam reforming

By the use of metal catalysts supported on thermostable carriers, hydrocarbons may be converted into synthesis gas, CO, CO₂ and H₂, by steam reforming.



For instance for methane:



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 [28]. These Ni-based catalysts may also be used in fluidised bed applications. Below in Figure 12, a schematic drawing of a gasification-steam reforming unit is shown.

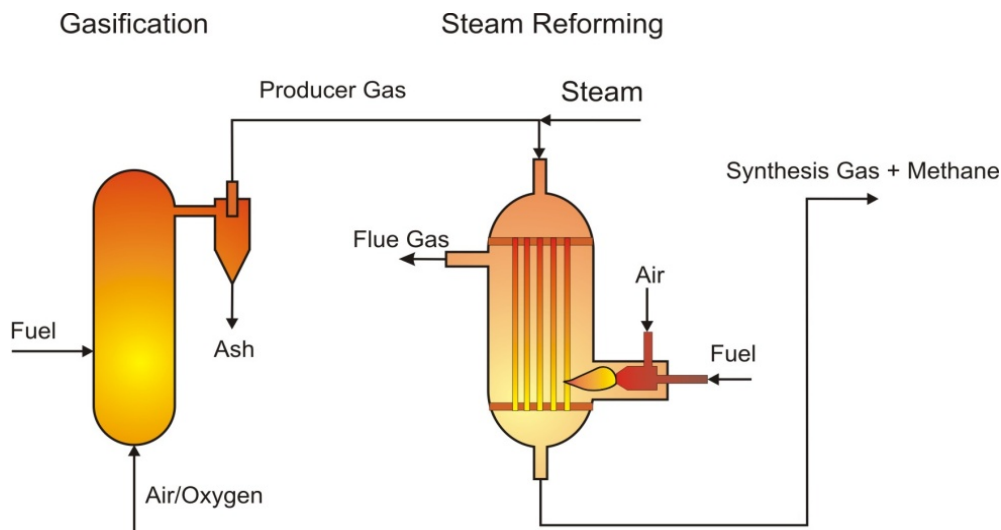


Figure 12. Schematic drawing of a gasification-steam reforming unit.

Since heat has to 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 13.

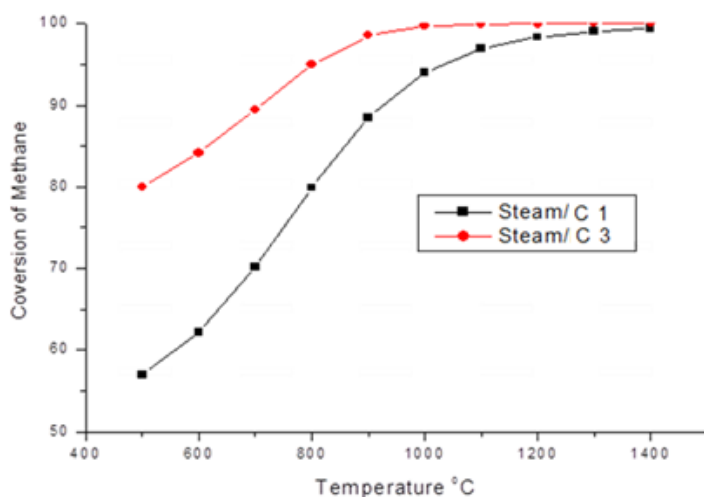


Figure 13. Steam reforming of methane at steam to carbon ratios 1 and 3, 101 kPa.

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 14.

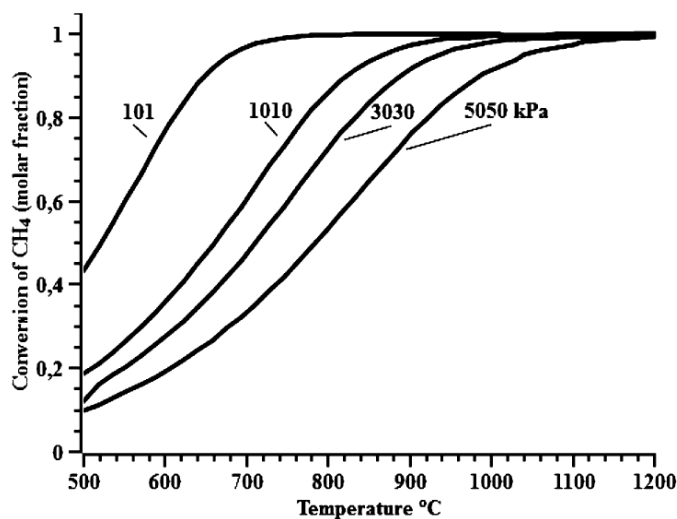


Figure 14. Steam reforming of methane at steam/C=3, pressure dependency of conversion.

In spite of 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/Nm³) or a monolithic bed (dusty gas 10-30 mg/Nm³) may be used [29]. 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 to the adsorption of hydrogen sulphide (H₂S) on the surface of the Ni crystallites, see Figure 15. 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.

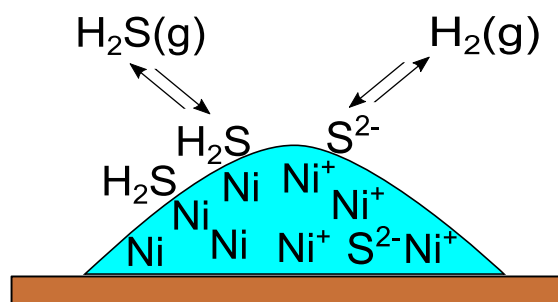


Figure 15. Adsorption of hydrogen sulphide on supported nickel.

The adsorbed hydrogen sulphide also oxidises the metallic Ni, in the bulk of the crystallite, into Ni⁺ under formation of hydrogen H₂. This leads to a gradual conversion of the metallic crystallite into NiS by incorporation of S²⁻ 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 16.

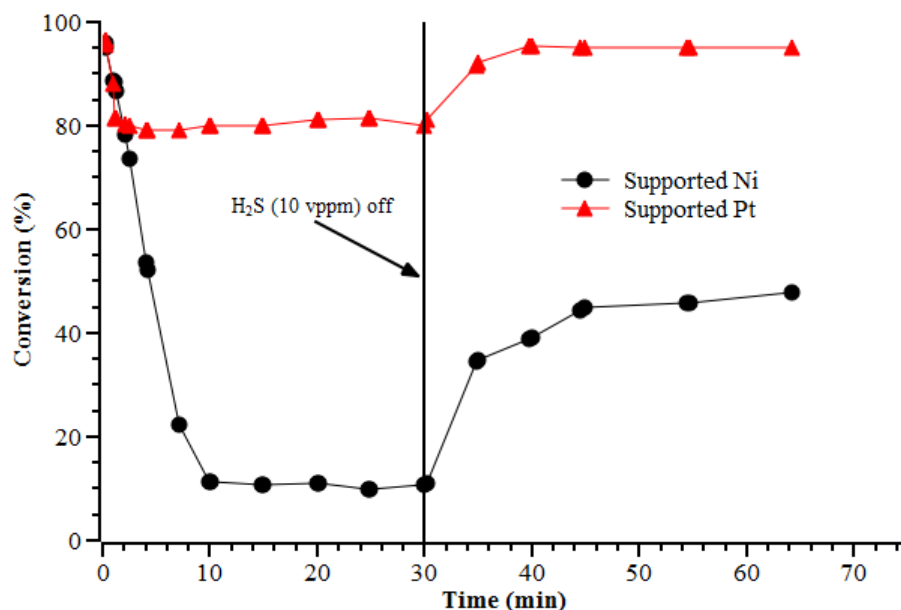


Figure 16. The hydrogen sulphide sensitivity of Ni and Pt supported catalyst. $T=800^{\circ}\text{C}$, GHSV $450\,000\text{ h}^{-1}$, gas composition: 64 dm^3 methane/h, 188 dm^3 /h steam, 150 dm^3 /h N_2 and 150 dm^3 /h H_2 [30].

In this experiment two different catalysts, one supported Pt and the other a supported Ni catalyst, are exposed to 10 vppm of H_2S in methane reforming. The activity decreases drastically, from almost 100 % down to 10 % for the Ni catalyst while for the Pt catalyst the activity falls down to 80 %. However, when the hydrogen sulphide is removed from the inlet after 30 min, the Pt catalyst regains its original activity while the Ni catalyst recovers from 10 to 40 % conversion. The difference is due to the fact that no bulk sulphide is formed in the Pt catalyst, only the surface is blocked, while it will take a long time to remove the sulphide from the nickel bulk.

The Pt catalyst is more resistant towards sulphur poisoning than the Ni catalyst. The spot market price for Pt (Aug 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 [31] is developing tar reforming catalysts for industrial use, see Figure 17. In dusty gas ($10\text{--}30\text{ g/Nm}^3$) cylindric megamonoliths, 1000 mm in height and 750 mm in diameter, are used. The megamonoliths are washcoated metal monoliths. The open canals allow the ash to pass the catalytic bed without clogging.

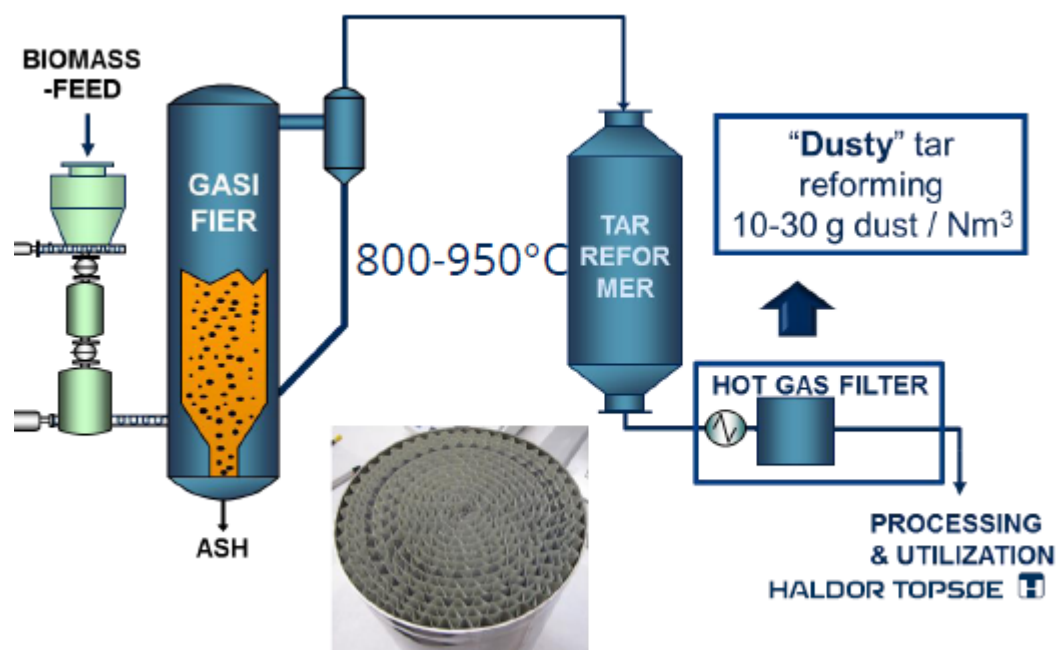


Figure 17. Tar reforming in dusty gas with Topsoe megamonoliths. (Courtesy of Topsoe AS)

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 Fjernvarme 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 %.

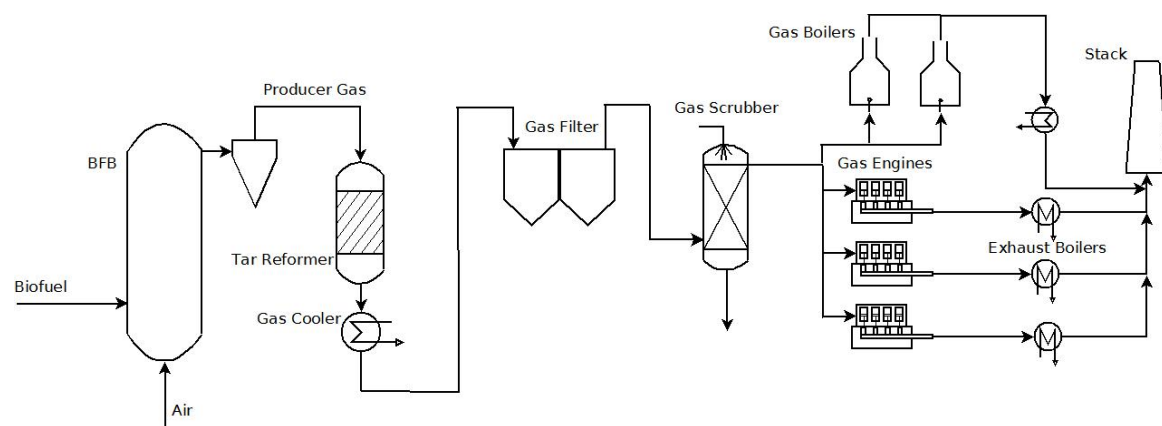


Figure 18. Schematic of the Skive plant (Carbona/Andritz) [32].

The operating temperature for the reformer is restricted by the stickiness of the ash, but in the range of 800-950°C and 0-20 bar in pressure. Typical hydrocarbon composition of the producer gas is C1-C3, benzene and 1-20 g/Nm³ 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 where the performance/size becomes an important factor, precious metal catalysts may be used [33].

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 19 shows results for a Ni-substituted β -hexaaluminate that is being developed. The hexaaluminate is a high-temperature stable material that has been used, substituted by various active materials, in high-temperature catalytic combustion. In [34] this catalyst was tested in a slip stream from a 100 kWt CFB. In Figure 19 the result of two different substitution levels (Ni-1 and Ni-2) are shown at 850°C and atmospheric pressure. The total amount of tars is in the range of 2-2.5 g/Nm³ and is measured at three different points with SPA. CFBG is after the gasifier but before the high-temperature filter, bef Cat is at the inlet of the reactor and after Cat 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.

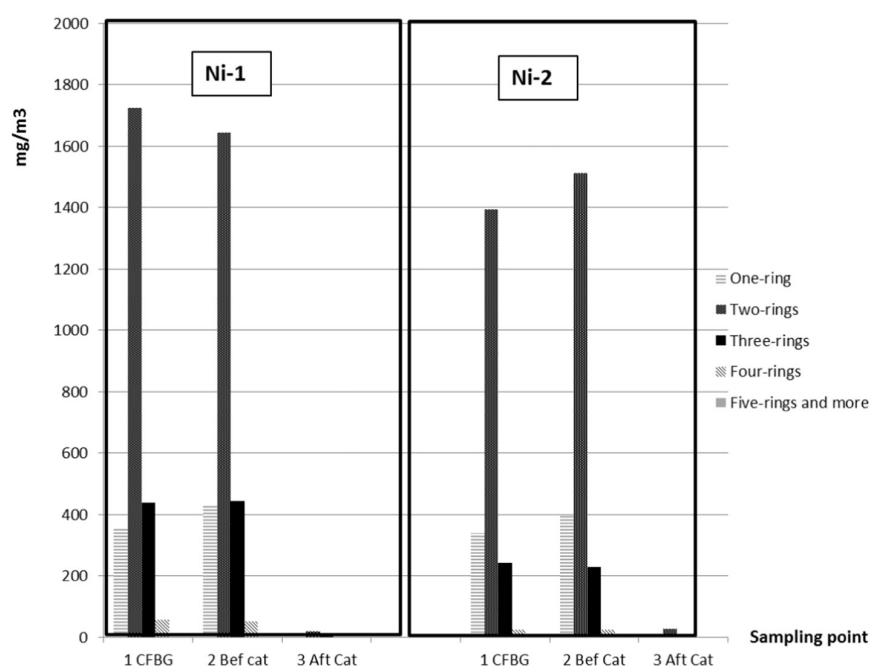


Figure 19. The diagram shows tar levels for a Ni-substituted hexaaluminate used for hydrocarbon reforming. The sampling point for CFBG is after the gasifier but before the high temperature filter, bef Cat is at the inlet of the reactor and after Cat is at the outlet of the reactor tested with two different substitution levels (Ni-1 and Ni-2) at 850°C and atmospheric pressure.

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

Autothermal reforming and partial oxidation

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 20 [35].

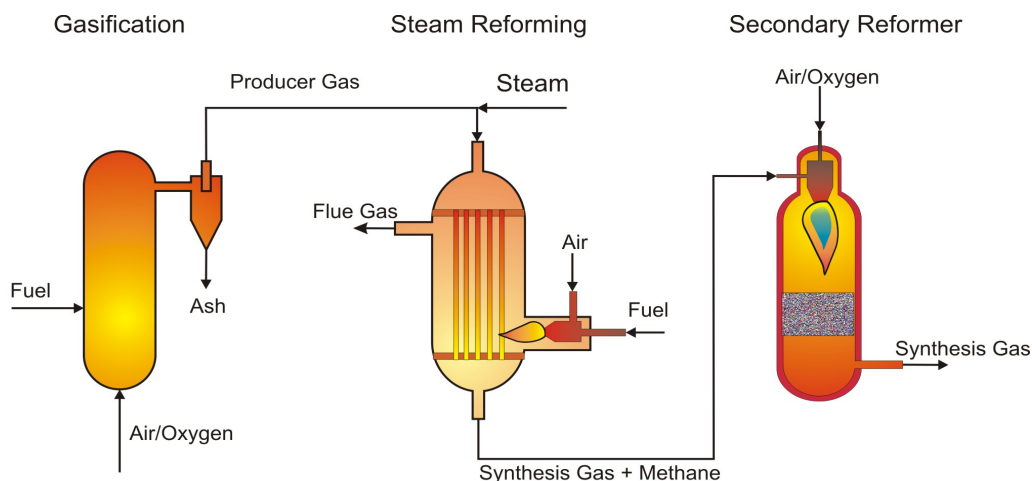


Figure 20. Gasification-steam reforming unit with a secondary reformer step.

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

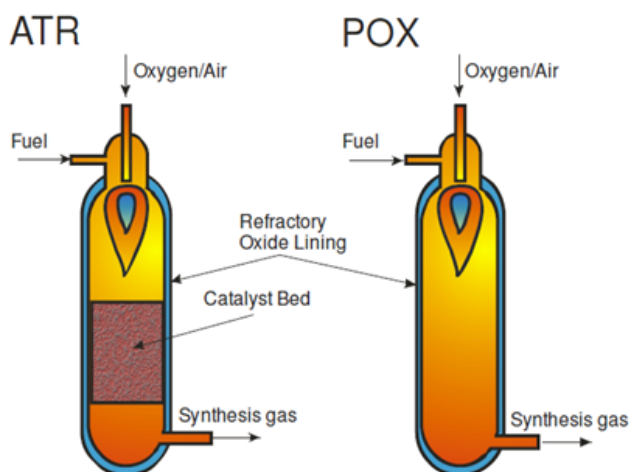


Figure 21. Comparison between ATR and POX reactors.

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 21. 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 has to be burnt than in the case of POX. While the ATR requires a temperature of 800-1000°C, the POX needs a temperature of 1200-1400°C for the homogeneous gas phase reactions [36].

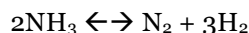
This means that the ATR process has higher efficiency, conserves more chemically bound heat in the gas, than does the POX process. However, the POX unit does not contain any catalyst that might be deactivated and needs to be replaced.

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 [37].

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 [38].



In Figure 22, the equilibrium for ammonia has been calculated for a stoichiometric amount of $\text{N}_2 + \text{H}_2$. 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 800-1000°C. 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.

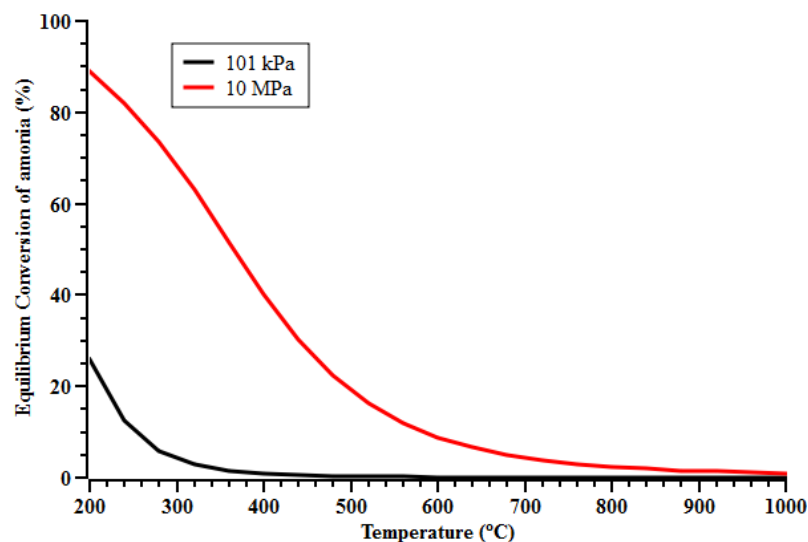


Figure 22. NH_3 equilibrium calculation of ammonia stability in a stoichiometric mixture of N_2 and H_2 .

In the Skive plant the ammonia reduction has gradually been increased during the development work, for instance in 2010 70 % reduction was reported [39] and lately ammonia slip-free conditions have been reported [40].

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 $\text{H}_2\text{O}/\text{CO}$ ratio and favoured at high temperatures: methanation (Eq. 2), CO disproportionation or decomposition (Eq. 3).



**reaction to the right*

An increase of the $\text{H}_2\text{O}/\text{CO}$ ratio lowers the risk of carbon formation. At ratios higher than $\text{H}_2\text{O}/\text{CO} = 2$, carbon will not exist in the equilibrium mixture when the reaction temperature is higher than 230°C. At ratio 1, the formation of carbon becomes thermodynamically favourable over the entire reaction temperature range. Methane formation is favoured between 200 and 450°C and at low $\text{H}_2\text{O}/\text{CO}$ ratios

[41]. Methane formation can be reduced by selectively removing the H_2 from the reaction stream (by means of a separation membrane) [42].

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 360–400°C, and Cu/ZnO– Al_2O_3 for low temperature shift, LTS, operating just above the dew point, the lowest possible inlet temperature is about 200°C for good performance under steady state conditions. Figure 23 shows a combined HT and LT shift steps, for production of gas containing high concentration of hydrogen, with cooling in between the two steps.

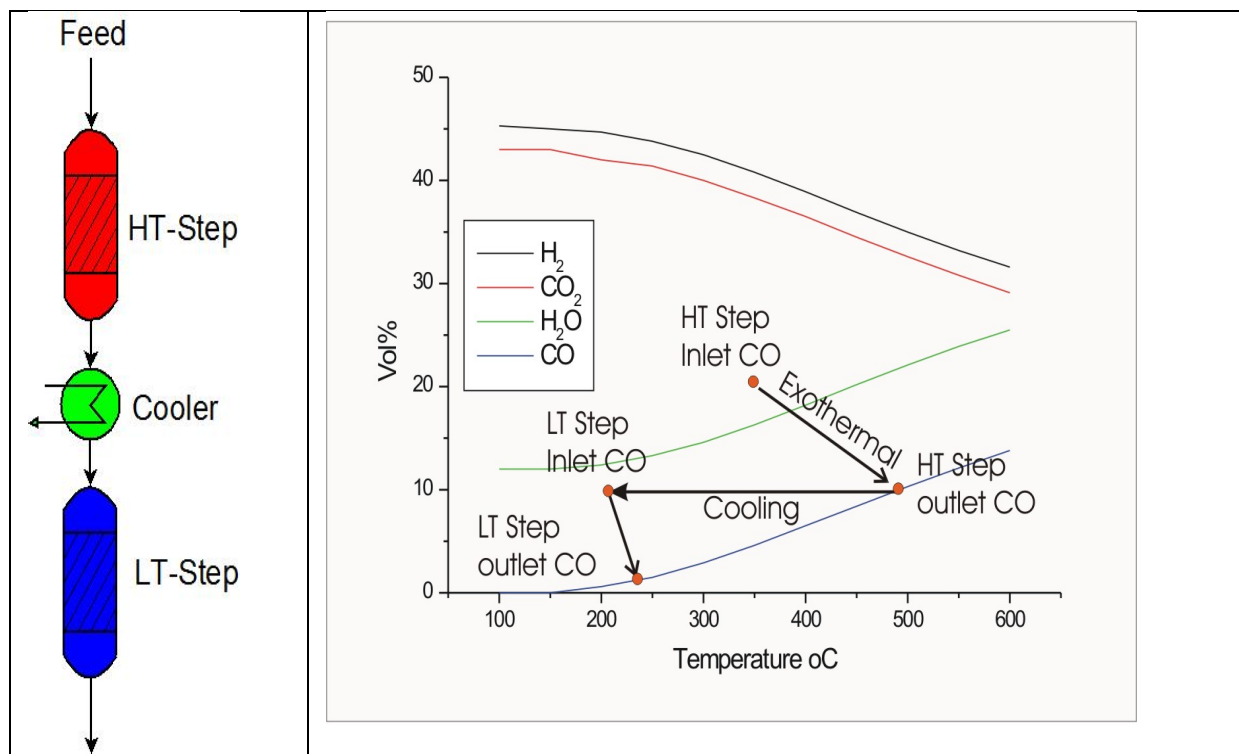


Figure 23. Two-step unit for production of gas containing high concentration of hydrogen [36].

At 500°C, the gas reaches equilibrium. To reach lower CO levels (higher H_2), the gas is cooled down, in this case to 200°C, 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.

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 [43]. These catalysts demonstrate WGS activity only at inlet temperatures above 300°C.

The average life is about 3–5 years. These catalysts are supplied in the oxidised condition (Fe_2O_3 , CrO_3) and have to be reduced in order to activate them. The reduction step is normally carried out in situ, Figure 24 [44], 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) [45].

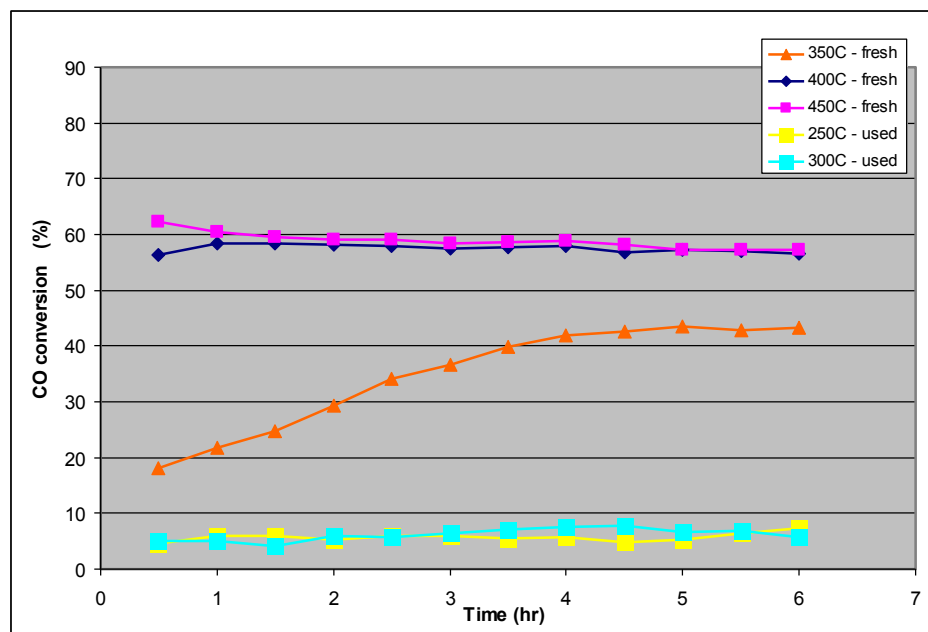


Figure 24. In situ activation of fresh and used FeCr catalysts in microreactor [44].

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

LT shift Cu/ZnO

Usually Cu/ZnO catalysts are used in the LT shift step (210-270°C). Although their activity increases with temperature, sintering proceeds so rapidly above 260°C (because of copper's low Hüttig temperature [46]), 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.

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 [47, 48, 49]. They exhibit a wide range of applications between ca 230 and 500°C. 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 [50], 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 [51] 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, [52]) 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.

Precious metal catalyst

Catalysts based on Pt/CeO₂ are reported [53] as active and non-pyrophoric, with activity higher than that of conventional WGS catalysts in the medium-temperature range (300–400°C). Work performed at Johnson Matthey on Pt/CeO₂ catalysts indicated that despite the high initial activity obtained in the medium–high temperature range (325–400°C), the catalyst loses activity under synthetic and real reformat 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/H₂ environment. In addition, methanation takes place on Pt/CeO₂, also seen at temperatures higher than 375°C, therefore, a Pt catalyst was developed by Johnson Matthey. This formulation is non-pyrophoric, has no methanation activity over a large range of temperatures (200–500°C) and has a much higher WGS activity and durability than a reference Pt–CeO₂ catalyst. Non-pyrophoric, precious metal–HTS catalysts further promoted to suppress methanation were also reported by Engelhard [54]. Ruthenium deposited on α-Fe₂O₃ has been mentioned in the literature [53] as giving promising WGS conversions with no methanation activity.

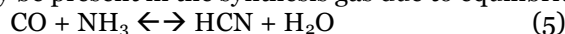
Hydrolysis and hydrogenation

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 CO₂ and H₂S at high temperature, reaction (4) [36]. In the form of COS the sulphur cannot be removed by absorption, by ZnO for instance.



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 NH₃.



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 H₂/CO-ratio should be tunable a separate hydrolysis step then becomes necessary as seen in Figure 25.

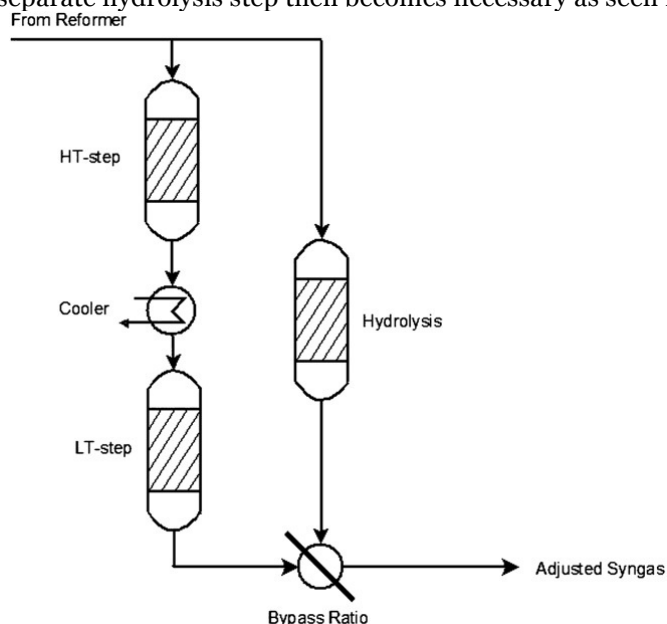


Figure 25. Combined HT-LT shift steps with tuneable H₂/CO ratio [36].

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.

CO₂-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.

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 CO₂, but also COS, CS₂, mercaptans, HCN and higher hydrocarbons. The low operating temperature is, however, a significant cost driver [54, 55]. The Selexol solvent has a high capacity for absorption of impurities such as sulphur as well as ammonia, HCN and other higher hydrocarbons. H₂S is up to nine times more soluble in the Selexol solvent than CO₂, which makes it suitable for selective removal of H₂S. 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 [54].

Analogous to the purification of anaerobic digestion, the use of water as a scrubbing agent is also possible. H₂S 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 [56, 57]; 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 CS₂, which deteriorates the solvent. If SO₂ and NO₂ are present in the gas this also causes solvent degradation due to reaction with the amine [58, 59].

As mentioned above, anaerobic digestion is a good analogue to removal of CO₂ 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 CO₂, compared to other alkanolamines and is therefore often activated by adding piperazine (PZ) as a promoter [60, 61].

Absorption of H₂S in MDEA solutions is a common technique for selective removal of H₂S from CO₂-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 CO₂, however, has a much lower heat of reaction than that of conventional amine solutions which leads to considerable energy savings [62]. The absorption is run at a low temperature, below 20°C, 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 [63].

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 [64]. A more thorough description of the PSA technology for biomethane enrichment may be found in SGC report 270 [65]. In the same report, a thorough description of membrane systems used for gas separation is also available.

Applications

In order to upgrade the raw product gas out from the gasifier to an appropriate syngas corresponding to the process specifications for an alternative fuel or the production of chemicals, first numerous clean-up steps are necessary.

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. The chapter is concluded by describing alternatives combining these methods.

Hydrogen

Hydrogen may be produced from a wide array of carbonaceous fuels, 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 H₂, CO, CO₂, CH₄, higher hydrocarbons and H₂O 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 CO₂ 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.

SNG

The first step in synthesising methane or SNG is the generation of synthesis gas. In order to further increase the CH₄ 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 exothermic and because of this, heat removal from the reactors employed is crucial [66]; a more extensive summary may be found in reference [67]. Methane from the methanation reactor is upgraded, by CO₂ 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 have to be employed to avoid hot spots and to limit the temperature. The temperature should also be kept low due to the equilibrium [68].



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 have to 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, < 200°C, and high partial pressures of CO. It is therefore important to have proper procedures for start-up and shutdown [66].

Carbon monoxide 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 carbon monoxide 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 [66].

Carbon dioxide, in reaction (2), is first converted to carbon monoxide with the reverse shift reaction. This formed CO is then reacted to methane according to reaction (1) [68]. 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 [66]. Typically the reaction is operated at inlet temperatures of 250-300°C and at pressures in

excess of 30 bar. The high pressure favours the equilibrium and also improves the kinetics. After upgrading the produced methane the concentrations is normally greater than 90 mol % and the heating value is typically higher than 33 MJ/m³ [69]. For upgrading to motor fuel standards, SNG for vehicles, the gas is additionally cleaned to nearly pure methane.

H₂/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) [70].

$$SN = \frac{V_{H_2}}{3V_{CO} + 4V_{CO_2} + 2V_{C_2H_4}} \quad (A)$$

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 700°C. This, however, does become a problem at lower SN. Lower SN also requires carbon dioxide removal to a greater extent upstream the methanation reactor.

Reactor Designs

In order 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 a number of 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 [67, 71].

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 26, 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 250-700°C. The catalyst is called MCR-2X and according to Topsoe has excellent durability [67, 72].

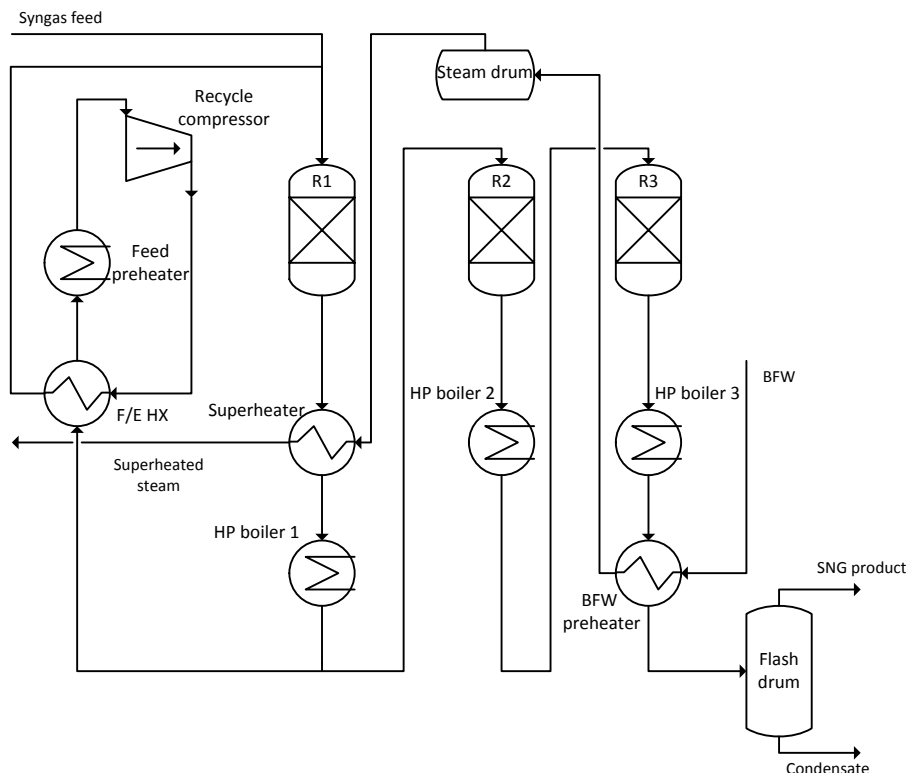


Figure 26. Haldor Topsoe's methanation process TREMP.

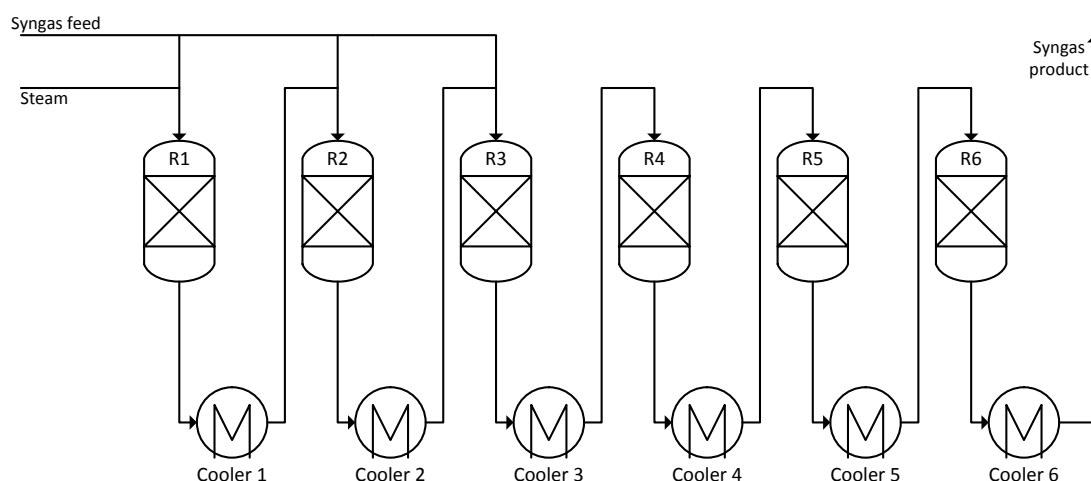
The disadvantage with recycling the product gas is the higher volume of gas that needs to be processed and the dilution of the reactant gases. It also increases the cost and energy loss due to the need to compress the recycled gas.

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 27 shows a TWR system [66].

The cooling method used in these types of reactors increases the difficulties of controlling the heat of reaction. As the methanation reaction is highly exothermic, 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 [66].

**Figure 27. Single-pass through wall-cooled methanation process [66].**

Fluidised-bed reactor

Methanation as well as other highly exothermic 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 was operated 1980-1985, for about 8,000 h and was developed by Thyssengas. 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 [73]. In addition to this, further work has been performed in recent years at the Paul Scherrer Institute [74, 75, 76]. 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.

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 [77], more specifically the type A quality. The motor octane

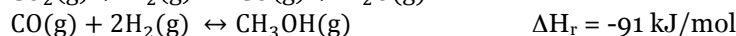
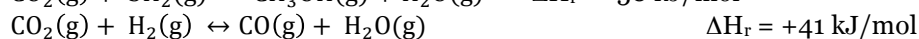
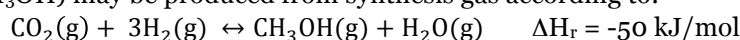
number is determined using calculations according to ISO 15403 [78]. The problem with using this definition in the present case is the hydrogen content. The standard does not take into account any hydrogen content in the gas. An alternative method is to use the definition in SAE 922359 [79]. However, 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.

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 and is among the best of all possible routes for syngas conversion, meaning that 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:



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 $\text{H}_2/\text{CO} = 2$. Instead it is the stoichiometric number $(\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)$ that should be 2 for ideal conversion [80]. However, a high CO_2 level limits the heat released by the exothermic reaction but produces more water, resulting in a diluted product.

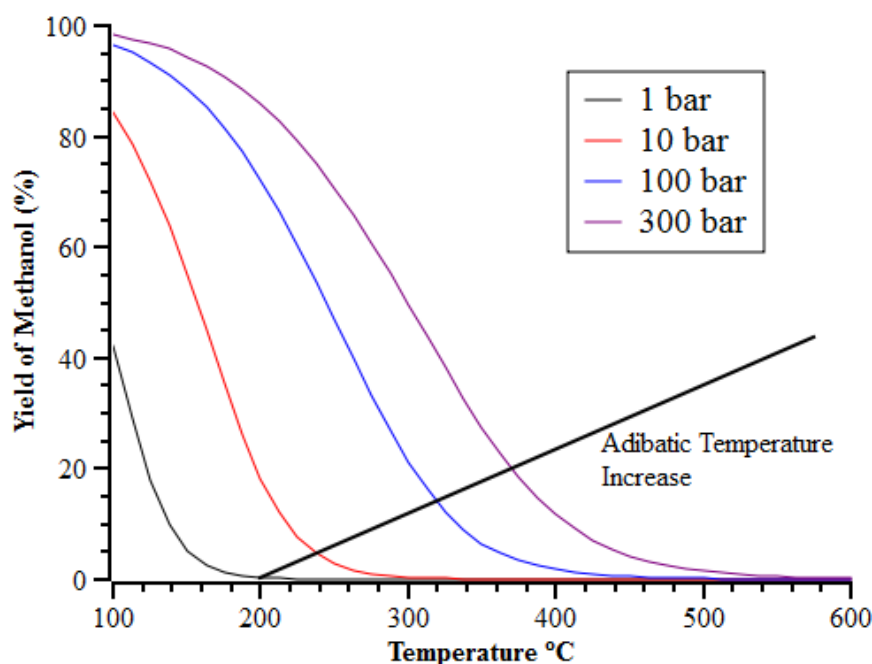


Figure 28. Equilibrium calculation of a $\text{CO}:\text{H}_2$ mixture with ratio 1:2 and the adiabatic temperature increase as function of conversion (assumed inlet temperature 200°C).

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 200°C .

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

Table 4. Feed composition [80].

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 H₂ 67, CO 22, CO₂ 8 and CH₄ 3 vol % and calculating the adiabatic temperature increase, then a full conversion (100 %) would correspond to a temperature increase of 880°C. This temperature increase is of course fictitious, the conversion is limited by the equilibrium, described above, and thereby also the obtainable temperature. In Figure 29 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 30. By doing so, it is possible to climb on the equilibrium curve, see Figure 29.

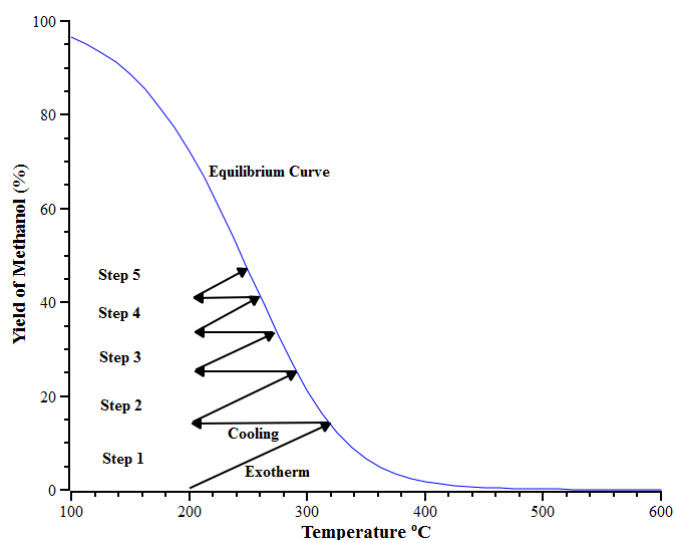


Figure 29. Improving methanol yield by multi-bed reactor with in-between cooling.

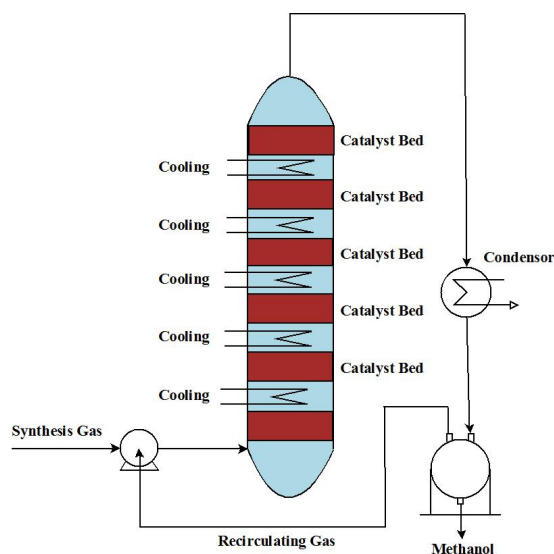


Figure 30. Multi-bed methanol reactor with in between bed cooling and gas recirculation.

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 31. 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 240-260°C and the yield of methanol, depending on operating pressure, may reach 30-40 % in a single pass.

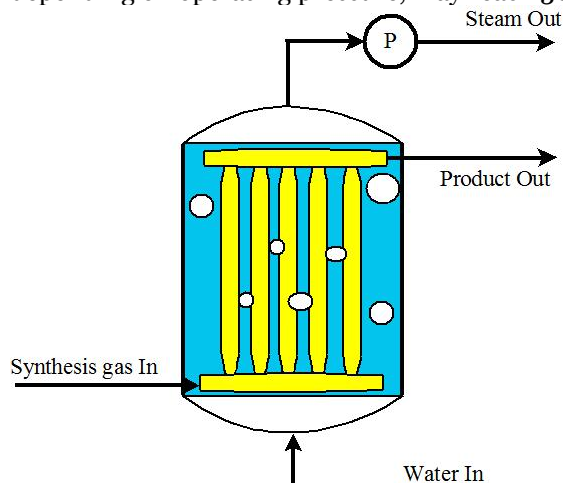


Figure 31. Lurgi boiling water reactor.

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.

Catalysts for the methanol process

Cu/ZnO/Al₂O₃

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 Al₂O₃. The catalyst is very sensitive towards sulphur and requires sulphur levels below 1 ppm. The H₂S 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 H₂S 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 [81]. Chlorine is a severe 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. Deposited on the catalyst they may act as Fischer-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, NH₃, HCN and CH₃CN seems not to affect the activity of the methanol catalyst.

MoS₂

In contrast to the Cu/ZnO catalyst, molybdenum disulphide (MoS₂) 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.

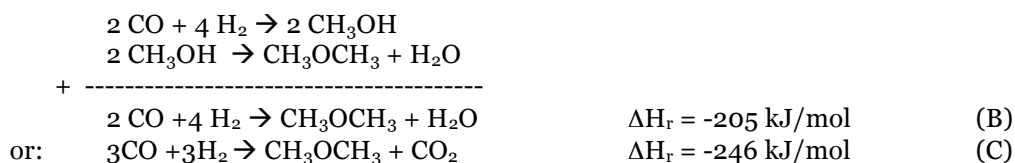
DME

DME, Dimethyl ether, is a gas with properties similar to those of Liquid Petroleum Gas (LPG). At Standard Temperature and Pressure (STP, 0 °C, 101 kPa) it is a gas, but condenses into a liquid at 506 kPa at 20 °C (270 kPa at 0 °C). The liquid density is about 0.67 kg/dm³ at 20 °C with a heat of combustion ΔH_c = 28 MJ/kg. Compared to diesel (35 MJ/dm³), DME has about half the energy density, 19 MJ/dm³, at 20 °C [82].

DME can be produced by dehydration of methanol over an acidic catalyst such as zeolites or modified γ-alumina. [83]



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.



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), 240-280 °C and 3-7 MPa [84].

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 300 °C 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 300 °C. 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.

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 [85] as "a surprising phenomenon in heterogeneous catalysis that attracts the interest of world experts: the gases CO and H₂ 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.

History

The FT process was developed in Germany in the first half of the 20th century [86]. 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 [87]. A FT process based on gasified biomass would probably have a total yield of up to 40 %.

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 32. This may be expressed mathematically and the results are to be found in Figure 33.

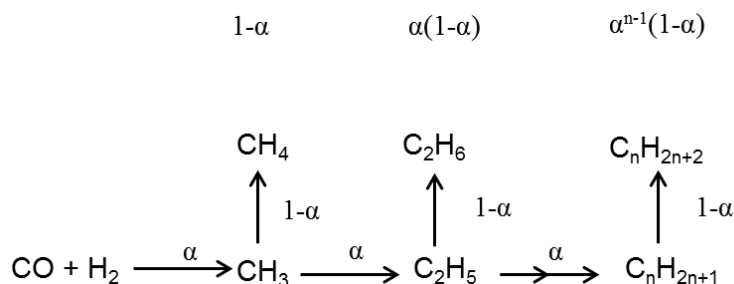


Figure 32. Logic behind ASF (Tunå, reproduced with permission).

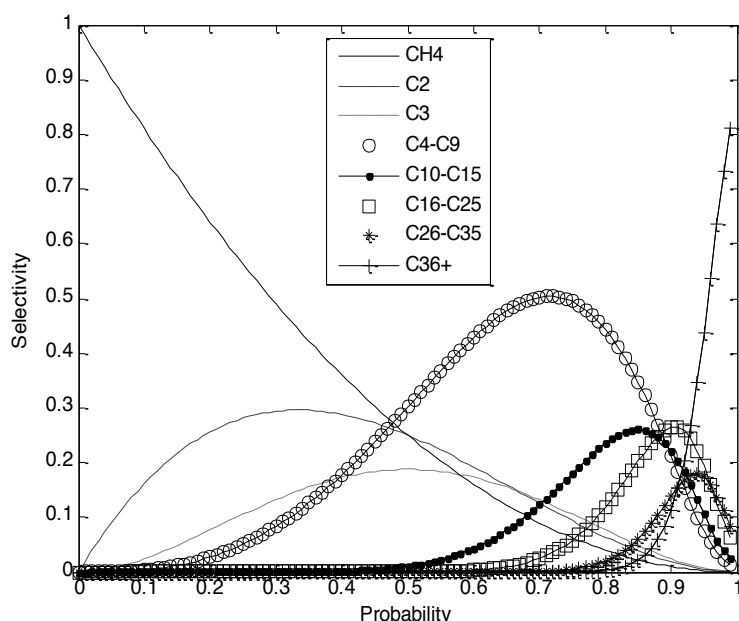


Figure 33. Distribution of hydrocarbons given different probability numbers (alfa number) (Tunå dissertation, reproduced with permission).

The emphasis for a modern FT wax process is to produce more long-chain straight hydrocarbons [88]. 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 [89]. 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/m³ will yield a significant catalyst deactivation [90].

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.

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 [91].

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 [92]. 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 [89].

g SiO ₂ / 100 g Fe	Unreduced			Reduced in H ₂			
	Pore volume /cm ³ g ⁻¹	Specific surface area/m ² g ⁻¹	Area in pores > 4.5 nm ² g ⁻¹	Pore volume/ cm ³ g ⁻¹	Specific surface area/m ² g ⁻¹	Area in pores > 4.5 nm ² 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.

^bNA 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 SiO₂, 5 g Cu and 5 g K₂O 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 [93].

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 [93]. The mass ratio was typically 100 Co: 18 ThO_2 : 100 kieselguhr. 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 and co-workers [94] 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/m³ poisoning is observed. The surface area of a fresh iron FT catalyst is approximately 200 m²/g. In a catalyst that has lost 50 % of its initial activity the remaining surface area is 50 m²/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.

Alcohols

Higher alcohol synthesis could be produced by a series of exothermic reactions, where syngas, i.e. CO and H₂, is converted into shorter alcohols over some specific catalyst:

1. Methanol:	$\text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$
2. Ethanol:	$\text{CO} + 4 \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$
3. Propanol:	$\text{CO} + 6 \text{H}_2 \rightleftharpoons \text{C}_3\text{H}_7\text{OH} + 2 \text{H}_2\text{O}$
4. Butanol:	$\text{CO} + 8 \text{H}_2 \rightleftharpoons \text{C}_4\text{H}_9\text{OH} + 3 \text{H}_2\text{O}$
5. Any alcohol	$n \text{CO} + 2n \text{H}_2 \rightleftharpoons \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1) \text{H}_2\text{O}$

Currently, the synthesis of higher alcohols is not applied commercially anywhere in the world. However, many interesting different conceptual processes do exist and are based on patented catalytic technologies [95]. Higher alcohol synthesis has been tested both in industrial plants and pilot plants or extensively tested in lab-scale reactors.

Challenges and On-going demonstrations

Research and development on using biomass as feedstock for production of different motor fuels 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.

As can be concluded there are many choices to be made before investing in a large 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 [37].

For biomass and waste gasification in pressurised fluidised bed systems the operating temperatures lie around 900°C, 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 [96, 97]. 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 [15], 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. In the section below we have chosen to shortly present three different latest approaches currently present/active in Sweden regarding gasification of biomass for biofuel production.

The first example is the approach of Cortus Energy, targeting smaller units with the possibility to use different kinds of biomass, which is not a large-scale solution as the others are. The second demonstration plant is the GoBigas solution aiming to produce methane for the natural gas grid, using an atmospheric indirect fluidising bed technique. The third plant is the Bio2G E.ON approach to demonstrate and produce biomethane in large scale by using pressurised gasification technology.

Cortus energy

The Swedish company Cortus Energy has developed their own gasification technology denominated Woodroll. The name originates from the fact that the biomass is dried and pyrolysed in rotating cylinders. In Figure 34 a schematic drawing of the process is shown.

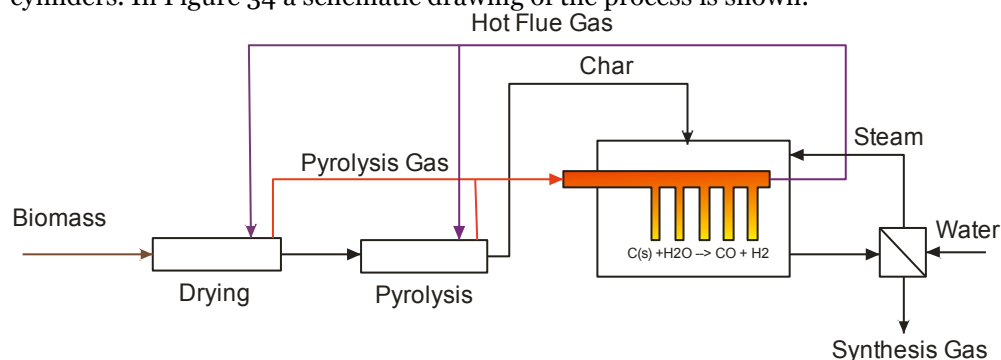


Figure 34. Schematics of Cortus Woodroll.

The biomass enters a rotating dryer and then a rotating pyrolysis unit that both are heated by combustion gases. The formed pyrolysis gases are separated from the formed char and burnt separately in recuperative burners from Kanthal, see Figure 35. The char is transported into a chamber where it is

gasified by steam and the heat that radiates from the recuperative burners. This produces a tar-free gas containing CO, CO₂ and H₂ [32]. The advantages of the Woodroll technique are that the syngas does not contain any nitrogen, and the heat management of the plant is integrated. The produced gas is used to pre-heat the water used as gasifying agent, while the hot flue gases are used to dry both the incoming biomass and to heat up the pyrolysis step. The syngas has a high hydrogen content and is suitable to be further refined into renewable natural gas (SNG) for which infrastructure and vehicles exist. The syngas can also be used as a feedstock to be refined into biodiesel, ethanol and other liquid fuels.

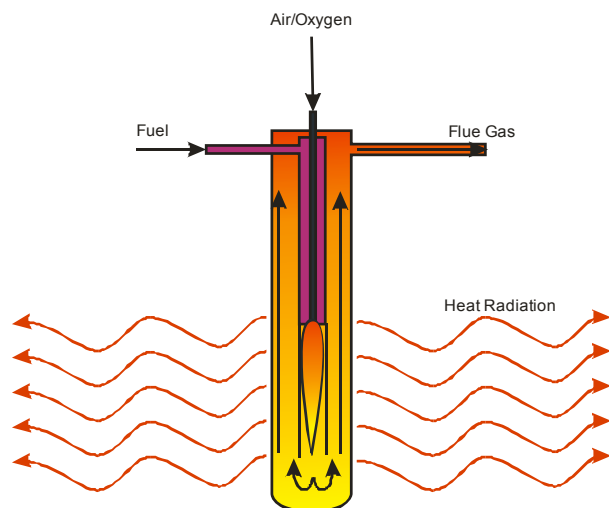


Figure 35. Schematics of a recuperative Kanthal burner used in Woodroll

Cortus Energy is about to commercialise this technique [98], [99].

GoBigas

The GoBiGas biogas project uses indirect gasification and focusing on producing biomethane (Bio-SNG) by thermal gasification of forest residues as branches, roots and tops. The goal is to reach 65 percent of the biomass into SNG, the first stage demonstration plant (20 MW_{gas}) is running in Gothenburg, a second stage (100 MW_{gas}) demo-plant is planned with some modifications. The process also aims at upgrading wet biomass to synthetic or substitute natural gas, see Figure 36. The incoming biomass is first milled and dried. Thereafter it enters into a fluidised bed gasifier (stream 2) using steam as the fluidising medium (stream 3). In the gasifier, the biomass is converted into syngas (stream 8) and char (part of stream 4). The fluidised bed material supplies the heat of reaction for the endothermic process. This fluidised bed material is heated in a combustor using char from gasification with air as oxidant (stream 5). The resulting syngas is cooled and residual dust is filtered out. This dust-free syngas is then scrubbed with RME to remove tar components, resulting in a syngas with lower tar content (stream 12). This stream is further cleansed with respect to tars in an activated carbon filter.

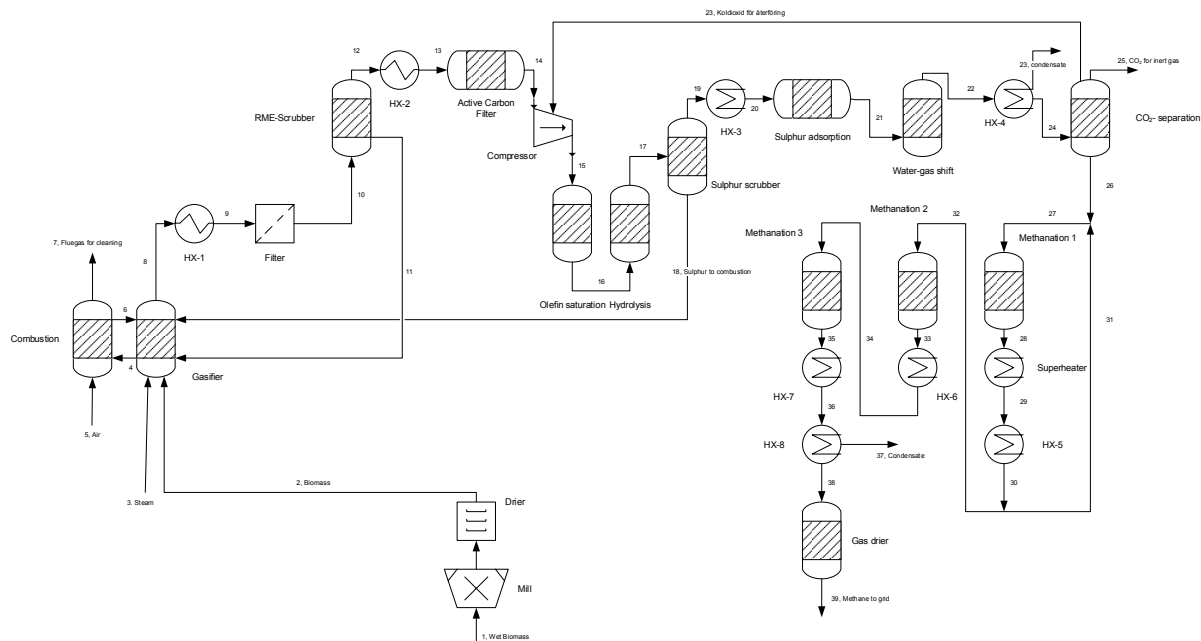


Figure 36. Schematics of the GOBIGAS process streams.

The tar-free syngas is then compressed up to 40 bar and mixed with a recycled CO_2 stream and passed through two consecutive reactors where the first reactor saturates olefins and the second reactor hydrolyses COS and CS_2 into H_2S (stream 17), as described in 3.6. This stream is then entered into a sulphur absorption system where the H_2S is removed along with some CO_2 . The stripped-off H_2S (stream 18) is returned to the combustor where it is oxidised into SO_2 and purified using traditional flue gas cleaning (reaction with lime). The purified syngas (stream 19) is heated and passed through a sulphur adsorption step, which is followed by a water-gas shift step to set the correct $\text{CO}:\text{H}_2$ ratio. The thus prepared syngas (stream 22) is cooled, condensate removed and passed on to CO_2 removal in an absorber, yielding a purified syngas with the correct CO -to- H_2 ratio for the methanation (stream 26). The methanation is performed in the TREMP system developed by Haldor Topsoe, which utilises a three-bed system with intercooling and recycling over the first reactor, described in Figure 26. The resulting methane-rich stream 37 is cooled, condensate is removed and then it is further dried in a temperature swing adsorption system to yield the final dry methane product (stream 39).

Bio2G E.ON

E.ON has been examining the possibility of building a plant for the production of methane by gasification of biomass. The plant is planned for up to 200 MW - or 1.6 TWh of energy products, with a fuel input of 345 MW_{th} . The work is being conducted in a project called Bio2G. The total efficiency of an integrated plant would be up to 80 %, with a biomass-to-methane-efficiency of 60-65 %. The biomass feed is to be forest residues, wood chips etc. Figure 37 shows the schematics of the Bio2G process streams including the hot gas-cleaning step after the pressurised gasification, the produced cleaned syngas is then further pressurised up to 20 bar for the methanation step.

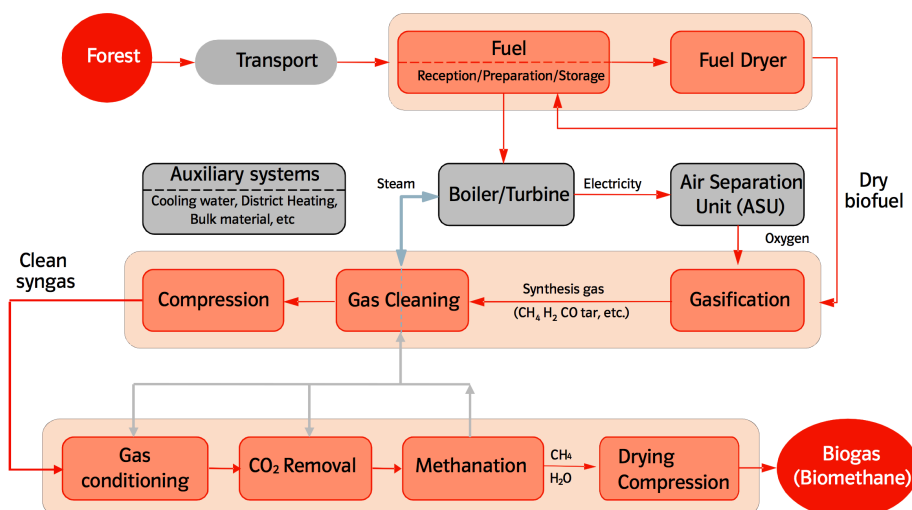


Figure 37. Schematics of the Bio2G process streams [100].

The process concept is mainly based on mature technology, but has some key features with innovative measures, with catalytic tar reforming, hot gas filtering, adiabatic methanation and heat integration. The pressurised oxygen-blown fluidised bed gasification will give a high yield of methane and downstream conservation of the methane is essential. The tar conversion step is non-selective for methane conversion and also the removal of both sulphur and CO₂ is selective without removal of CH₄. The hot gas filtering is designed for ~700°C allowing later upgrade to >800°C. The challenges are within the filter materials and design, avoiding filter blinding - sticky filter cake, blocking of inner structure of candles. Currently the plans for building the Bio2G plant have been put on hold, but not yet abandoned.

References

- ¹ Heyne, S., Liliedahl, T., Marklund, M. Biomass Gasification - A Synthesis of Technical Barriers and Current Research Issues for the Deployment at Large Scale, Report No 2013:5, f3 - The Swedish Knowledge Centre for Renewable Transport Fuels, Sweden, 2013, 71.
- ² van der Drift, A. and Boerrigter, H. Synthesis gas from biomass for fuels and chemicals, 2006, ECN-C-06-001.
- ³ Engvall, K., Kusar, H., Sjöström, K. and Pettersson, L.J. Upgrading of Raw Gas from Biomass and Waste Gasification: Challenges and Opportunities, *Top Catal*, 2011, 54: 949-959.
- ⁴ Stevens, D.J. Hot gas conditioning: Recent Progress with Larger-Scale Biomass Gasification Systems, 2001, NREL/SR-510-29952.
- ⁵ Brage, C., Yu, Q., Chen, G. and Sjöström, K. Use of amino phase adsorbent for biomass tar sampling and separation, *Fuel*, 1997, 76(2): 137-142.
- ⁶ Devi, L., Ptasiński, K.J., Janssen, F.J.J.G., van Paassen, S.V.B., Bergman P.C.A. and Kiel, J.H.A. Catalytic decomposition of biomass tars: use of dolomite and untreated olivine, *Renewable Energy*, 2005, 30(4): 565-587.
- ⁷ Reed, T.B. and Das, A. "Handbook of Biomass Downdraft Gasifier Engine Systems 1988: Biomass Energy Foundation"; 140.
- ⁸ Cummer, K.R. and Brown, R.C. Ancillary equipment for biomass gasification, *Biomass and Bioenergy*, 2002, 23(2): 113-128.
- ⁹ Barr-Rosin Ltd. 2007; Available from: <http://www.barr-roisin.com/english/products/super-heated-steam-drying.htm> [cited 2015-02-18].
- ¹⁰ Olofsson, I., Nordin A., and Söderlind, U. Initial Review and Evaluation of Process Technologies and Systems Suitable for Cost-Efficient Medium-Scale Gasification for Biomass to Liquid Fuels, ETPC Report 05-02, University of Umeå/Mid Sweden University, Umeå, 2005, 90.
- ¹¹ Paysly, M.A. and Overend, R.P. The SilvaGas Process From Future Energy Resources – A commercialization success. In 12th European Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection, 2002, Amsterdam, The Netherlands.
- ¹² Basu, P. "Biomass Gasification and Pyrolysis: Practical Design and Theory", Academic Press Burlington, MA, 2010.
- ¹³ Hamelinck, C.N., Faaij, A.P.C., den Uil, H. and Boerrigter, H. *Energy* 2004, 29, 1743.
- ¹⁴ Dayton, D. A Review of the Literature on Catalytic Biomass Tar Destruction, National Renewable Energy Laboratory (NREL), Technical Report, Golden, CO, Report, 2002, NREL/TP-510-32815.
- ¹⁵ Yung, M.M., Jablonski, W.S. and Magrini-Bair, K.A. Review of catalytic conditioning of biomass-derived syngas, *Energy and Fuels*, 2009, 23: 1874.
- ¹⁶ Kumar, A., Jones D.D. and Hanna, M.A. Thermochemical Biomass Gasification: A Review of the Current Status of the Technology. *Energies*, 2009, 2: 556.

-
- ¹⁷ Perry, Perry's chemical engineering handbook, New York: McGraw-Hill, 2007.
- ¹⁸ Meva Energy, Available from: www.mevaenergy.com [cited 2015-10-18].
- ¹⁹ Tuomi, S, Kurkela, E., Simell, P. and Reinikainen, M. Behaviour of tars on the filter in high temperature filtration of biomass-based gasification gas, *Fuel*, 2015, 139, 220-231.
- ²⁰ Engström, F. Hot gas clean-up, *Biomass Bioenergy*, 1998, 15, 259-262.
- ²¹ Simone, E., Nacken, M., Haag, W. and Heinreich, S. Filtration performance at high temperature and analysis of ceramic filter elements during biomass gasification, *Biomass and bioenergy*, 2011, 35, 87-104.
- ²² Nacken, M., Ma, L., Engelen, K., Heidenreich, S. and Baron, G.V. Development of a Tar Reforming Catalyst for Integration in a Ceramic Filter Element and Use in Hot Gas Cleaning, *Ind Eng. Chem. Res.*, 2007, 46, 1945-1951.
- ²³ Hermann, H., Reinhard, R., Klaus, B., Reinhard, K. and Christian, A. Biomass CHP plant Güssing – a success story, Expert meeting on pyrolysis and gasification of biomass and waste. October 2002 Strasbourg, France.
- ²⁴ Moersch, O., Spliethoff H. and Hein, K.R.G. Tar quantification with a new online analyzing method *Biomass and Bioenergy*, 2000, 18: 79.
- ²⁵ Bergman, P.C.A., van Paasen, S.V.B and Boerrigter, H. The novel OLGA technology for complete tar removal from biomass producer gas, In *Proceedings of the Expert Meeting on Pyrolysis and Gasification of Biomass and Waste*, Ed. A.V. Bridgwater, Strasbourg, 2003.
- ²⁶ Abu El-Rub, Z., Bramer, E. A., Brem, G. Review of Catalysts for Tar Elimination in Biomass Gasification Processes, *Ind. Eng. Chem. Res.*, 2004, 43 (22): 6911–6919.
- ²⁷ Sutton, D., Kelleher, B. and Ross, J.R.H. Review of literature on catalysts for biomass gasification, *Fuel Process. Technol.*, 2001, 73: 155.
- ²⁸ Gerber, M.A. Review of Novel Catalysts for Biomass Tar Cracking and Methane Reforming, Report PNNL-16950, National, Technical Information Service, U.S. Department of Commerce Springfield, 2007.
- ²⁹ Skov Sköt-Rassmusson, M. Biomass gasifier – Gas conditioning and conversion, SGC International Seminar on Gasification, Malmö October 2014.
- ³⁰ Hultberg, C. Hydrogen, an Energy Carrier of the Future, Thesis, Department of Chemical Engineering, Lund University, 2007, ISBN: 978-91-628-7337-0.
- ³¹ Haghighi Moud, P., Granstrand, J., Dahlin, S., Nilsson, M., Andersson, K., Pettersson, L. and Engvall K. The role of alkali in heterogeneous catalysis for gas cleaning in stationary and mobile applications, ASC National Meeting 2015, Denver, CO.
- ³² Brandin, J., Tunér, M. and Odenbrand, I., Small Scale Gasification: Gas engine CHP for biofuels, Rapport Linnaeus University, Växjö, 2011, ISBN: 978-91-86983-07-9.

-
- ³³ Ghenciu, A. F. Review of fuel processing catalyst for hydrogen production in PEM fuel cell systems, *Current Opinion in Solid State and Materials Science*. 6 (5) 2002: 389-399.
- ³⁴ Parsland, C., Larsson, A., Benito, P., Fornasari, G. and Brandin, J. Nickel-substituted bariumhexaaluminates as novel catalysts in steam reforming of tars, *Fuel Processing Technology*, 2015, 140, 1–11.
- ³⁵ Dybkjare, I. Tubular reforming and autothermal reforming of natural gas-an overview of available processes, *Fuel Processing Technology*, 1994, 42: 85-107.
- ³⁶ Brandin, J. and Liliedahl, T. Unit operations for production of Clean Hydrogen-Rich Synthesis gas from gasified biomass, *Biomass and bioenergy* 2011, 35, S1: 8-17.
- ³⁷ Higman, C. and van der Burgt, M. *Gasification*, 2nd ed. Gulf Professional publishing, Elsevier Science, Burlington, 2008.
- ³⁸ Lipman, T., Shah, N. Ammonia as an alternative energy storage media for hydrogen fuel cells: Scientific and technical review for near-term stationary power demonstration projects, final rapport, UC Berkeley Transportation sustainability research center, UCB-ITS-TSRC-RR-2007-5, 2007.
- ³⁹ Carbona Gasification Technologies, Biomass Gasification Plant in Skive. *Gasification* 2010, SGC, 28-29 October Scandic Crown, Gothenburg, Sweden.
- ⁴⁰ Hansen, J. B. Syngas Routes to Alternative Fuels from Renewable Sources, Haldor Topso, Task 33 Thermal gasification of biomass, Karlsruhe, Nov 4, 2014.
- ⁴¹ Navarro, R. M., Penea, M. A. and Fierro, J. L. G. Hydrogen production from carbon feedstocks: Fossil fuels and biomass, *Chem. Rev.* 2007, 107: 3952-3991.
- ⁴² Sanchez, J. M., Barreiro, M. M. and Marono, M. Hydrogen enrichment and separation from synthesis gas by the use of a membrane reactor, *Biomass and bioenergy* 2011, 35, S1: S132-S144.
- ⁴³ Xue, E., O'Keeffe, M. and Ross, J. R. H. Water-gas Shift Conversion Using a Feed with a Low Steam to Carbon Monoxide Ratio and Containing Sulphur, *Catalysis Today* 1996, 30: 107-118.
- ⁴⁴ Einvall, J., Parsland, C., Benito, P., Basile, F. and Brandin, J. High temperature water-gas shift step in the production of clean hydrogen rich synthesis gas from gasified biomass, *Biomass and bioenergy* 2011, 35, S1: S123-S131.
- ⁴⁵ Twigg, M. V. (Ed), *Catalyst Handbook*, Wolfe publishing Ltd London, UK 1989.
- ⁴⁶ Twigg, M. V. and Spencer, M.S. Deactivation of supported copper metal catalysts for hydrogenation reactions, *Applied Catalysis A: General* 2001, 212 (1-2): 161-174.
- ⁴⁷ Mellor, J. R., Copperthwaite, R. G. and Coville, N. J. The selective influence of sulfur on the performance of novel cobalt-based water-gas shift catalysts, *Applied Catalysis A: General* 1997, 164: 69-79.
- ⁴⁸ Hakkarainen, R. and Salmi, T. Water-gas shift reaction on a cobalt-molybdenum oxide catalyst, *Applied Catalysis A: General* 1993, 99:195-215.

-
- ⁴⁹ P. Hou, P., Meeker, D. and Wise, H. Kinetic studies with a sulfur-tolerant water gas shift catalyst, *Journal of Catalysis* 1983, 80: 280-285.
- ⁵⁰ Li, Y., Wang, R., Chang, L. *Catalysis Today* 1999, 51, p. 25-38.
- ⁵¹ Laniecki, M., Malecka-Grycz, M. and Domka, F. Water-gas shift reaction over sulfided molybdenum catalysts I. Alumina, titania and zirconia-supported catalysts, *Applied Catalysis A: General* 2000, 196: 293-303.
- ⁵² Andreev, A. A., Kafedjisky, V. J. and Edreva-Kardjieva, R. M. Active forms for water-gas shift reaction on NiMo-sulfide catalysts, *Applied Catalysis A: General* 1999, 179: 223-228.
- ⁵³ Basińska, A., Kepiński, L. and Domka, F. The effect of support on WGS activity of ruthenium catalysts, *Applied Catalysis A: General* 1999, 183: 143-153.
- ⁵⁴ Ruettinger, W., Lampert, J., Korotkikh, O. and Farrauto, R. J. Non-pyrophoric water-gas shift catalysts for hydrogen generation in fuel cell applications, *ABSTR AP AM CHEM S* 221, April 1 2001.
- ⁵⁵ Lurgi, Available from: www.lurgi.com [cited 2015-09-11].
- ⁵⁶ Persson, M., Jönsson, O. and Wellinger, A. Biogas Upgrading to Vehicle Fuel Standards and Grid Injection, 2006, IEA Bioenergy Task 37.
- ⁵⁷ Benjaminsson, J., Nya renings- och uppgraderingstekniker för biogas, Svenskt Gastekniskt Center, Report SGC, 2006, 163.
- ⁵⁸ Derks, P.W. Carbon Dioxide Absorption in Piperazine Activated N-Methyldiethanolamine, University of Twente: Enschede, 2006, 244.
- ⁵⁹ Bishnoi, S. and Rochelle, G.T. Thermodynamics of Piperazine/Methyldiethanolamine/Water/Carbon Dioxide, *Industrial and Engineering Chemistry Research*, 2002, 41(3): 604-612.
- ⁶⁰ Figueroa J.D., Fout T., Plasynski S., McIlvried H. and Srivastava R.D. Advances in CO₂ capture technology - The U.S. Department of Energy's Carbon Sequestration Program. *Int J Greenhouse Gas Control*, 2008, 2: 9-20.
- ⁶¹ Kozak, F., Petig, A., Morris, E., Rhudy, R. and Thimsen, D. Chilled Ammonia Process for CO₂ Capture, *Energy Procedia*, 2009, 1: 1419-1426.
- ⁶² Smith, K. et al., Recent developments in solvent absorption technologies at the CO₂CRC in Australia, *Energy Procedia*, 2009, 1: 1549-1555.
- ⁶³ Thee, H., Suryaputradinata, Y.A., Mumford, K.A., Smith, K.H., Silva, G., Kentish, S.E. and Stevens, G.W. A kinetic and process modeling study of CO₂ capture with MEA-promoted potassium carbonate solutions, *Chem Eng J*, 2012, 210: 271-279.
- ⁶⁴ Grande, C.A. Biogas Upgrading by Pressure Swing Adsorption, *Biofuel's Engineering Process Technology*, InTech, Rijeka, 2011, chap. 3, 65-84.
- ⁶⁵ Bauer, F., Hulteberg, C., Persson, T. and Tamm D Biogas upgrading - Review of commercial technologies, SGC Report 270, 2013, Available: www.sgc.se/ckfinder/userfiles/files/SGC270.pdf

-
- ⁶⁶ Elvers, B., Ullmann's Encyclopedia of Industrial Chemistry - 7th Edition in Print / Sample Volume 2011: Wiley-VCH Verlag GmbH.
- ⁶⁷ Kopyscinski, J., Schildhauer, T.J. and Biollaz, S.M.A. Production of synthetic natural gas (SNG) from coal and dry biomass – A technology review from 1950 to 2009, *Fuel*, 2010. 89(8): 1763-1783.
- ⁶⁸ Lackner, M. Combustion Science and Technology, in Kirk-Othmer Encyclopedia of Chemical Technology 2000, John Wiley & Sons, Inc.
- ⁶⁹ van der Meijden, C.M. Veringa, H.J. and Rabou L.P.L.M. The production of synthetic natural gas (SNG): A comparison of three wood gasification systems for energy balance and overall efficiency, *Biomass Bioenergy*, 2010, 34: 302.
- ⁷⁰ Gassner, M. and Maréchal, F. Thermo-economic optimisation of the integration of electrolysis in synthetic natural gas production from wood. *Energy*, 2008, 33(2): 189-198.
- ⁷¹ Bengtsson, K. Twin-Bed Gasification Concepts for Bio-SNG Production, Dept. of Chemical Engineering, 2007, Lund University.
- ⁷² Topsoe, H. From Solid Fuels to Substitute Natural Gas (SNG) Using TREMPTM; Haldor Topsoe: Lyngby, Denmark, 2009.
- ⁷³ Duret, A., Friedli, C., and Maréchal, F. Process design of Synthetic Natural Gas (SNG) production using wood gasification, *Journal of Cleaner Production*, 2005, 13 (15): 1434-1446.
- ⁷⁴ Kopyscinski, J., Schildhauer, T. J., and Biollaz, S. M. A. Methanation in a fluidized bed reactor with high initial CO partial pressure: Part I—Experimental investigation of hydrodynamics, mass transfer effects, and carbon deposition, *Chemical Engineering Science*, 2011. 66 (5): 924-934.
- ⁷⁵ Kopyscinski, J., Schildhauer, T. J., and Biollaz, S. M. A. Methanation in a fluidized bed reactor with high initial CO partial pressure: Part II— Modeling and sensitivity study, *Chemical Engineering Science*, 2011. 66 (8): 1612-1621.
- ⁷⁶ Rüdisüli M, Schildhauer, T. J., Biollaz, S. M. A. and van Ommen, J. R. Monte Carlo simulation of the bubble size distribution in a fluidized bed with intrusive probes, *International Journal of Multiphase Flow*, 2012. 44 (0): 1-14.
- ⁷⁷ Standards, S.I.f., SS 15 54 38, Motorbränslen - Biogas som bränsle till snabbgående ottomotorer, 1999, SIS.
- ⁷⁸ ISO, ISO 15403-1:2006, Natural gas -- Natural gas for use as a compressed fuel for vehicles -- Part 1: Designation of the quality, 2001.
- ⁷⁹ SAE, Effect of Gas Composition on Octane Number of Natural Gas Fuels, Society of Automotive Engineers, Inc., SAE 922359, 1992.
- ⁸⁰ Lange, J. P. Methanol synthesis: a short review of technology improvements, *Catalysis Today*, 2001, 64: 3–8.
- ⁸¹ Ali, K. A., Abdullah, A.Z., and Mohamed, A. R. Recent development in catalytic technologies for methanol synthesis from renewable sources: A critical review, *Renewable and Sustainable Energy Reviews*, 2015, 44: 508-518.

-
- ⁸² Fundamental Aspects of Dimethylether. Alternative Fuels Data Center, Available from: www.afdc.energy.gov/pdfs/3608.pdf [cited 2015-06-11].
- ⁸³ Bellussi, G., Millini, R. and Pollesel, P. An industrial perspective on the impact of Haldor Topsøe on research and development in catalysis by zeolites, *J. Catal.* 2015, 328: 11-18.
- ⁸⁴ Ogawa, T., Inoue, N., Shikada, T. and Ohno, Y. Direct Dimethyl Ether Synthesis, *Journal of Natural Gas Chemistry* 2003, 12: 219-227
- ⁸⁵ Schulz, H. Short history and present trends of Fischer–Tropsch synthesis, *Applied Catalysis A: General.* 1999,186: 3-12.
- ⁸⁶ de Klerk, A., Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., 2000.
- ⁸⁷ Dry, M.E. Practical and Theoretical Aspects of the Catalytic Fischer-Tropsch Process, *Appl. Catal. A*, 1996, 138: 319.
- ⁸⁸ Tsakoumis, N.E., Rønning, M., Borg, Ø., Rytter E. and Holmen, A. Deactivation of cobalt based Fischer–Tropsch catalysts: a review. *A. Catal. Today*, 2010, 154: 162.
- ⁸⁹ Ertl, G., Knözinger H., Schüth, F. and Weitkamp J. *Handbook of Heterogeneous Catalysis*, 8 Volumes, John Wiley & Sons, 2008.
- ⁹⁰ Barrientos, J., Montes, V., Boutonnet, M. and Järås, S. Further insights into the effects of sulfur on the activity and selectivity of cobalt-based Fischer-Tropsch catalysts, *Catalysis Today*, In Press, Corrected Proof, Available online 1 December 2015.
- ⁹¹ Borg, Ø., Hammer, N., Eri, S., Lindvåg, O.A., Myrstad, R., Blekkan, E.A., Rønning, M., Rytter E. and Holmen, Fischer-Tropsch synthesis over un-promoted and Re-promoted γ -Al₂O₃ supported cobalt catalysts with different pore sizes, *A. Catal. Today*, 2009 142: 70.
- ⁹² Dry, M.E. The Fischer-Tropsch Synthesis, in *Catalysis Science and Technology*, eds. J.R. Anderson and M. Boudart, Springer-Verlag, New York, 1981, 159-256.
- ⁹³ Storch, H.H., Golumbic, N. and Anderson, R.B. *The Fischer-Tropsch and related synthesis*, John Wiley & Sons, Inc., New York, 1951.
- ⁹⁴ Kogelbauer, A., Goodwin, J. and Oukaci, R. Ruthenium Promotion of Co/Al₂O₃ Fischer-Tropsch Catalysts. *J. Catal.*, 1996, 160: 125-133.
- ⁹⁵ Andersson, R. Catalytic conversion of syngas to higher alcohols over MoS₂-based catalysts, TRITA-CHE Report 2015:2 ISSN 1654-1081 ISBN 978-91-7595-392-2.
- ⁹⁶ Sharma, S.D., Dolan, M., Park, D., Morpeth, L., Ilyushechkin, A., McLennan, K., Harris, D.J. and Thambimuthu, K.V. A Critical Review of Syngas Cleaning Technologies – Fundamental Limitations and Practical Problems, *Powder Technol.*, 2008, 180: 115.
- ⁹⁷ Sharma, S. D., Dolan, M., Ilyushechkin, A.Y., McLennan, K.G., Nguyen, T. and Chase, D. Recent developments in dry hot syngas cleaning processes, *Fuel* 2010, 89: 817.
- ⁹⁸ Redeye, Bolagsanalys Cortus Energy, Available from: <http://www.redeye.se/resultat/o/cortus> [cited 2015-03-01].

⁹⁹ Cortus Energy, Månadsbrev, Available from:

<http://investor.cortus.se/releasedetail.cfm?ReleaseID=933162> [cited 2015-09-25].

¹⁰⁰ Fredriksson Möller, B. Status of Bio2G and Gasification testing at GTI, SGC International Seminar on Gasification Oct. 14-15 2014.