Recovery of excess heat from methanation into WoodRoll® gasification and modelling of an integrated heat and mass balance

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Thesis to obtain the Master of Science Degree in

Energy Engineering and Management

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July 2015

Acknowledgments

I would like to express my gratitude to Cortus' colleagues for sharing their knowledge with me and providing guidance along my internship period and thesis work, as well as to my thesis coordinator Maria Cristina de Carvalho Silva Fernandes, for her valuable input and support throughout the thesis.

Abstract

This objective of this master thesis work is to explore which are the possible fuels that can be converted starting from the clean syngas produced by WoodRoll® technology. Syngas can be raw material for hydrogen, diesel, methanol, DME and SNG production. For each of these fuels, state-of-the-art technology is presented, showing thermodynamic parameters, configurations and catalytic materials that are commonly adopted in the industry. In the framework of Cortus' collaboration with KIC InnoEnergy with the aim of synthetizing CH_4 from 100% renewable waste biomass feedstock, the focus in the literature review is mainly on methane conversion from hydrogen-rich syngas; Cortus and KIC Innoenergy have tested the joint operation of methane from biomass gasification in Köping pilot plant. Further objective of the thesis is to model integrated systems, which are able to maximize the thermodynamic efficiency of the SNG production process from raw biomass. Firstly, the simplest case with standard WoodRoll® technology connected to methanation unit, with no waste heat recovery, is shown. Here, results are compared to the results of a VBA model developed by Cortus, yielding a small deviation. Secondly, an integrated case has waste heat from methanation supplied to a steam cycle with the aim of combined production of electricity and methane. Thirdly, the option of processing fibre sludge from paper mills with 70% moisture content is analysed: the waste heat is here supplied to the drier. These models are compared to each other in efficiency and impact on the environment.

Key words

Gasification, methane, syngas, biomass.

Resumo

O objectivo deste trabalho é explorar a produção de combustíveis obtidos do gás de síntese produzido pela tecnologia WoodRoll®, como por exemplo hidrogénio, diesel, metanol, DME e gás natural sintético (SNG). No âmbito da colaboração Cortus 'com KIC InnoEnergy o objetivo principal foi estudar a síntese do metano a partir de matéria-prima 100% renovável, utilizando um gás de síntese rico em hidrogénio, produzido na unidade de gasificação numa unidade piloto em Köping.

Outro objectivo da tese é modelar sistemas integrados, capazes de maximizar a eficiência termodinâmica do processo de SNG a partir da biomassa. Em primeiro lugar, foi analisado um caso base, correspondente à integração da tecnologia padrão WoodRoll® com a unidade de metanação, não incluindo a recuperação do calor excedentário. Os resultados estão em concordância com os obtidos a partir do modelo desenvolvido em VBA pela Cortus. Em segundo lugar, foi simulada a integração do excesso de calor processo de metanação com um ciclo de vapor com o objectivo da produção combinada de energia eléctrica e de metano. Em terceiro lugar, a opção da secagem das lamas de fibra, com 70% de humidade, e resultantes do processamento do fabrico de papel também analisado: o calor residual é aqui fornecido ao secador. Estes modelos são comparados uns com os outros em termos de eficiência térmica e impacto ambiental.

Key words

Gasificação, metano, gás de síntese, biomassa, optimização.

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List of abbreviations and symbols

Abbreviations	Meaning
BM	Biomass
DME	Dimethyl Ether
FG	Flue gases
LHV	Lower Heating Value
M.U.	Mass Units
P	Electrical power
P.U.	Power Units
PG	Pyrolysis Gas
Syn	Syngas
TGA	Thermo Gravimetric Analysis
w	Moisture content
WGS	Water Gas Shift

Symbol	Meaning
$\dot{E}$	Chemical energy associated to a mass flow, calculated as material mass flow times LHV
$\dot{Q}$	Heat flow transferred between two mass flows
$\dot{m}$	Mass flow
c_p	Heat capacity of a gas at constant pressure
T_{evap}	Temperature of evaporation

Δh_{water}^{evap}	Enthalpy of evaporation of water at atmospheric pressure
$\Delta h^{0}{}_{React}$	Enthalpy of reaction with products at 25°C and 1 atm

1. Introduction

1.1. Background

Bioenergy is supplying 10% of the world total primary energy supply. In the industrialized world, biomass residues are used in thermal plants to yield electricity and heat; while anaerobic digesters and fuel conversion units are used to achieve combustible gaseous or liquid fuels, easing storage, consumption and distribution.

Energy conversion from biomass resources might not yet always be competitive with power generation from fossil fuels. However, new bioenergy policies are in the EU target for Horizon 2020, as it is of primary importance to move towards a cleaner, more decentralized and more sustainable energy-supply chain.

On a global level, bioenergy production is expected to experience a robust annual increase about +7%. The International Energy Agency foresees a world biomass yearly energy production ten-fold increase up to 3000 TWh by 2050, while biomass use for heat supply will ramp up to 24 EJ per year by 2050.

In order to promote the technological development of biomass-based application for heat and electricity production and fuel conversion, EU is fostering the aggregation of research centres and industries across the European territory. As a matter of example, Task33, promoted by the International Energy Agency, and the Biofuel Research Infrastructure for Sharing Knowledge (BRISK) are supporting innovative projects in the field of biomass conversion technology, which have prospects of improving of the current state-of-the-art (IEA - Bioenergy, 2015).

1.2. Research focus and Process description

In Sweden, with abundant forest resources and a thriving settled forest industry, bioenergy plays an important role in reaching the EU targets for renewable energy incorporation in the country's energy consumption mix.

Figure 1 Nordkalk industrial area, located in Köping (Sweden), hosts Cortus' pilot plant

Patented by Cortus Energy AB, the WoodRoll® is a gasification technology which produces clean syngas with high-energy content. The company is running a 500 kW pilot test plant in Köping in order to gain knowledge about the process and build the first commercial version of the system.

Figure 2 Sweden: Stockholm and Köping location

The WoodRoll® process is divided in three steps - drying, pyrolysis and gasification. The principle behind is to separate the solid material flow from the pyrolysis gas in the pyrolysis reactor and burn the latter gas to heat the gasification process indirectly. The separation of solid and gases enables the process to become cleaner and more efficient than state-of-the-art. In Figure 3, a scheme of the process is presented.

The incoming biomass is grinded, dried and then fed to a slow pyrolysis reactor. The resulting char is gasified at high temperature with steam into an externally-heated reactor. Consequently, the syngas is clean from condensable tars and nitrogen and, therefore, is very suitable for combustion in power production units or cost-effective bio-methane production. The total thermal efficiency of the system can reach up to 80%.

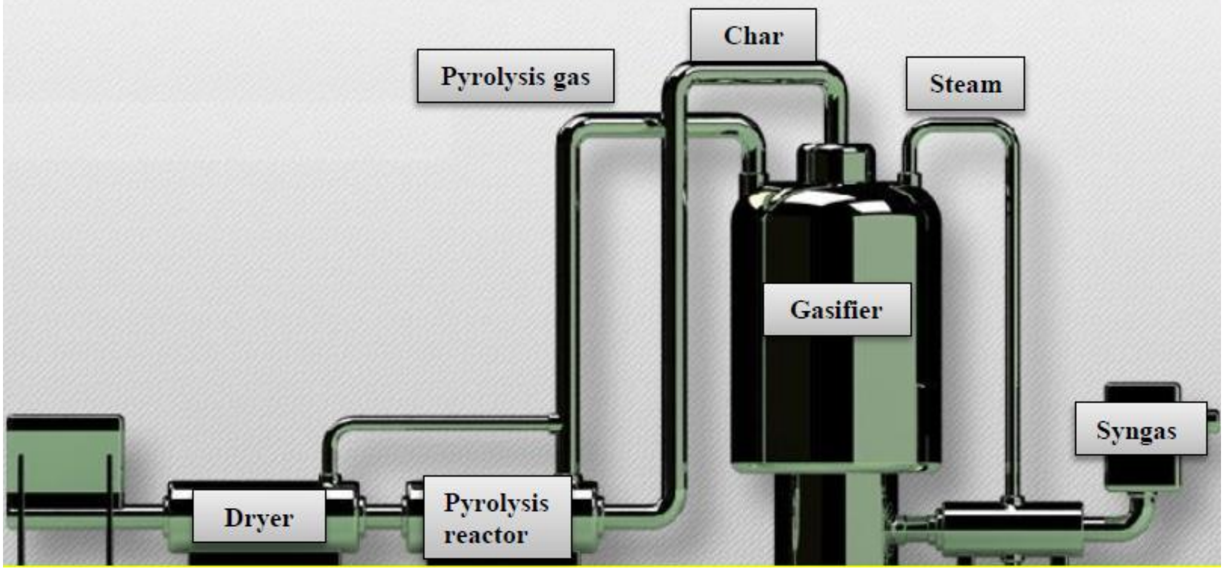

Figure 3 Representation of WoodRoll® system

The process has been tested with more than 100 types of feedstock, ranging from wood, to microalgae and sludge.

The syngas typically presents the following composition:

- H_2: 55-60%
- CO: 25-30%
- CH_4: 1-2%
- CO_2: Remainder

Cortus Energy actively works on cost efficient green energy for power, process and transport industries. Hydrogen from a completely green source and in industrial scale is becoming necessary to realize the vision of the non-pollution cars driven by fuel cells.

Cortus has got a new patent granted in the USA for a process solution where the WoodRoll® biomass gasification technology can integrate a water gas shift process in order to generate a clean renewable hydrogen. The hydrogen level from the WoodRoll® process is normally 55 - 60% but the newly patented process increases the hydrogen level to almost 100% of the energy from gasification of biomass.

Cortus Energy AB has established a partnership with KIC InnoEnergy in order to test out its syngas in the DemoSNG methane synthesis unit developed by Karlsruhe Institute of Technology. Under the umbrella of the DemoSNG project, there is also an attempt of including the Power-to-Gas technology and make use of the surplus electricity injected into the grid from the increasingly popular Intermittent Renewable Energy sources; however, this branch of the system is not considered in the present work, as no data is available yet.

1.3. Objectives and Thesis outline

The present work has the objective of exploring what are possible configurations in terms of process integration for the two systems. In the literature review, the concepts of gasification and syngas are outlined.

It is in the interest of Cortus Energy to learn about the fuel conversion processes that require syngas as raw material. These processes are: hydrogen separation, diesel, methanol, DME and methane synthesis. For each of these fuels, follows an overview on the conversion technology, ranging from temperature and pressure ranges of operation, desired H_2/CO ratios of the fed syngas and type of catalyst adopted.

The methodology part shall focus on the improvement of the integration between the WoodRoll® system and the methanation unit developed by the Karlsruhe Institute of Technology. The work of improvement begins on the field, at Cortus' pilot plant, with the risk analysis, commissioning and automation programming phase.

Now, the primary objective of the thesis is to explore different alternatives for the integration of WoodRoll® technology and the methanation unit. Working three months on the pilot plant gave the possibility to collect experimental data about the operation of the 500 kW system. This, together with information provided by Cortus' team, allowed building a Simulink model of the larger commercial version for three different arrangements.

The Case I model allows quantifying the heat demand and the temperature range of the drier, pyrolysis reactor, gasifier and steam boiler. Starting from the estimation of how much heat can be extracted from the methanation process and knowing which are the heat-loads on the rest of the system, it is possible to explore several configurations. Then, Case I model's results were compared with a Visual Basic model, developed by Cortus.

Amongst the proposed suggestions, Case II combines the conversion of electricity and methane. The heat from methanation produces saturated steam, while the heat released by the syngas cooling provides heat to the drier; pyrolysis gas burns in the gasifier's burner and in a boiler for steam superheating purposes, which then expands through a steam turbine for electricity conversion. The cooler syngas flow is purified in the gas-cleaning unit and undergoes methanation synthesis downstream.

Case III model aims at methane production from paper mills' sludge at 70% humidity: the fuel has very low grade and heating content, which would allow Cortus to be paid for processing it. In this setting, the methanation unit provides heat to the drier and flue gases, out of the gasifier, supply heat to the pyrolysis reactor, preheating the air and water needed.

Eventually, every scenario is compared on the basis of fuel conversion efficiencies, the amount of heat released to cold sinks and pyrolysis temperature (which sets a certain proportion between the char and the pyrolysis gas produced).

2. Literature Review

2.1. Background information

The declining petroleum resources, combined with increased demand for petroleum by emerging economies, and political and environmental concerns about fossil fuels are imperative to develop economical and energy-efficient processes for the sustainable production of fuels and chemicals. In this respect, biomass allows, through a variety of mechanisms, the synthesis of biofuels. Biofuels are the only current sustainable source of liquid and gaseous fuels and they can retrofit more traditional fossil fuels used in the transportation and power production sector. They generate significantly less greenhouse gas emissions than fossil fuels do and can even be greenhouse-gas-neutral if efficient methods for biomass collection and conversion are developed (Klass, 2004).

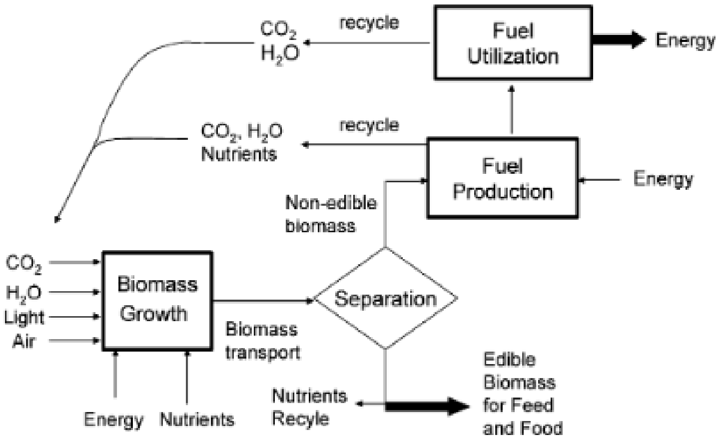

Figure 4 Sustainable production of transportation fuels from biomass in an integrated biomass production-conversion system (Klass, 2004).

Figure 4 shows an idealized biomass growth and manufacturing scheme in which CO_2, H_2O, light, air, and nutrients are the inputs for biofuel production, and energy to power transportation vehicles and food are the outputs. The three main technologies necessary for a carbohydrate economy are growth of the biomass feedstock, biomass conversion into a fuel, and fuel utilization. In this review, we focus on biomass conversion into a fuel, while recognizing that research in biomass production and fuel utilization are also very important.

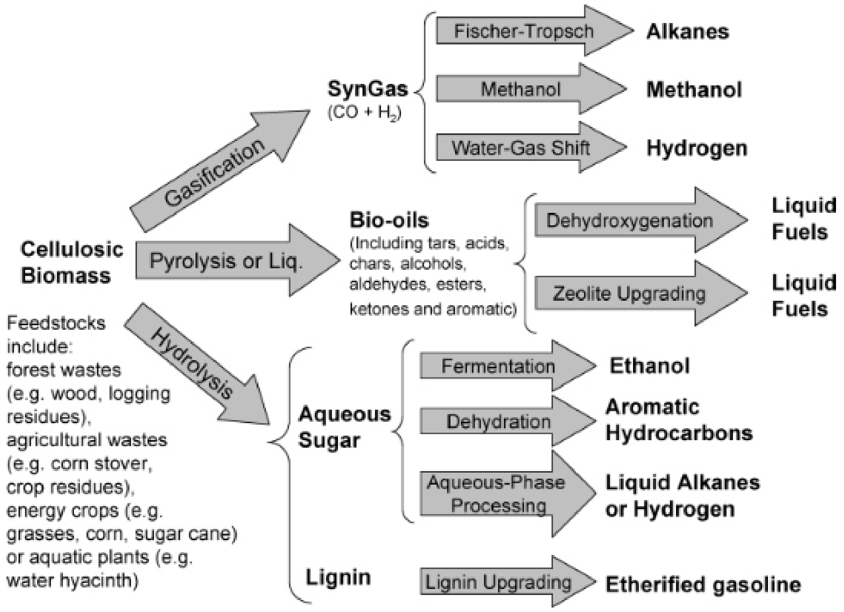

Figure 5 Strategies for production of fuels from lignocellulosic biomass (Huber & Dumestic, 2006).

Lignocellulosic material can be converted into liquid fuels by three primary routes, as shown in Figure 5, including syngas production by gasification, bio-oil production by pyrolysis or liquefaction or hydrolysis of biomass to produce sugar monomer units. Syngas can be used to produce hydrocarbons (diesel or gasoline), methanol, and other fuels (Huber & Dumestic, 2006).

The transition to the carbo-hydrate economy is already occurring with many companies, including traditional oil and chemical companies, such as Shell, UOP, Petrobras, Conoco-Phillips, Dupont, Dow and BP, developing the technology and infrastructure for biofuels and biochemicals production. Governmental leaders are also recognizing the importance of this fledgling industry by providing tax breaks, money, and mandates. The European Commission has set a goal that by 2010, 5.75% of the transportation fuels in the EU will be biofuels (K.EU-25, 2005).

2.1.1. Gasification and syngas

In this thesis, one can understand gasification as the process of converting a solid raw material, of some heating value, into a gaseous fuel, called syngas. The process is clean, highly efficient and it can convert a broad range of feedstock, such as coal, natural gas, biomass and different types of waste, allowing a wide range of applications, as shown in Figure 6; however, on industrial scale, only coal and natural gas are used. (Rostrup-Nielsen J. R., 2002).

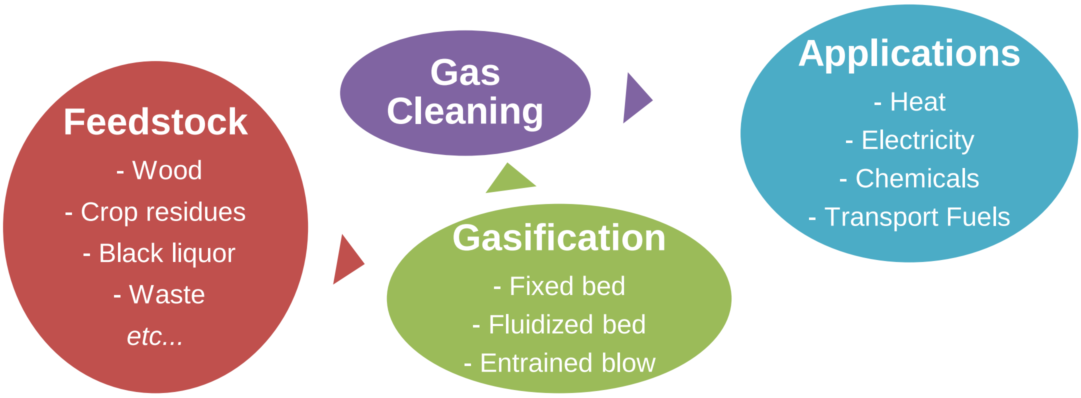

Figure 6 Biomass gasification overview

Syngas is generally a mixture of gases including H_2, CO, CO_2, CH_4 and H_2O in different proportions, depending on the process settings. The solid fuel reacts with a gasification agent, which can be oxygen, steam, air or carbon dioxide. Gasification reactions can be endothermic or exothermic; therefore, whenever the fluidizing agent is a reducing gas, it is necessary to either introduce an oxidizing agent to release some heat allowing endothermic reactions to occur, or to keep an entirely reducing atmosphere and supplying the heat externally. Gasification can be regarded as the intermediate step between pyrolysis and combustion. Firstly, the volatile matter is evaporated at temperatures below 600°C, with no need for oxidizing agent; afterwards, the fixed carbon of the biomass, namely char, is gasified through reactions with oxygen, steam and hydrogen. (IEA, 2015) The temperature range in the reactor can vary from 700°C to over 3000°C (above 1500°C only plasma gasification) and the reactor can operate at atmospheric pressure or in pressurized conditions. The higher are the temperatures and the pressures in the reactor, the faster are the kinetic rates of reaction.

The following steps are important in the conversion of biomass to syngas: biomass storage and transport, size reduction, drying, feeding, gasification, product gas conditioning, and ash disposal or recycling. Biomass particle size affects the gasification reaction rate and the product gas composition. Size control is expensive and energy intensive, and there is a trade-off between the optimal biomass particle size and the gasification process. Specialized equipment is used to feed the solid biomass into a gasifier. Screw feeders, where the screw forms a compact, pressure-retaining plug, are used for atmospheric gasifiers, and lock-hopper feeder or a lock-hopper/screw-piston feeder for pressurized gasifiers. Inside the gasifiers the following sequence of events occurs: drying, heating, thermal decomposition (combustion and pyrolysis), and gasification. The high moisture feedstock content of the feedstock has a negative influence on the thermal process efficiency and is usually the most energy intensive part of the gasification process.

The reactors can have different designs:

- **Fixed bed:** small-scale applications ranging from 10 kW to 10 MW of thermal power. The fuel is held on a grate, while the gasification agent flows from the top or the bottom (depending on whether it is an updraft or downdraft configuration). The simple design makes it a cheap solution; however heat transfer is not optimal and there is formation of agglomerates.
- **Bubbling bed:** up to 25 MW of thermal power. The gasification agent is blown from the bottom to achieve partial fluidization of the bed of solid particles. The heat exchange is more favourable.
- **Entrained flow:** thermal power higher than 100 MW. The turbulent flow allows rapid fuel conversion; the particle size can be as low as few micrometres; the syngas is free of tars and can behave flexibly on the type of feedstock in use.

The inorganic components of the gasification feedstock are converted into bottom ash, which is removed from the bottom of the gasification reactor, or into fly ash, which leaves the reactor with the product gas. The composition of the ash includes CaO, K_2O, P_2O_5, MgO, SiO_2, SO_3, and Na_2O_2. Ash melts around 1000°C[1], and it is important to keep the operating temperature below this value to avoid ash sintering and slagging (Bauen, 2004). Therefore, ashes can represent a problem, since they have a melting temperature after which sintering and corrosion of components can seriously damage the equipment. Tars, heavy hydrocarbons, are often undesired by-products, lowering the energy content of the syngas and causing corrosion problems after condensation in the pipes. If the purpose is power production, they can be burnt together with the syngas, but they need to be cracked or separated if other conversion steps are to follow. (Basu, 2010)

2.2. Different conversion processes

Having an overview of biomass gasification over the world through years, two relevant main periods can be identified in the development of the technology. The first one, between 1981 and 1988, is due to the oil crisis and the second period of activity takes place in the late 1990 with climate change being the major driver, with a clear peak of development in 2008. Canada, Finland, Sweden and the USA have been initially involved in the development of biomass gasification, since each of them has large woody biomass and/or peat resources. The 1990s brought increased awareness of climate change and European countries became increasingly involved. Germany and Austria have joint Sweden and Finland as leading countries, while many others became involved in development and implementation, including Netherlands, Italy, UK, Switzerland and Denmark; especially in countries with strong support for renewables and with availability of biomass (Kirkels, 2011).

The syngas is used for production of fuels and chemicals, and many industrial routes for utilization of syngas exist such as production of H_2 by the water gas shift reaction, diesel fuel by

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[1] However, the ash melting point is dependent on the type of biomass, decreasing down to even 700°C for herbaceous biomass

Fischer Tropsch Synthesis (FTS), methanol by methanol synthesis, and methanol-derived fuels, as described in Figure 7.

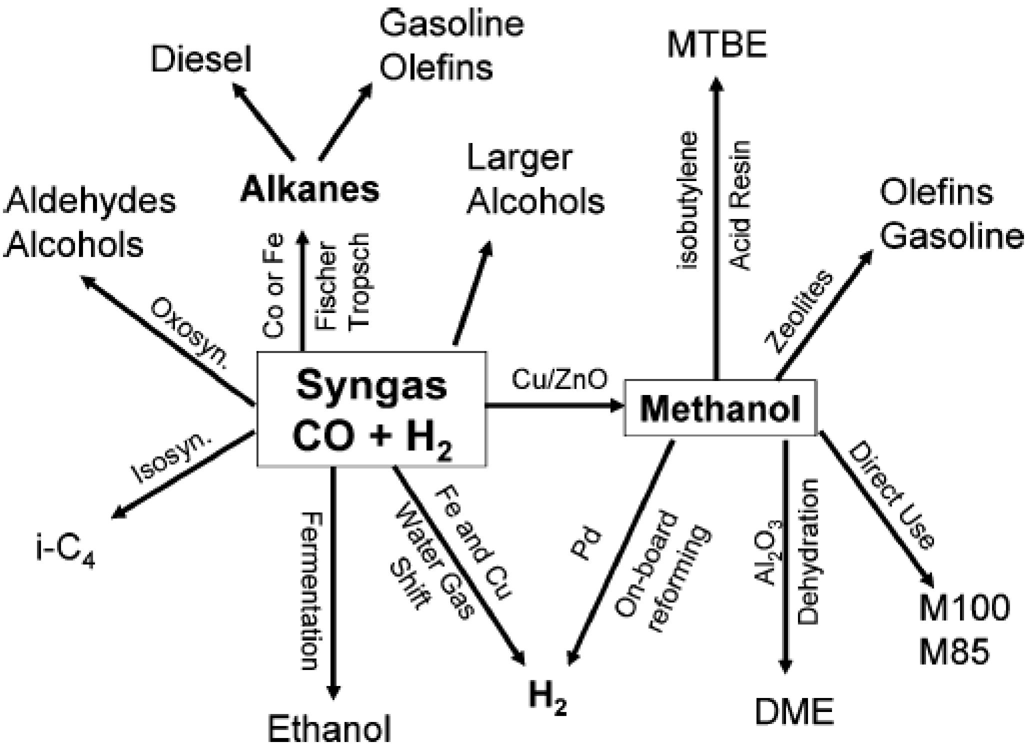

Figure 7 The H_2/CO ratio in the syngas is the parameter to be tuned in order to accomplish a specific fuel synthesis. In the following table there is a summary of the operative conditions to be adopted for each fuel (Anderson & Boudart, 1981)

Table 1 Summary of operating parameters industrially adopted in the conversion of syngas to hydrogen, diesel, methanol, DME and methane

	H_2/CO	Temperature range	Pressure range
Hydrogen	Any	21 – 38 °C	4-30 bar
Diesel	>1	220 – 350 °C	<27 bar
Methanol	2	275 – 350 °C	50 – 100 bar
DME	1-2	250 °C	70 bar
Methane	3	250 – 700 °C	10 – 50 bar

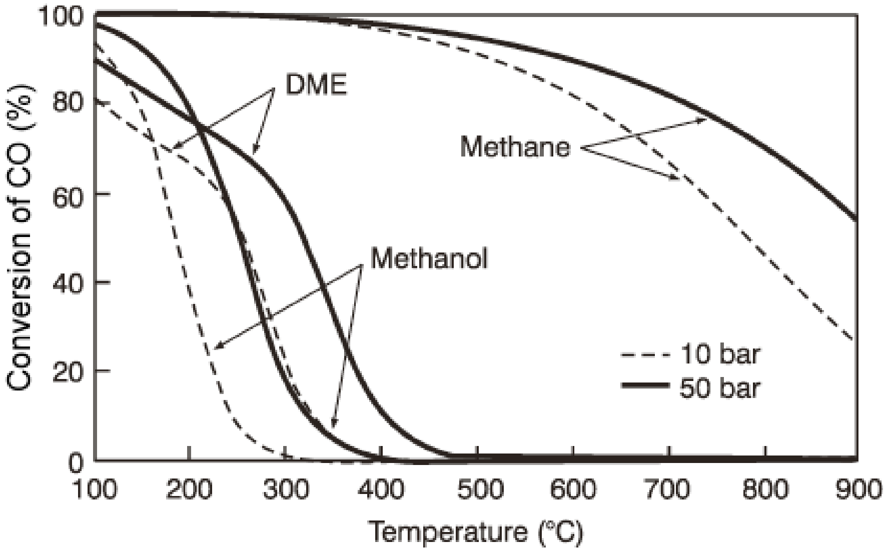

Figure 8 CO conversion efficiency in case of DME, Methanol and Methane at different temperatures and 10 and 50 bar (Rostrup-Nielsen & Winter-Madsen, 2008)

The graph in Figure 8 shows the influence of pressure on syngas conversion processes: higher pressures enable better CO conversion rates at higher temperatures; furthermore, every process is characterised by a certain temperature range, after which the CO conversion worsens.

As discussed through this section, syngas is a gaseous fuel, which can be raw material for the synthesis of a number of other different fuels, which are going to be discussed in more detailed:

- Hydrogen
- Diesel
- Methanol
- DME
- Methane

2.2.1. Syngas to H_2

Hydrogen is an important raw material in the petrochemical industry, used by ammonia and methanol manufacturers. The main applications of the remainder are in food, electronic, chemicals and metal refineries industries. Increasing restrictions on light hydrocarbons, sulphur content and unsaturated compounds have led to even higher demands for hydrogen (Rostrup-Nielsen, 2011). If hydrogen is the objective of the production of syngas, the output H_2/CO ratio should be as high as possible. To maximize it, CH_4 steam reforming reaction is performed, mainly, on Nickel-based catalysts (Liu Ke, 2009). Water-gas shift reaction is also run to increase H_2 content.

There are few methods allowing hydrogen separation:

- Pressure Swing Adsorption (PSA) technique accounts for 85% of hydrogen production. A feedstock with 60 - 90% molar fraction can yield very high purity (98 - 99.999%) through PSA, which is already considered state-of-the-art technology. The impurities contained in the gas mixture are selectively adsorbed by porous solid adsorbents when the syngas flow is compressed into a column. Subsequently, the hydrogen-rich gaseous phase that has not been adsorbed can be removed from the column. A pressure release will allow the impurities to be desorbed, thus regenerating the porous matrix. The process takes place at 4-30 bar pressure range and 21 - 38 °C temperature range. The waste gas stream containing the unrecovered H_2, other gaseous species and impurities can be combusted to make good use of its heating value. PSA can only work in batch mode and proves to be economically convenient on the large scale.

- The water-gas shift reaction occurs in two steps. First of all, high temperature shift reaction removes CO on chromium-promoted magnetite. Afterwards, low-temperature shift reaction removes further CO down to 0.2 - 0.4 % concentration with Cu/ZnO or CoMo catalyst. CO_2 scrubbing follows these steps.
- Membranes of various kinds, such as polymeric materials or porous (ceramic, carbon and metal) materials, are also in use to separate hydrogen. They both work thanks to a pressure gradient that pushes the small H_2 molecules through the sieve, while all the other bigger size molecules are held back.

With preferential oxidation reaction or methanation reaction, it is possible to remove CO and CO_2 traces. Consequently, H2 purity is improved up to 97% (Liu Ke, 2009).

2.2.2. Syngas to diesel

The key steps to form diesel out of syngas are cleaning of syngas and Fischer-Tropsch synthesis (FTS) process.

The Fischer-Tropsch synthesis (FTS) is an industrial process aiming at alkanes production from syngas using Co-, Fe-, or Ru-based catalysts. This technology was first developed in the early 1900s and used by Germany during the 1930s and 1940s to produce liquid fuels from syngas-derived coal (Anderson & Boudart, 1981) (Anderson R. B., 1984). Several oil companies are currently using or building FTS units to produce liquid fuels from natural gas derived syngas in remote locations. The overall reaction in FTS is shown in equation (1). The Water Gas Shift (WGS) reaction, and the reverse of the WGS reaction, occur during FTS (particularly on Fe catalysts) adjusting the H_2/CO ratio, particularly when low values are used.

The synthesis of liquid hydrocarbons from syngas through FTS processes is well performed when $H_2/CO > 1$. Hence, it proves to be particularly interesting in the case of steam gasification, for which H_2 concentrations are much higher. It is important to remove tars, impurities, hydrogen sulphide, carbonyl sulphide, ammonia, hydrogen cyanide, alkali and dust particles to prevent contamination and poisoning of the FTS catalytic material.

Catalytic production of diesel through FTS process involves the formation of a broad range of straight-chain hydrocarbons. The choice of the catalytic material will determine which fraction will be prevailing. The diesel formation reaction can be written as:

$$n\,CO \;+\; (2n+1)\,H_2 \;\rightarrow\; C_nH_{2n+2} + nH_2O \qquad (1)$$

All these reactions are exothermic ($\Delta h^0_{React} = -165\;kJ/mol_{CO}$) (Ram B. Gupta, 2010).

The product distribution of the hydrocarbons is described by Anderson-Schulz-Flory as:

$$x_n = (1-\alpha)\cdot\alpha^{n-1} \qquad (2)$$

where α is the chain growth probability, which is influenced by the thermodynamic condition and composition of the syngas.

Higher hydrocarbons such as diesel show higher tendency to form carbon depositions on nickel catalyst than methane. Therefore it is more suitable to use catalysts containing alkali or rare earth metals, or based on active magnesia support (Ram B. Gupta, 2010).

Fe catalysts are used in the production of diesel, as they are the cheapest catalytic material available on the market. With Fe-based catalysts and considering the activity of the water-gas shift reaction, 0.7 is the H_2/CO ratio required. From the operative point of view, they present high tolerance to sulphur compounds; however, the products tend to be rich in olefins and alcohols and their lifetime is limited to 8 weeks. (Ram B. Gupta, 2010)

Depending on whether it is low temperature or high temperature FT process, the operative temperature are within the range 220-240°C or 350°C (Axens.net, 2015). The pressure can range from 1 to 27 bar (Fischer Tropsch Synthesis, 2015)

2.2.3. Syngas to methanol

Methanol, which is one of the top 10 chemicals produced globally, is converted by the methanol synthesis reaction from syngas feedstocks, usually with Cu/ZnO-based catalysts, at 220-300°C and 50-100 bar. Methanol synthesis is a combination of two exothermic reactions, the WGS reaction and hydrogenation of CO_2 to methanol, equations (3) and (4), respectively (Chinchen, Denny, Jennings, Spencer, & Waugh, 1988) (K. Klier, 1982). The net reaction of these two reactions is shown in equation (5). Methanol can be produced from H_2-CO or H_2-CO_2 mixtures, but the rate of methanol production is 7 times higher for H_2-CO-CO_2 mixtures than pure H_2-CO mixtures (Klier, K. et al, 1982). Transient in-situ kinetic experiments suggest that at industrial operative conditions, methanol synthesis occurs via hydrogenation of CO_2 (Muhler, M.; Tornqvist, E:; Nielsen, L. P.; Clausen, B. S.; Topsoe, H. et al, 1994). For activity and selectivity reasons, the desired stoichiometric ratio for the syngas, defined as $(H_2 - CO_2)/(CO + CO_2)$, should be slightly above 2 (Dybkjaer & Christensen, 2001).

Methanol is used as intermediate step to produce:

- Acetic acid

- Dimethyl carbonate
- Formaldehyde
- DME
- Olefins
- Gasoline
- Biodiesel
- MTBE

The chemical reactions involved are WGS, methanol synthesis from CO_2 and from CO:

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \tag{3}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \tag{4}$$

$$CO + 2H_2 \rightleftharpoons CH_3OH \tag{5}$$

The global synthesis reaction (5) is exothermic, with $\Delta h^0{}_{React} = -90.84\, kJ/mol_{CO}$. Higher pressures and lower temperatures allow higher yields. The proper ratio to achieve maximum methanol yields is $H_2/CO = 2$; however, CO_2 concentrations above 2.5÷3.5% and below 12% are required for kinetic reasons. In fact, it can be proven that methanol synthesis from CO_2-free syngas is not possible. CO_2 is source of C to methanol formation and it also prevents consumption of the copper catalysts, impeding ZnO reduction, leading to brass formation. It is normal practice to recycle back the unreacted synthesis gas up to 3-7 times than the inlet volume flow. (Supermethanol.eu, 2015)

Methanol synthesis is thermodynamically favourable at low temperatures and high pressures. By-products of the methanol synthesis reaction include methane, dimethyl ether, methyl formate, higher alcohols, and acetone. One of the challenges in using methanol synthesis is to design reactors that efficiently remove the heat from this exothermic reaction.

Since 1920, when the process was discovered, chrome-oxide catalysts were used at 300 bar and 320-380°C. Later on, copper-based catalysts allowed pressures as low as 50 bar and 235-270°C ranges. The tendency seemed to be that of reducing operational pressures as much as possible to try to avoid high costs for thick pipes and equipment to compress the syngas. However, high pressures favour kinetic rates and reduce the need for large syngas recycle stream.

Low selectivity and crystallization of the catalyst limit the operational temperature of copper catalysts respectively below 230°C and over 270°C. Higher temperatures affect product distribution, producing unwanted species such as CH_4, DME, methylformate and higher alcohols; besides, high temperatures also cause catalyst sintering.

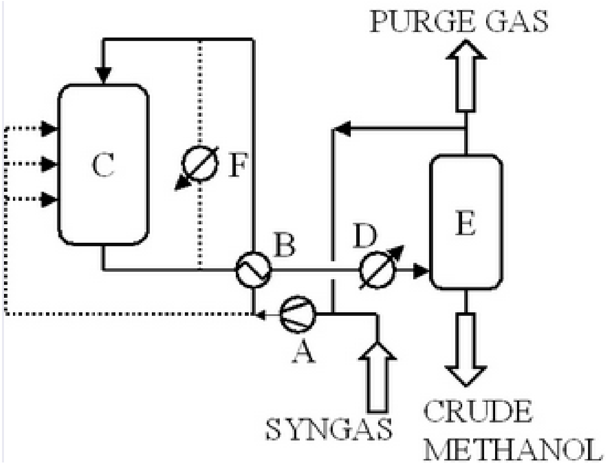

Figure 9 Schematic representation of a methanol synthesis system. A=Recycle compressor; B=Heat exchanger; C=Reactor; D=Cooler/Condenser; E=Methanol separator; F=Start-up heater.

In Figure 9 there is a representation of the basic scheme of a methanol system. A stream of syngas is mixed with the recycled syngas at the inlet of the reactor and heated up to about 220-230°C. The gas at the outlet is about 250-270°C. The mixture is then cooled to separate methanol and recycle syngas. The operational pressures range from 50 to 100 bar. The water fraction in methanol depends on the CO_2 concentration of the feed gas. After the synthesis of methanol, a distillation step is required to achieve higher purity. (Supermethanol.eu, 2015)

Methanol also can be converted to olefins or gasoline (Stöcker, 1999). This process was first discovered in the 1970s by Mobil scientists who showed that zeolite catalyst, such as ZSM-5, could convert methanol into dimethyl ether (DME) followed by light olefins, and then higher olefins, paraffins, aromatics, and naphthenes.

Since MeOH is often an intermediate step to the production of other fuels, it is convenient to integrate the steps in a single system. For example, MTG (Methanol to Gasoline) requires condensation and re-evaporation of methanol. (Rostrup-Nielsen, 2011)

2.2.4. Syngas to DME

DME (dimethyl ether) is a clean, colourless gas that has a broad number of applications: it can be used as engine fuel for the transportation sector, electricity conversion and be burnt in households for heating and cooking.

DME has been used for decades in the personal care industry (as a benign aerosol propellant), and is now increasingly being exploited for use as a clean burning alternative to LPG (liquefied petroleum gas), diesel and gasoline. In fact, as LPG, DME is gaseous at normal temperature and pressure, but changes to a liquid when slightly compressed or cooled, which allows easy liquefaction, storage and distribution. It has high oxygen content, lack of sulphur or other noxious compounds, which make it a very clean fuel.

Dimethyl ether (DME) can be used as a diesel fuel and is produced in a two-step process involving formation of methanol, followed by dehydration. Recent improvements in DME involve the development of bifunctional catalysts to produce DME in a single gas-phase step (Peng, Wang, Toseland, & Tijm, 1999) (Ge, Huang, Qiu, & Li, 1998) or the use of a slurry reactor (Lee & Sardesai, 2005) (Sardesai & Lee, 1998). Higher alcohols, including ethanol, 2-propanol, and butanol are made from syngas with catalysts consisting of Cu, Zn, Mo, or Cr, promoted with alkali metals.

DME can be synthetized directly from syngas in one single step (Liquid Phase DME) according to:

$$3\,CO\ +\ 3\,H_2 \rightleftharpoons (CH_3)_2O + CO_2 \qquad (6)$$

$\Delta h^0{}_{React} = -246\ kJ/mol_{CO}$.

Alternatively, it can be produced out of methanol by dehydration, according to:

$$2\,CO\ +\ 4\,H_2 \rightleftharpoons 2CH_3OH \qquad (7)$$

$\Delta h^0{}_{React} = -181\ kJ/mol_{CO}$

$$2CH_3OH \rightleftharpoons (CH_3)_2O + H_2O \qquad (8)$$

$\Delta h^0{}_{React} = -23\ kJ/mol_{CH_3OH}$ (Rostrup-Nielsen, 2011).

Synthesis of dimethyl ether from syngas (the LPDME process) can be carried out in the liquid phase at moderate temperature and pressure, 250 ˚C and 70 bar. It makes use of dual catalysts dissolved in a liquid oil medium. The bi- functional catalyst consists of a mixture of methanol synthesis catalyst ($Cu/ZnO/Al_2O_3$) and methanol dehydration catalyst (gamma-Alumina).

DME is considered to be an environmentally clean substitute for Chlorofluorocarbons (CFC), which are of target of retrofitting in the refrigeration sector, as they heavily contribute to ozone's layer depletion; it is also of common use in the sector of households' products. Given its cetane number, around 50-60, it has proved to be a good substitute in diesel engines. Among other uses, it can be introduced as an additive to methanol to improve its combustion properties and it can serve as raw material to obtain aromatics, methyl acetate, acetic acid, premium gasoline, oxygenates and other ethers (Lee, 2015).

2.2.5. Syngas to methane

Methane (CH_4) is considered to be an environmentally clean fuel, as it releases more heat per mole CO_2 produced than other longer chain hydrocarbons; it burns without formation of soot, it is easy to store, distribute and sell to the national grids. The methanation technology offers a promising potential to feed the already existent SNG grid with bio-generated methane. Methanation reactions are the reverse reactions of steam reforming. The overall reaction is exothermal (11), reason for which the removal of heat from the reactor is often a technical challenge. Carbon dioxide methanation takes place according to:

$$CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2\,H_2O \tag{9}$$

With $\Delta h^0{}_{React} = -165\ kJ/mol_{CO}$.

There is also carbon monoxide methanation:

$$2\,CO + 2\,H_2 \rightleftharpoons CH_4 + CO_2 \tag{10}$$

With $\Delta h^0{}_{React} = -247\ kJ/mol_{CO}$.

Yielding the global reaction:

$$CO + 3\,H_2 \rightleftharpoons CH_4 + H_2O \tag{11}$$

With $\Delta h^0{}_{React} = -206\ kJ/mol_{CO}$

Additionally, Water-Gas Shift (3) and carbon deposition (12) (13) are also part of the mechanism:

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \tag{3}$$

$$2\,CO \rightleftharpoons CO_2 + C \tag{12}$$

$$CH_4 \rightleftharpoons C + 2\,H_2 \tag{13}$$

The methanation process can be carried out also for H_2/CO=1, but only on sulphide catalysts, which have proven to exert beneficial influence on carbon deposition (Rostrup-Nielsen J. , 2011). Equation (11) shows that the methanation reaction is volume reducing. The conversion of syngas into methane is not a flexible process: load and syngas composition should remain constant to ensure good conversion efficiencies. The optimal condition to maximize the process' efficiency needs temperatures around 620 - 750 °C. Consequently, there is a need for thermally stable catalysts that maintain high activity level even if operated at low T (Jensen, Poulsen, Andersen, 2011).

The H_2/CO ratio is of primary importance to meet the carbon/hydrogen proportion in the desired product. WGS reaction allows an increase of the H_2/CO ratio; it is carried out either at 650-700 K with Fe or Cr catalysts, or at 450-500 K with Cu-ZnO-Al_2O_3 catalysts. As in the case of nitrogen, also water and carbon dioxide should be removed to avoid too low CO and H_2 partial pressures and unnecessary costs of equipment (Ojeda, 2010).

Methanation is enhanced by high-Ni content in the catalyst, but it is inhibited by increasing particle size. The higher the steam content present in the raw gas, the higher will be the CO taking part in the WGS reaction. With regard to impurities, H_2S, HCl, NO_x and NH_3 cannot enter the methanator, as they poison the catalyst. At elevated gas pressures, Ni tends to form $Ni(CO)_4$.

When choosing the catalyst for methanation, activity, selectivity and lifetime are the important indicators. The higher the activity, the smaller the size of the reactor, which means lower costs associated to it. Selectivity is defined as the fraction reactant that yields a desired product. In other words, the catalyst should not promote the consumption of CO and H_2 to for other species than CH_4. Metals of the VIII group are very common catalysts for methanation (Mills & Steffgen, 1974). The metal with the highest activity is Ruthenium, which is too expensive to be used on a commercial scale. Also Fe and Co can be good catalysts for methanation, but they also favour the formation of longer chain hydrocarbons. So far, Ni has proved to be the best compromise in terms of costs, activity and selectivity (Mills & Steffgen, 1974). There are, however, limitations on the adoption of Ni as catalyst: first of all, particles tend to sinter at high temperatures. Then, it is sensitive to carbon deposition in the form of graphite or other structures; unlike Fe materials, it proves to be easily affected by sulphur concentrations in the feed syngas, in the form of COS and H_2S (Dacheng Hu, 2012). For what regards the supporting material, alumina (Al_2O_3) is by far the most common solution commercially adopted because it improves the thermal and mechanical properties of the catalyst.

If there is no gas cleaning higher expenses on the catalyst replacement occur, while higher investment on the gas cleaning section can postpone the purchase of new catalyst: the extent to which gas cleaning is carried out is always a matter of economical trade-off. However, 1 ppm is the maximum concentration allowed for the sum of nitrogen/sulphur containing compounds.

Ammonia can be removed from the raw syngas by catalytic destruction or wet scrubbing, together with halides thanks to a water washer. H_2S can be removed by conversion to elementary sulphur (Claus process). Eventually, H_2S, COS and HCN in low quantities are trapped at the last stage by ZnO guard beds (Liu Ke, 2009). There are no specific limits to the concentration of tars; however, it is important to consider the operative pressures in FTS reactors and consequently keep lower concentrations than dew point concentrations to avoid clogging phenomena. Tars are not only an issue to the syngas conversion process, but they also represent a fraction of the total available energy. Therefore, it is always preferable to convert them instead of stripping them off the syngas. This conversion is labelled as tar-cracking and it can happen through Nickel catalyst or via thermal route at approx. 1400 K with steam or oxygen. As for the solid particulates, the removal must be nearly complete, since it provokes fouling of the catalytic system. A 15 % level is considered as upper limit to the concentration of inert gases in the syngas, since higher levels impact on the size and cost of the equipment. Especially N_2 should be avoided, as it is particularly expensive to remove (Liu Ke, 2009).

Considering the global methanation reaction, about 20% of the heating value is lost as waste heat, if the syngas has $H_2/CO = 3$. To give an idea of the extent of heat production, considering the case of $H_2/CO=3$ and 30 bar reactor and assuming adiabatic reactor conditions, an inlet flow at 300°C would result in 923°C flow (Harms, H. G. et al, 1980), introducing also the risk of carbon deposition and threatening the lifetime of the catalyst. This issue can be addressed by a number of possible solutions. The methane produced could be cooled and mixed with the inlet syngas: in this way the temperature can be kept below 450°C (Jensen, Poulsen, Andersen, 2011) (Rostrup-Nielsen, 2011). The main drawback is the high cost of compression in the first methanation stage to be faced in order to perform recirculation. However, it would be possible to recycle enough flow to maintain 700°C at the outlet, but this condition does not allow good product quality, since low temperatures are needed for thorough conversion of CO and CO$_2$. Alternatively, the process can be broken down step-wise, allowing heat removal through several heat exchangers. Throughout the steps, water is removed to shift the reaction towards product formation. Afterwards, the product is cooled, dried and compressed in order to meet the grid requirements (Jensen, Poulsen, Andersen, 2011).

In the ADAM-EVA project around 1980, this high temperature methanation process (TREMP) in which heat was recovered as superheated steam generation was explored.

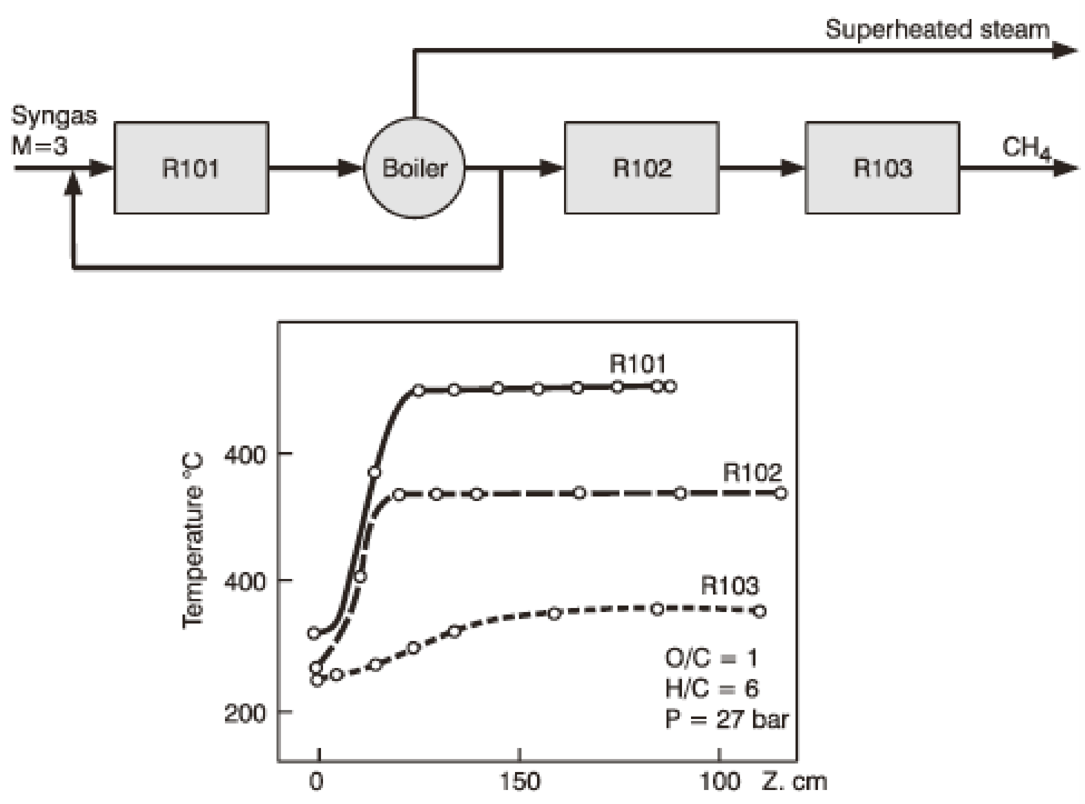

Figure 10 TREMP process. R101, R102 and R103 are methanation reactors (Rostrup-Nielsen, 2011).

As shown in Figure 10, only the higher temperature step exchanges heat with a steam boiler, while the lower temperature reactors releases heat to lower temperature sinks. Generally, the catalyst can exhibit good stability at high or low temperatures; there is still margin for improvement in the search of a material with good behaviour on both ranges.

With regards to low temperature operations (250-300°C) the Ni catalyst proves to have short lifetime: the TREMP process has enacted the use of a Ni/non-Ni mixture of catalyst to make its use more durable. On the high temperature side, there is risk of Ni sintering and carbon deposition.

As for the typology of reactor, the fluidized bed type of reactor is considered superior in performance to the fixed bed one. Experiments (Jiao Liu et al, 2013) have proven that for different temperatures, CO conversion and CH$_4$ selection are always higher in the fluidized bed arrangement than in the fixed bed one. The authors simulate atmospheric pressure methanation in a quartz reactor and pressurized methanation in a stainless steel reactor, while the operative condition are simulated by blowing N_2, H_2 and CO in controlled quantities. The catalyst used is NI-Mg/Al_2O_3. The reason for improved performance are lower heat and mass transfer coefficients, lower amount of surface available for reactions (since the catalyst particles are packed together) and poor surface refreshment. Even for different space velocity values[2], fluidized bed showed CO conversion levels up to 87%, with only 4% decrease at higher flows, while the same operative conditions produce 82% maximum CO conversion with 46% drop at higher flows. With regard to the operative pressure, the fluidized bed concept behaves steadily over the 10-30 bar range, presenting CO conversion levels from 85% to 90.5%. The fixed bed arrangement, instead, improves the conversion values from 24% to 40%. It has also been noticed that the carbon deposition occurred in the fluidized bed is much easier to oxidize to CO_2: catalyst deactivation is quicker when the bed is fixed (Jiao Liu et al, 2013).

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[2] Space velocity is defined as the volume of outlet dry gas per hour at standard conditions of 15.6°C and 1 atm, given per volume of catalyst. (L., 1975)

3. Analysis of the WoodRoll® gasification and methanation unit

In this chapter, there is a section dedicated to the description of the pilot plant located in Köping and an explanation of what the work in Cortus has been over the 5-months-internship. Following up, the calculation model is described and the commercial version of WoodRoll® is modelled on Simulink, with the Thermolib toolbox. The base case will be described in this chapter. Then, out of five different integration alternatives, only three scenarios will be modelled flow Tables and flow diagrams reported and ultimately, compared on the basis of a global energetic analysis, including heat and cold utilities, and electrical power consumption.

This chapter analyses the large-scale conversion of low-quality wood into synthetic natural gas (SNG) by indirect gasification, gas cleaning, and methane production. However, there are several world projects, some of those will be described hereafter, that foresee the production of bioenergy through the use of Bio-SNG.

1. The GoBiGas facility was inaugurated on 12 March 2014. The facility converts waste wood to SNG via gasification, followed by gas cleaning and methane production. In December 2014, GoBiGas started injecting methane into the natural gas grid.

Figure 11 GoBiGas facility in Göteborg.

On 18 December 2012 it was announced that GoBiGas Phase 2, Sweden, had been selected to receive counterpart funding of €58.8m under the first call for proposals of the NER300 funding programme for innovative low-carbon technologies. The Project will demonstrate the large-scale conversion of low-quality wood into high quality synthetic natural gas (SNG) by indirect gasification at atmospheric pressure, gas cleaning, methane production (via nickel catalyst), pressurization and injection of the product into the regional gas network. The Project will make use of pulpwood and forest residues harvested from the surrounding areas of Göteborg, the Lake Vänern and Baltic region. The volume of ~0.5 Mt/year of wet biomass will be used in the Project, which has an installed capacity of ~100 MWth to produce 800 GWh/year of gas (SNG) (BiofuelSTP.eu, 2015).

2. The Biomass CHP Plant Güssing, which started operation in 2002, has a fuel capacity of 8 MW and an electrical output of about 2 MWel with an electrical efficiency of about 25 %. Wood chips with a water content of 20 – 30 % are used as fuel. The plant consists of a dual fluidized bed steam

gasifier, a two-stage gas cleaning system, a gas engine with an electricity generator, and a heat utilization system, offering a complete value chain demonstration from woody biomass to SNG.

Figure 12 Güssing facility in Austria.

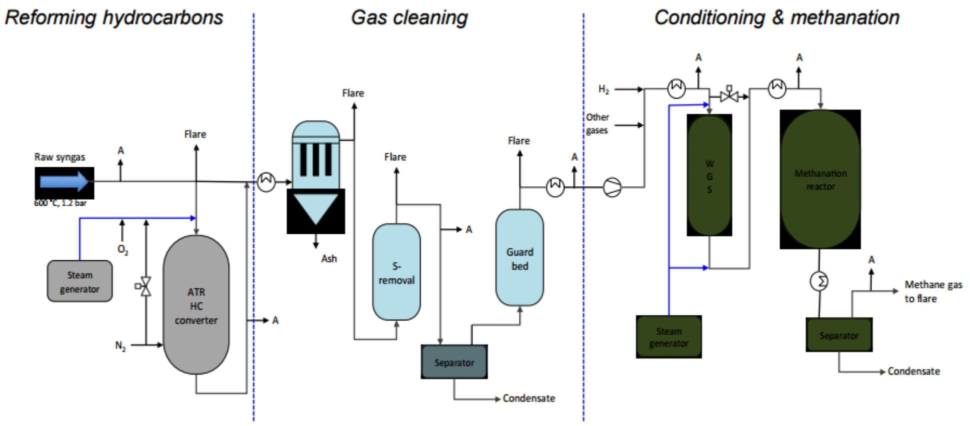
Commercial bio-SNG plants are expected to be in the scale of 20 to 200 MW. In the initial conversion step i.e. in the biomass gasification process wood chips are converted into a syngas or more general into a product gas. The FICFB gasification process has operated in Güssing since 2002 for a combined heat and power (CHP) plant and in this time has been in operations for many 10000s of hours. The product gas is delivered at ambient pressure, has a high content of CH_4, higher hydrocarbons and tars. This product gas, after proper conditioning, can be suitable for SNG production. The final conversion step consists of three sub-steps: gas conditioning, SNG synthesis and gas upgrading. R&D work over the first 8 years at Güssing focused on gas conditioning and SNG synthesis. The pilot scale showed that fluidized bed SNG synthesis is possible. The whole process chain reaches high conversion efficiencies and has the potential for lower investment and lower operation costs than conventional SNG synthesis technology (NER300-SWD-224, 2012).

3. ECN (Energy resource Center of the Netherlands) has been developing a system for the conversion of dry lignocellulosic biomass into natural gas quality gas: BioSNG or Substitute Natural Gas from biomass. Technology choices have been based on the desire of having large-scale BioSNG plants with high overall efficiency. The ECN concept is based on so-called MILENA indirect gasification and OLGA tar removal. The ECN concept offers 70% efficiency from biomass to BioSNG. A lab-scale system is available at ECN. A 1 MW pilot system at ECN is under commissioning for the two main parts of the system: the MILENA gasifier and the OLGA tar removal. HVC is a waste company, which is expanding its activities towards renewable energy. Joining the development of the BioSNG-concept perfectly fits in with HVC’s ambitions in the medium and long term. HVC intends to

realize two demonstration plants to demonstrate the ECN-concept. The first demo plant will be a ~10 MW CHP plant to demonstrate the combination of the MILENA and OLGA-processes. The second demo plant will be a ~50 MW SNG plant in which the MILENA and OLGA are up-scaled and further gas cleaning and methanation will be added. (Zwart, 2015)

3.1. Description of the InnoEnergy system

Cortus Energy AB has a partnership with KIC InnoEnergy to provide clean high-hydrogen-yield syngas to the DemoSNG pilot plant built by the Karlsruhe Institute of Technology (KIT), installed in Köping next to the gasification pilot plant. The joint operation of WoodRoll® 500 kW and Demo SNG is currently being tested for a fraction of the total syngas flow.



- Demonstration of process at Cortus
- Tests of system components
- Intermittent/Stable feeding of additional H_2

- Raw gas capacity 12 – 14 Nm^3/h
- Removal of HC, S and N – compounds, ash, etc

Figure 13 Scheme of the InnoEnergy gas cleaning system, conditioning and methanation system (Engvall, 2015)

A substream of syngas of 12-14 Nm^3 at 430°C is extracted from the main outlet of the gasifier after the glycol-cooled cyclone.

After extraction, it passes through a filter with 6 stainless steel cylindrical cartridges with 2 micron porosity, removing all the dust with densities within 2 - 10 g/m^3 and above. The filter is periodically back-flushed with CO_2 at 4 barg in order to destroy the cake that is formed by the continuous deposition of ashes and dusts; the cake fragments will fall on the bottom and will be removed at each programmed stop of the plant.

The gas leaves the filter from the top and runs through a pipe, which is kept under temperature control by use of a heating cable wrapped around the pipe under the insulation coating. This device can provide 2 kW power and make sure the syngas can enter the next stage, zinc-oxide bed, at the proper temperature of 400°C. The operative temperature is crucial at this stage to ensure thorough elimination of sulphur compounds (H_2S and COS) and avoid poisoning of the catalytic materials in the DemoSNG. The ZnO bed can accept sulphur content as high as $H_2S < 200$ ppm and guarantee outlet concentrations such as $H_2S < 0.05$ ppm. For traditional woody biomass, however, the sulphur content is always found to be below 5% mass of the dry composition, normally not above 1%.

The gas is then condensed in an external heat exchanger with water-glycol mixture at 45% volume as a heat carrier; the heat is transferred from syngas to the cooling fluid and discharged to the atmosphere through convection, driven by an air fan for 1 kW power. A pump, working at constant speed, ensures the flow of cooling fluid. Eventually, the condensate is drained out, together with additional impurities.

After cooling, the gas is blown through an active carbon bed of 40cm height, with particle average dimension of 3 mm. This material is placed here to trap potential gases and impurities that manage to come through the previous cleaning steps.

Before the interface to the DemoSNG container, a syngas fan with 373 W power, provides the necessary pressure difference to win the resistances encountered across filter, pipes and beds. The fan is placed just outside Cortus' shed and has a provisory chimney on top of it, ensuring that syngas leakages do not represent a danger.

Safety issues are never neglected:

- In the design phase, a 5 barg nitrogen inlet is situated in the section where syngas enters the system, so as to allow quick inertization of the pipes and rinsing of syngas to the flaring system of the WoodRoll®. Additionally, to take into account the occurrence of a power failure, the system can also be evacuated by means of a compressed-air-driven ejector. In case of power failure or pneumatic failure, all the valves reach their safety mode (Fail Open or Fail Close), blocking inlet of syngas and outlet to Demo SNG and opening the way in to nitrogen and all the bypasses to the flare.
- The flare system is always kept above 750°C whenever there is syngas production to ensure self-ignition of the fuel without risks for explosions.

The syngas composition is a key requisite to flow to the Demo SNG container. Whenever the composition is not stable and acceptable for the methane conversion unit, the flow is temporarily routed to a bypass line to the flare. The measurements are carried out in multiple points: through Gas Chromatography station in the WoodRoll® side and in the DemoSNG container.

3.2. Commissioning of the InnoEnergy system - Improvements

The improvement of a system does not only take place in the design phase of the system, but it continues over the commissioning, risk assessment and programming phase. The activities in the pilot plant were focused on the commissioning of the Innoenergy cleaning gas section, built for Cortus, in order to purify the syngas produced by the WoodRoll® up to purity levels that are acceptable for methanation in the DemoSNG container, located next to the pilot plant.

The risk analysis evaluates the likelihood and impact of possible hazards on:

- Human health
- Environment
- Cost.

It is a procedure aiming at considering all the possible causes of failure or ill operation for every component in the system; each of these causes is going to have an effect on the rest of the system, in a direct or indirect way. In the process, all the possible failures are associated to several possible causes for that failure, and again, for each of previous mentioned scenarios, there is a consequence. These consequences are assessed on a scale ranging from 1 to 5 on the following three main parameters listed above. E.g. CO leakages from the syngas pipe are poisonous and not detectable by the workers; a pump circulating glycol can break and release large quantities of the substance to the environment; a flow heater overheats for out-of-range operations and melts down inside: this does not pose any hazard to humans or to the environment, but it is, in fact, an expensive component to be replaced. To every consequence, there is an action for improvement that is detected and the risk is newly assessed to quantify the impact of this measure.

The procedure for designing a system goes through the basic engineering design, which cares mostly about the process values, ensuring that heat and mass balances are possible to be fulfilled. Secondly, a more detailed approach follows and the whole equipment must be sized; after several reviews of the project, the team purchases components. Every item arriving at the plant needs to be installed and connected according to the original intent of the designers; however it might occur that the equipment was over- or under-sized or even that unexpected problems show up, which had not been accounted for during the design phase. It is here important to have knowledge of the process and brainstorm with the team to find a post-design alternative. As matter of example, the zinc-oxide bed for sulphur removal should already be up in temperature when the first syngas enters the system, so as to avoid steam condensation and clogging. During the design phase, this aspect had not been considered; the team found a solution to it, purging nitrogen through electrically heated pipes and warming up the bed indirectly.

Once the system is commissioned, it is time to think of how can it be safely operated, preventing hazardous manoeuvring from a new operator who is not entirely familiar with the system or any other spontaneous cause of hazard foreseen in the risk analysis. Programming instructions are written on the base of the experience gained over commissioning tests. These commands were written for InnoEnergy Gas Cleaning, Pyrolysis and Drying blocks, with the intent of achieving safety in automation and minimum consumption of resources. As for the steady state operations, any time there is a thermodynamic value that should be maintained (e.g. incoming temperature of flue gases to the drier), a *Control loop* with PID control needs to be implemented. *Interlocking* of components are meant to prevent hazards caused by wrong operations (e.g. block manoeuvring of the gasification system when the flare is not in the safe temperature range). Finally, for every object there are limits on the analogic/digital output describing the status of the component: alarms and alarm suppressions are set to each of them to communicate a malfunction to the operator. When it comes to transitional states, the system has to be instructed on how to start from cold conditions, or to stop from normal operative conditions: this is done through *Start-up* and *Stop sequences*. An *Inerting sequence* is what brings the system to a safe state in which all pipes and reactors are emptied of combustible substances and inerted with nitrogen. It is equivalent to a stand-by mode and can be quickly brought back to steady state. Finally, a *Trip sequence* takes place when system is suddenly stopped from the emergency buttons placed in the plant. It interrupts all moving parts and electrically heated elements in case someone got hurt.

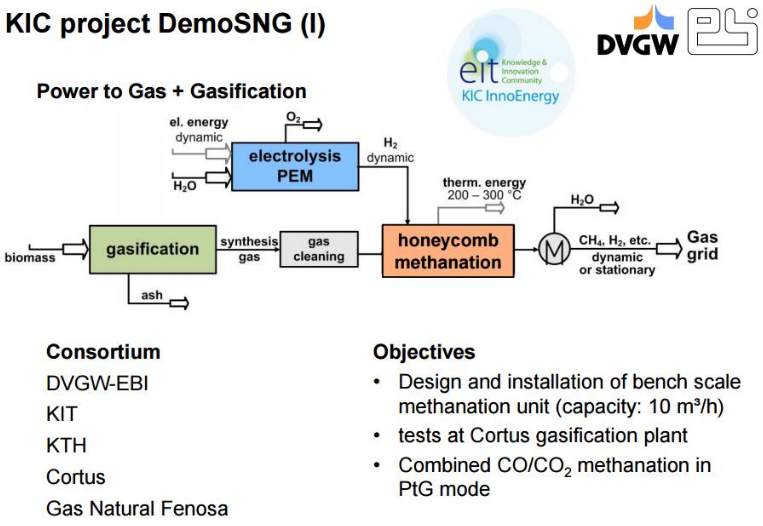
In order to guarantee a safe commissioning, a set of programming instructions was developed. Here is an example of how the control system works through the programming instructions: The air fan cooler, which discharges the condensation heat of steam in the syngas to the environment, is equipped with a variable speed engine. Nevertheless, the thermal load on this condenser is variable depending on the temperature of the incoming syngas, mass flow of syngas and mass flow of the cooling medium transferring heat from the condenser to the cooler. The easiest way to commission this component would be setting the cooling fan at constant maximum speed, which ensures thorough cooling at any condition of the syngas. However, the team set this as target for improvement: the load on the syngas line was modified, tracking several variables - the temperature and the mass flow of the gas; the cooling pump of the cooling medium was held at constant speed. The air fan cooler was tested for every set of conditions to the value that returns the desired temperature on the downstream side of the condenser. The values were then fitted in a curve, written in the programming instructions and handed to the programmer. This measure will minimize the energy spent for cooling needs, dynamically following the system.

3.3. DemoSNG - Estimation of heat availability

Here follows a short description of the methanation system, which will not be a target for improvement, with the exception of the heat deducted by the methanation reactors.

Figure 14 Cortus' gasifier on the left, methanation module from KIT and DVGW on the right.

At the beginning of the methanation container, the syngas undergoes two-staged compression up to 2 bar. Once compressed, the inlet syngas has the possibility to mix with pure N_2, CO, CO_2, H_2 and CH_4 from gas bottles stored outside the container and adjust its composition. The gas mixture is later driven through an electrical heater to bring it up in temperature and enters the Water Gas Shift reactor (WGS), where the H_2/CO ratio can be adjusted with steam, produced on spot through electrical heating. Downstream, the syngas is led to six methanation reactors that can be arranged (in series and/or in parallel).



KIC project DemoSNG (I)

Power to Gas + Gasification

Consortium

DVGW-EBI
KIT
KTH
Cortus
Gas Natural Fenosa

Objectives

- Design and installation of bench scale methanation unit (capacity: 10 m³/h)
- tests at Cortus gasification plant
- Combined CO/CO_2 methanation in PtG mode

Figure 15 Schematic flowTable for the global project, merging Cortus, KIC Innoenergy DemoSNG unit.

The methanation reactors are the honeycomb type, Figure 18 and 19. They show a small variability on the temperature profile at the external layer of the reactor, at about 260°C, while the temperature radially increases to the axis (Figures 16, 17, 19).

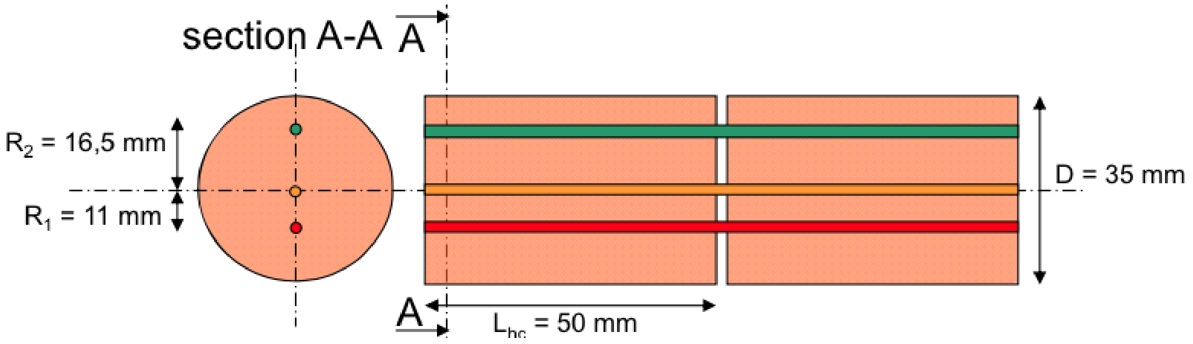


Figure 16 Methanation reactor's section (Buchholz, 2015).

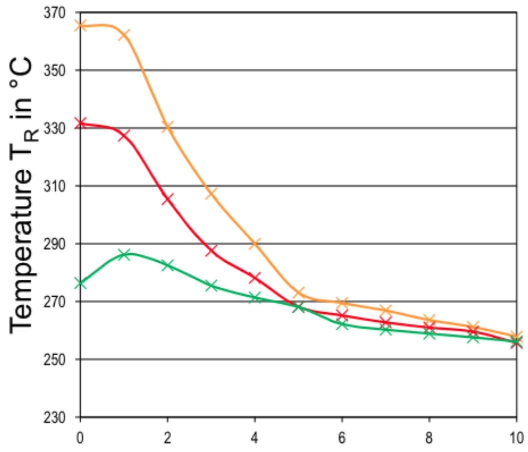


Figure 17 Methanation radial temperature profile. On the x axis, the length of the reactor, 10 corresponding to the full length. Yellow corresponds to the temperature profile on the central axis of the reactor, red corresponds to an axis which is 11 mm far from the center, green corresponds to an axis which is 16,5 mm far from the center (Buchholz, 2015).

The methanation reactions in the previous chapter show that these types of reactions are exothermic. With the purpose of estimating the waste heat availability from the methanation, only the global reaction will be considered:

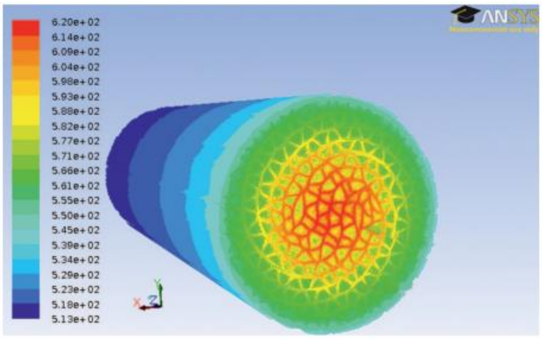
$$CO + 3\,H_2 \rightleftharpoons CH_4 + H_2O - 206\,\mathrm{kJ/mol} \qquad (14)$$

(Rostrup-Nielsen, 2011)

As displayed in the above equation (14), the optimal H_2/CO ratio for methanation is 3. However, the syngas produced from the WoodRoll® has a ratio equal to 2. Since the Water-Gas-Shift reaction does not change the volume flow, it is possible to calculate the volume flow at the outlet of the WoodRoll® system and obtain the waste heat from methanation using the same initial volume flow of syngas, disregarding the heat lost in the WGS reactor and the difference in volume composition.

Figure 18 Honeycomb methanation reactor (Buchholz, 2015).

Figure 18 and 19 show the structure of the honeycomb reactor, implemented by KIT, together with a Computational Fluid Dynamic analysis of the temperature profile.



Methanation in metallic honeycomb catalysts (Temperature T in K).

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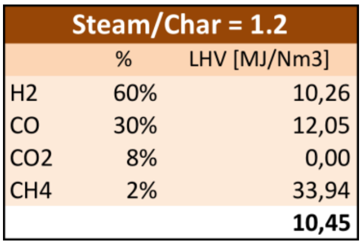
Figure 19 Computational simulation of temperature profile inside the honeycomb reactor (Buchholz, 2015)

By introducing the gas volume composition that is experimentally obtained adopting a ratio Steam/Biomass equal to 1.2 and by using the LHV of the pure gases (see Table 2), follows that:

$$LHV_{syngas} = \sum_{i} x_i \cdot LHV_i = 10{,}45\ MJ/Nm^3 \qquad (15)$$

Table 2 Syngas composition and LHV, for Steam/Char ratio equal to 1.2 and gasification temperature equal to 1100°C, calculated at Cortus



Steam/Char = 1.2		
	%	LHV [MJ/Nm3]
H2	60%	10,26
CO	30%	12,05
CO2	8%	0,00
CH4	2%	33,94
		10,45

The waste heat available from methanation can be found as:

$$\dot{Q} = \dot{V}_{tot} \cdot x_{CO} \cdot \Delta h = \left(\frac{\dot{E}\ [MW]}{10{,}45}\frac{Nm^3}{s}\right) \cdot 0{,}30 \cdot \left(-0{,}206\ \frac{MJ}{mol}\right) \cdot \left(\frac{1}{0{,}022414}\frac{mol}{Nm^3}\right) \tag{16}$$

$$= 0{,}2638 \cdot \dot{E}\ [MW]\ MW$$

Given a certain syngas flow, equation (16) says how much of the heating value contained in the syngas is lost in the methanation conversion step. In other words, how much less energy it is possible to extract from complete combustion of methane, compared to complete combustion of syngas before the conversion step.

In the current DemoSNG setup in Köping, the heat is extracted as a thermal oil flow at 250°C, which is then forced through an air cooler. In the commercial plant, the temperature will also be 250°C and the flow will be calculated in the Simulink model.

3.4. Calculation model tool

The section contains modelling of several alternatives for the process integration of WoodRoll® technology and the methanation unit. A heat and mass balance is implemented in order to obtain thermodynamic values (temperatures, pressures, mass flows, heat flows) and assess if the proposed design for the system is feasible or not, at least in theory.

The simulation is carried out in Matlab, making use of Simulink Thermolib toolbox. These tools have a clear graphic interface, which helps the user visualize all the flows and parameters in this highly integrated system. This library is designed to provide the user with the building blocks of the most frequent components that are found in a power plant, allowing agile modelling on a simple level. The very good aspect about this software is that it always allows looking inside the code and intervening on how calculations are performed. It is possible to produce an entirely user-defined block and also add chemical property databases.

There are several points of the system where it is important to specify thermodynamic values a priori. Hence, during the simulation, the software is set to meet several targets:

1. Temperature inside the drier should never be above 110°C. Higher temperatures would cause hazardous ignitions.
2. Temperature inside the gasifier needs to be at 1100°C to allow fast rates of reaction
3. The thermal balance always needs to be satisfied. Namely, the energy associated with the pyrolysis gas flow must always equal the sum of the heat requirement of the gasifier, pyrolysis and drier. The goal is to achieve a steady operative condition that does not require additional heat inputs from fossil sources.
4. The outlet chimney temperature should be not be lower than 130°C to avoid condensation of flue gases
5. The pressure drops are neglected over the entire system.

6. Only steady state conditions are considered, thermal inertias are neglected

In the following section, the modelling of the commercial arrangement is carried out. Then, out of all the alternatives presented in the last section, two cases will be presented.

Table 3 Summary for input and output variables in each block

Blocks	**Variable In**	**Variable Out**
Drier	• Wet BM mass flow • Humidity (inlet) • Humidity (outlet) • T drying • No pressure drops	• Heat load
Pyrolysis	• Dry BM mass flow • Heat loads from gasification, pyrolysis and drying • No pressure drops	• T pyrolysis
Char handling	• Char mass flow • Grinder specific energy consumption	• Grinding power load
Gasifier	• Steam mass flow • Char mass flow • T gasification	• Heat load from PG • Combustion air mass flow • FG mass flow
Steam production	• Syngas mass flow • T steam • p steam	• Steam mass flow
Electrical power consumption	• Mass flows • Fans electrical consumptions • Pumps electrical consumption • Screws electrical consumption	• Power consumption

3.5. Case I: WoodRoll®

3.5.1. Description Case I

Drier

The drier is a rotating drum that acquires heat from a flow of flue gases. This flow is circulating counter-wise on the external jacket of the drier, where a shell & tube configuration improves the heat exchange with the biomass. The amount of heat to be supplied equals to:

$$\dot{Q}^{in}_{Drier} = \dot{m}_{BM\,in} \cdot c_{p_{BM\,in}} \cdot \left(T_{evap} - T_{BM\,in}\right) + \dot{m}_{BM} \cdot \left(\frac{(1 - w_{BM\,in})}{(1 - w_{BM\,out})} \cdot w_{BM\,out}\right) \cdot \Delta h^{evap}_{water} \quad (17)$$

with $\dot{Q}^{in}_{Drier}$ heat to be supplied to the drier, $\dot{m}_{BM\,in}$ mass flow of biomass entering the reactor, T_{evap} evaporation temperature of water at atmospheric pressure, $T_{BM\,in}$ temperature of biomass as it enters the reactor, $w_{BM\,in}$ and $w_{BM\,out}$ moisture of biomass in and out the reactor, Δh^{evap}_{H2O} specific enthalpy for evaporation of water.

The TGA data regarding the biomass water content before and after the drying process are validated by a humidity scale device, measuring the weight loss of the sample over a period of time at 105°C, then yielding the moisture content of the sample.

The humidity is removed due to a warm airflow that circulates through the drier. Afterwards, the stream is cooled down and the condensate is separated from the air to avoid spilling possible contaminants present in the biomass to the environment.

$$\dot{Q}_{Drier\,cond} = \dot{m}_{humidity} \cdot (\Delta h^{evap}_{water} + c_{p\,water} \cdot (T_{evap} - T_{out})) \quad (18)$$

Where, $\dot{Q}_{Drier\,cond}$ is the heat required to condensate humidity from the drier, $\dot{m}_{humidity}$ is the evaporated mass of water, T_{evap} equals to 100°C and T_{out} is the outlet temperature of the condensate.

$$\dot{Q}_{Drier\,cond} = \dot{m}_{Cooling\,water} \cdot c_{p\,water} \cdot (T_{Water\,in} - T_{Water\,out}) \quad (19)$$

The cooling medium is water extracted from a natural source. The assumption is to take it out at 5°C and return it at 25°C. However, the environmental regulation on the return temperature of cooling water flows is region dependent and should be seen case by case.

The ventilation airflow is modelled on the software as *Wet air*, which allows simulating the psychometric behaviour of air.

Pyrolysis

The pyrolysis step is the milestone of the whole WoodRoll® process, as it produces the gaseous fuel that feeds every endothermic process in the system. The reactor is a rotary drum that receives heat from the flue gases stream. The flow takes place counter-wise on the external jacket surrounding the reactor. As the first dry biomass enters the reactor, the temperature increases up to about 400°C, at which thermal decomposition begins. Under the process conditions, biomass is mainly transformed into char with about 80% fixed carbon (depending on the feedstock in use) and a gaseous fuel with high percentage of condensable tars. The char coming out of the pyrolysis reactor brings along the whole ash present in the initial biomass.

The heat supplied to the pyrolysis reactor has the main purpose of warming up the biomass to the desired temperature, while the thermal decomposition has proved to be nearly adiabatic. However, this heat is calculated as:

$$\dot{Q}_{pyro}^{in} = \dot{m}_{dry\ BM} \cdot \left[\Delta h_{BM}^{pyro} + c_{p_{BM\ in}} \cdot \left(T_{pyro} - T_{dry\ BM\ in}\right)\right] \qquad (20)$$

With $\dot{Q}_{pyro}^{in}$ thermal power required by pyrolysis process, Δh_{BM}^{pyro} overall enthalpy of reaction, $c_{p_{BM\ in}}$ heat capacity of biomass at the inlet of the reactor, T_{pyro} temperature of pyrolysis process and $T_{dry\ BM\ in}$ temperature of biomass after drying process.

The thermal decomposition of biomass is considered to be adiabatic, hence $\Delta h_{BM}^{pyro} = 0$. Basically, there is no additional heat to be supplied to the reactor apart from the sensible heat that is necessary to increase the temperature of dry biomass. Given the complexity of the phenomenon of the biomass thermal decomposition, chemical reactions are not computed in this model, as biomass is always a very heterogeneous fuel. It is instead preferable to take a sample of the fuel, run a TGA analysis under the same operative condition of the real process and use the Gas Chromatography to obtain concentrations of all species; thanks to the TGA, it is also possible to gain knowledge on the melting point of the tars, thermal capacity of the gas. The bomb calorimeter test determines the LHV of the fuel. Here is the behaviour of LHV of pyrolysis gas with variations on the pyrolysis operative temperature:

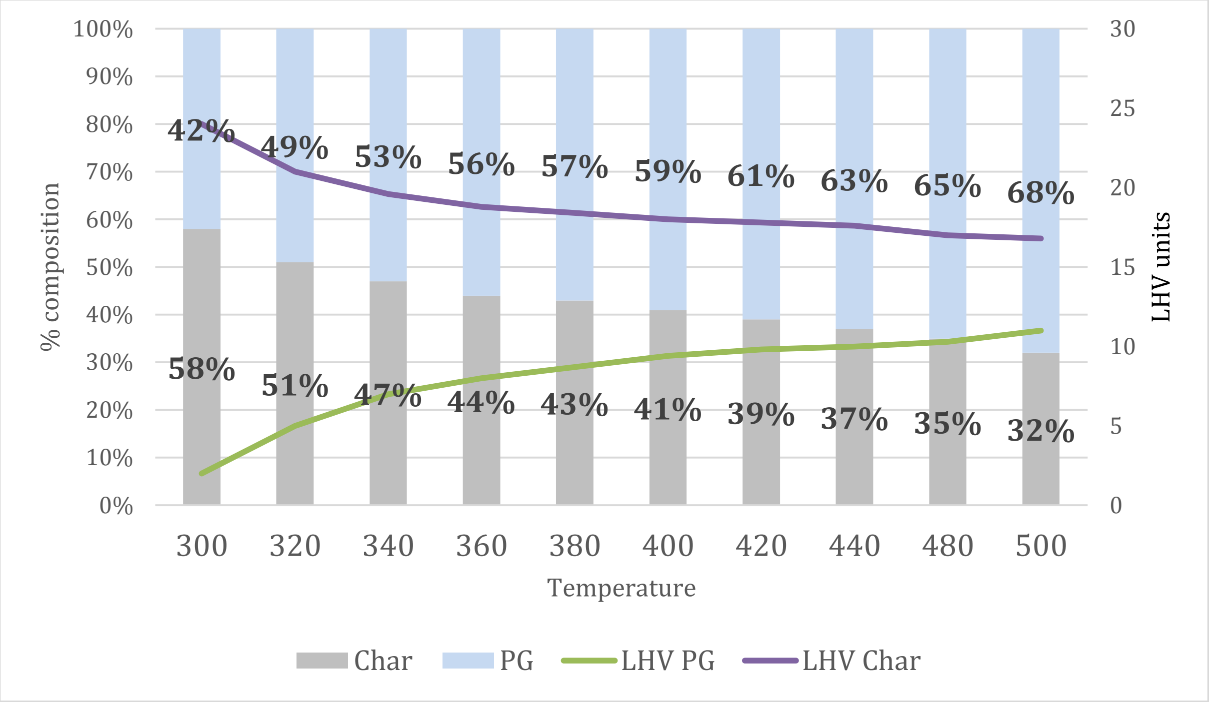


Figure 20 Curve describing the pyrolysis process. Lower pyrolysis temperature yields more char, with higher heating value and less PG with lower heating value.

Figure 20 shows how the pyrolysis process occurs in a wide range of temperature. Depending on the reaction temperature, a certain amount of volatile matter is evaporated as PG, leaving the remaining mass in the form of char. Assuming that the residence time in the reactor is the same in every case, the trend for the pyrolysis process is that of increasing the yield of char as the pyrolysis temperature decreases. The energy content of char is higher at lower temperature, while PG formed at low temperature is less energetic than PG produced in high-temperature pyrolysis. Obviously, the sum of the heating value of pyrolysis gas and char produced equals the heating value in the incoming biomass, in accordance with mass and energy conservation laws. The pyrolysis gas contains a high percentage of condensable tars, which are modelled as benzene molecules. Hence,

$$LHV_{PG} = \sum x \cdot LHV_i \tag{21}$$

the LHV of the char is calculated from the elemental analysis, through the formula (Coalspot.com, 2015):

$$LHV_{Char} = 337 \cdot C + 1442 \cdot \left(H - \frac{O}{8}\right) + 93 \cdot S \tag{22}$$

where C, H, O and S are percentages from the dry ash free char and [MJ/kg] are dimensional units of LHV_{Char}.

Afterwards, the validation of the calculations carried out above is done through the energy balance:

$$LHV_{Char} = \frac{m_{test\ BM} \cdot LHV_{BM} - m_{PG} \cdot LHV_{PG}}{m_{Char}} \tag{23}$$

The heat capacity of char is assumed to be 1.24 kJ/kgK, independent of temperature.

Char handling

After char is removed from the pyrolysis reactor, an externally cooled screw brings down the temperature to 30 °C to minimize risks for ignition. In addition, nitrogen is always purged into the transportation screws for solid materials, as char would easily ignite under oxidative atmosphere.

The flow is then conveyed to a grinder that reduces its size to ease the reaction rates in the gasifier. This step is not included in the thermodynamic model; only its power consumption will be considered in the final evaluation of the scenario. In fact, this is the highest electrical-energy-intensive process in the system.

Parameters: Grinding specific energy consumption - 260 kJ/kg_{Char}

Gasifier

In the gasifier, finely grinded char and steam are injected together in the gasifier of Cortus' own design. The temperature in the reactor is kept at 1100°C through combustion of the pyrolysis gas formerly produced in irradiative burners. The ashes separate in the fast-rate gasification and fall down to the cyclone. The operation is always over-stoichiometric to avoid the deposition of unreacted char, which represents an unnecessary energy loss. The temperature in the gasification reactor is a rigid parameter. The mass and energy balance for this block is:

$$\dot{m}_{Char} + \dot{m}_{Steam} = \dot{m}_{Syngas} \tag{24}$$

$$\begin{aligned}\dot{Q}_{PG} = \dot{m}_{Char} \cdot c_p(T) \cdot (T_{React} - T_{in}) + \dot{m}_{Steam} \cdot (\mathrm{h}_{React}^{1\ bar} - h_{165°C}^{7\ bar}) \\ - \dot{m}_{Syngas} \cdot c_p(T) \cdot (T_{React} - T_{out}) + \dot{m}_{Char} \cdot \Delta h_{Gasif\ React}\end{aligned} \tag{25}$$

Where $\dot{m}_{Syngas} = \sum_i \dot{m}_i \cdot y_i$, with i being gas in the syngas and y_i mass percentage for each gas; $\Delta h_{Gasif\ React}^{T_{React}}$ is the enthalpy of reaction of carbon gasification with water at the reaction temperature, 1100°C.

Steam production

Syngas comes out of the cyclone at around 700°C. The flow is cooled down to 30°C in a shell&tube boiler, where saturated steam at 7 barg is continuously produced to feed the gasifier, from water pumped from atmospheric to 7 bar pressure. Hence, the condensate is removed from the flow. The water consumed in the process is taken form the municipal pipes: therefore, it needs to be purified from all the minerals. The heat exchanger has a counter-flow arrangement, modelled on Thermolib by a predefined component. The model does not account for pressure losses in the tubes.

UA global between two fluids	1000 W/K

External temperature	5°C
UA to environment	200 W/K

Electrical power consumption

The plant consumes electrical power mainly in the grinder, gas fans for recirculation of flue gases and heating cables for temperature control of areas where condensation of hydrocarbons needs to be avoided. The fans in the system are connected to variable speed engines, accounting for a total power consumption of 221 Power units (PU). The heating cables are extensively used in the start-up phase of the plant, but the steady state operation is entirely self-sustaining. Therefore their contribution is not considered in the total energy balance.

3.5.2. Result Case I

The flow Table below presents the solution to the optimized system. To better protect the internal knowledge of the company with regards to the heat and mass balance, power and mass flow data have been multiplied by two different constants.

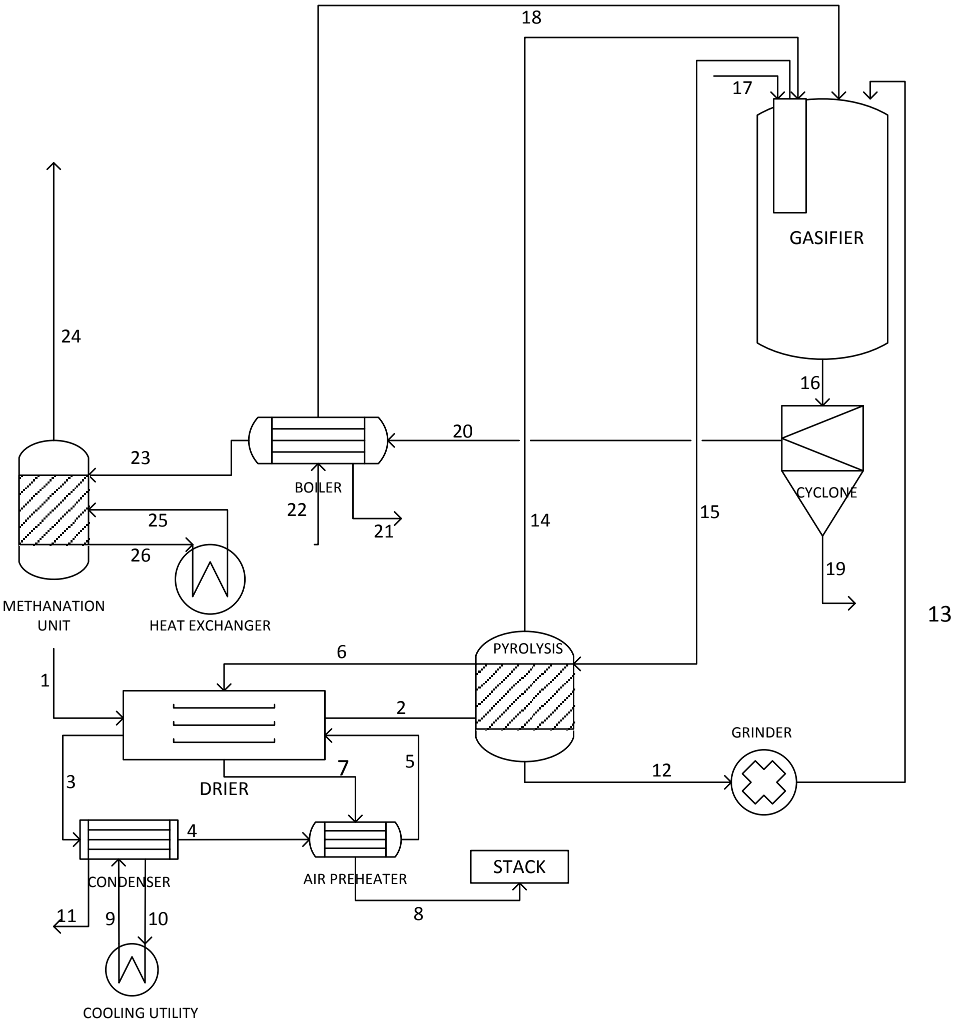


Figure 21 Standard WoodRoll® scheme connected to methanation unit, without recovery of the waste heat

Table 4 FlowTable for Case I: WoodRoll®

Flow N.	Description	Compounds	T	p	Mass flow
			°C		Units
1	Wet biomass	-	5	Atm	231
2	Dry biomass	-	100	Atm	170
3	Humid ventilation air	N2, O2	130	Atm	210
4	Ventilation air	N2, O2	40	Atm	149
5	Ventilation air	N2, O2	110	Atm	149
6	Flue gases	N2, CO2, H2O, O2	400	Atm	908
7	Flue gases	N2, CO2, H2O, O2	150	Atm	908
8	Flue gases	N2, CO2, H2O, O2	139	Atm	908
9	Cooling water	H2O	5	Atm	937
10	Cooling water	H2O	25	Atm	937
11	Condensate	H2O + pollutants	40	Atm	60
12	Char	Mainly C, also O and H	400	Atm	70
13	Char	Mainly C, also O and H	400	Atm	70
14	Pyrolysis gas	H2, CO, CO2, CH4, H2O,Tars	400	Atm	101
15	Flue gases	N2, CO2, H2O, O2	550	Atm	908
16	Wet syngas	H2, CO, CO2, CH4, H2O	700	Atm	163
17	Combustion air	N2, O2	5	Atm	369
18	Steam	H2O	165	2 bar	97
19	Ashes	-	400	Atm	3
20	Wet syngas	H2, CO, CO2, CH4, H2O	700	Atm	167
21	Condensate	H2O + pollutants	30	Atm	28
22	Process water	H2O	5	2 bar	31
23	Dry syngas	H2, CO, CO2, CH4	30	Atm	136
24	Methane	CH4	14	Atm	56
25	Thermal oil	-	82	Atm	578
26	Thermal oil	-	235	Atm	578

The temperature in the pyrolysis reactor is 400°C. Of the dry biomass, 40,93% is converted into char and 59,06% in pyrolysis gas, accounting for, respectively, 63.51% and 36.49% of the energy yield. The fuel conversion efficiency is calculated as:

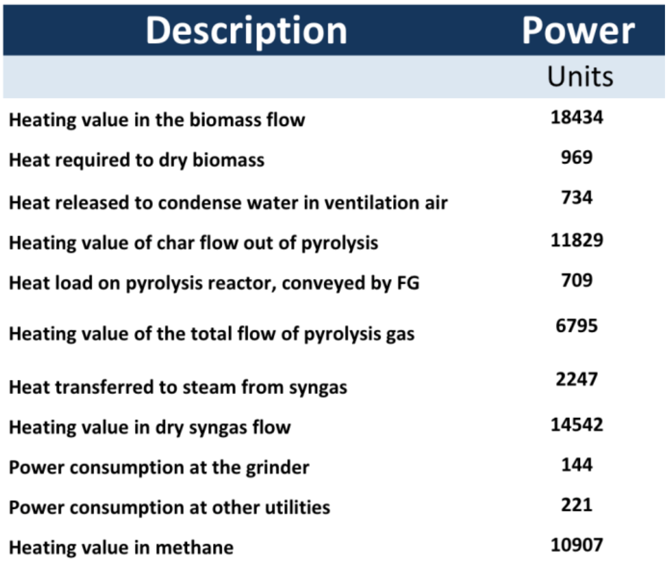
$$\eta_{BM\ to\ Syn} = \frac{\dot{E}_{Output\ fuel}}{\sum \dot{E}_{Inputs}} = \frac{\dot{m}_{Syngas} \cdot LHV_{Syngas}}{\dot{m}_{Dry\ BM} \cdot LHV_{Dry\ BM} + P_{El\ engines}} = \frac{14542}{18434 + 365} = 77{,}4\% \tag{26}$$

The simulation converged to the solution, which means that the energy from biomass is sufficient to the self-sustainment of the system with no need for further input of fossil fuels.

$$\eta_{BM\ to\ CH4} = \frac{\dot{E}_{Output\ fuel}}{\sum \dot{E}_{Inputs}} = \frac{\dot{m}_{Methane} \cdot LHV_{Methane}}{\dot{m}_{Dry\ BM} \cdot LHV_{Dry\ BM} + P_{El\ engines} + \dot{E}_{Steam\ WGS}} = \frac{10907}{18434 + 365 + 1257} = 54{,}4\% \tag{27}$$

Results concerning the energy flows in the system are reported in Table 5. The power values associated to a flow of combustible material such as BM, char or PG, are always meant as chemical energy (referred to as $\dot{E}$), that is the energy that could be released after complete combustion and cooling of product gases to 150°C. $\dot{Q}$ values are, instead, heat loads transferred between two different flows; while electrical power is referred to as P.

Table 5 Power Table for Case I: WoodRoll®



Description	Power
	Units
Heating value in the biomass flow	18434
Heat required to dry biomass	969
Heat released to condense water in ventilation air	734
Heating value of char flow out of pyrolysis	11829
Heat load on pyrolysis reactor, conveyed by FG	709
Heating value of the total flow of pyrolysis gas	6795
Heat transferred to steam from syngas	2247
Heating value in dry syngas flow	14542
Power consumption at the grinder	144
Power consumption at other utilities	221
Heating value in methane	10907

The water consumption of the process is 97 Mass Units, while 70 Mass Units are collected as condensate, which needs to be disposed of in a regulated fashion. With regards to the cooling, the plant has to take in 537 Mass Units of water, which is returned to the natural water source at 25°C. Alternatively, there can be a cooling evaporating tower or an air fan cooler, which can however decrease the total efficiency of the plant. In fact, based on the experience of the equipment used in the test plant, we can consider that:

$$\frac{\dot{Q}_{Removed}}{P_{El\ cooler}} = 29{,}16\ P.U._{th}/P.U._{El} \tag{28}$$

This implies that, in order to cool 734 P.U.:

$$P_{El\ cooler} = 734/29{,}16 = 25{,}17\ P.U. \tag{29}$$

In this case, the total efficiency decreases to:

$$\eta_{BM\ to\ Syn} = \frac{\dot{E}_{Output\ fuel}}{\sum \dot{E}_{Inputs}} = \frac{\dot{m}_{Syngas} \cdot LHV_{Syngas}}{\dot{m}_{Dry\ BM} \cdot LHV_{Dry\ BM} + (P_{El\ engines} + P_{El\ cooler})} \tag{30}$$

$$= \frac{14542}{18434 + 365\ +\ 25{,}17} = 77{,}25\%$$

The electrically driven air fan cooler might be an option. For a large commercial system, however, it is preferable to adopt water-cooling from a natural stream or an evaporative cooling tower. This component removes the heat by sprinkling a small stream of water over the bundle of tubes coming out of the condenser in a closed loop. The water is heated up touching the surface of the tubes and partially evaporates to the air. An airflow is established by natural convection thanks to the difference in temperature and height of the tower. This solution can be feasible for a large commercial plant, but not for low capacities, as they require large size to work properly, they are costly and they require pumps.

The result of the simulation is in good agreement with the calculation model carried out inside the company on Microsoft Excel Visual Basic. The values have been compared and deviations have been calculated between the outcomes as:

$$\varepsilon_{Rel} = \left|\frac{x_{Simulink} - x_{VBA}}{x_{VBA}}\right| \tag{31}$$

Where ε_{Rel} is the relative mismatch between the Simulink model and the Visual Basic model, and $x_{Simulink}$ and x_{VBA} are the values of a certain parameter resulting from, respectively, the Simuling and the VBA model. From the comparison, $\varepsilon_{Rel_{Max}} = 6{,}24\%$ relatively to the heat released to condensate the water in the ventilation air. The reason for this gap could be found in Simulink's ability to compute c_p heat capacity coefficients for all the gases as a function of temperatures; while in the VBA simulation, they are averaged over the temperature gap of interest for a certain heat exchanger. However, the reason of this mismatch requires further investigation.

This fact only proves that the Simulink Model is in very good agreement with the VBA model, but it does not say that the results of any of them are valid. In fact, the confirmation of the validity of these models can only come from the measurements of thermodynamic values of the real plant.

4. Process integration alternatives: Results and discussion

After the comparison of the base case WoodRoll® model and the estimation of how much heat it is possible to extract from the methanation exothermic process, it follows a list of ideas for the integration of the two processes:

a. One possibility is to supply the heat to the drier system and preheating of combustion air of pyrolysis gas. In this case, there would be no need for producing the pyrolysis gas that can be saved. Therefore, pyrolysis operative temperature can be modulated in order to achieve a different char/PG ratio, which leads to higher char yield. This alternative aims at produce the smallest possible changes on the present configuration.

b. The methanation reactors can be cooled by producing steam for district heating at 120°C and be fed into the city grid. The temperature level of methanation waste heat has a high grade when it comes to district heating application since it is high enough to cope with the higher loads of the winter season. This configuration could supply about 75% of the power in the form of methane into the national gas grid and 25% as heat to households.

c. One of the biggest limitations of the biomass conversion processes is the fuel quality. In Sweden there is abundance of fibre sludge coming from pulp mills, where it represents a waste to be disposed of. It is then possible to get paid for withdrawing this feedstock, drying it with the excess waste heat from methanation and then feeding it to the WoodRoll® system. This type of waste is not very appealing as a solid fuel since it can have up to 70% moisture content and it requires too much heat to dry up the whole biomass down to 5% moisture content. However, the negative cost of the fuel would compensate for the inefficiency introduced by a more moist fuel. In case the feedstock is still too wet for the process, it can be mixed with recycled wood residues in order to make it processable.

d. District cooling: absorption refrigerators can make use of the heat from methanation to cool water that will be distributed to households, restaurants, hotels and hospitals, providing stable cooling capacity.

e. Alternatively, there could be combined production of electricity and methane. A heat exchanger where the waste heat conveyed from the methanation process at 250°C, together with a boiler fed on PG could bring a water flow to superheated steam conditions at 350°C and 40 bar. Then, a steam flow can be stripped at 7 bar and be introduced into the gasifier to produce new syngas. The rest of the flow is expanded through a steam turbine to produce electricity.

The strength of the paper industry in Sweden suggests that the integration outlined in case **c** could open the doors to a number of business possibilities for Cortus. Installations of isolated grid systems are becoming more and more frequent, especially in developing countries where waste biomass is often an abundant and scarcely valued resource. It seems reasonable to develop an integrated design able to deliver methane and electricity supply on 100% renewable, locally based feedstock: case **e** is also explored in detail.

4.1 Case II: Electricity and methane

4.1.1 Description Case II

The flows have been rearranged from the original system, as shown in the flow diagram below. Recirculation fans and pumps for cooling loops have been omitted from the drawing to simplify it.

The choice of the pressure in the steam cycle is aimed at establishing an efficient heat exchange between the methanation reactors and the steam cycle. In fact, the heat exchange takes place at constant $\Delta T = 10\,°C$, between 260°C at which the heat is available, and 250°C, saturation temperature of the steam at 40 bar. The superheating phase of the cycle receives heat from a burner fed on pyrolysis gas. Then, the steam expands into a steam turbine with 60% isentropic efficiency. A flow of superheated steam at 7 bar is extracted and fed to the gasifier. The remaining steam expands to 7385 Pa (saturation pressure for 40°C) and is cooled in a heat exchanger with cool water from a natural source. A feedwater stream is added to the condensed steam and the flow is pumped to 40 bar. Then, it enters another heat exchanger, where it is warmed up from 40°C to 250°C through the heat released by the flue gases.

The remaining part of the pyrolysis gas is burnt into the irradiative burners of the gasifier. The flue gases coming from the burner on the gasifier are added to the superheating steam boiler.

Part of the flue gases collected after pyrolysis gas combustion in the boiler are conveyed to a mixing chamber, regulating the inlet temperature of the flue gases entering the external jacket of the pyrolysis reactor and warming up biomass to the optimal pyrolysis temperature. This parameter is target of the improvement, as it will determine in which proportion the heating value of the biomass will be divided between the char flow and the pyrolysis gas flow.

The syngas produced in the gasifier, leaving the cyclone, undergoes separation of smaller ashes and particulate in the filter and cools down into the drier passing through the tubes inside the rotary drum, where the steam that has condensed is separated.

4.1.2. Results Case II

This arrangement aims at converting biomass into both methane and electricity. The flow sheet is displayed below, together with the thermodynamic values resulting from the Simulink model.

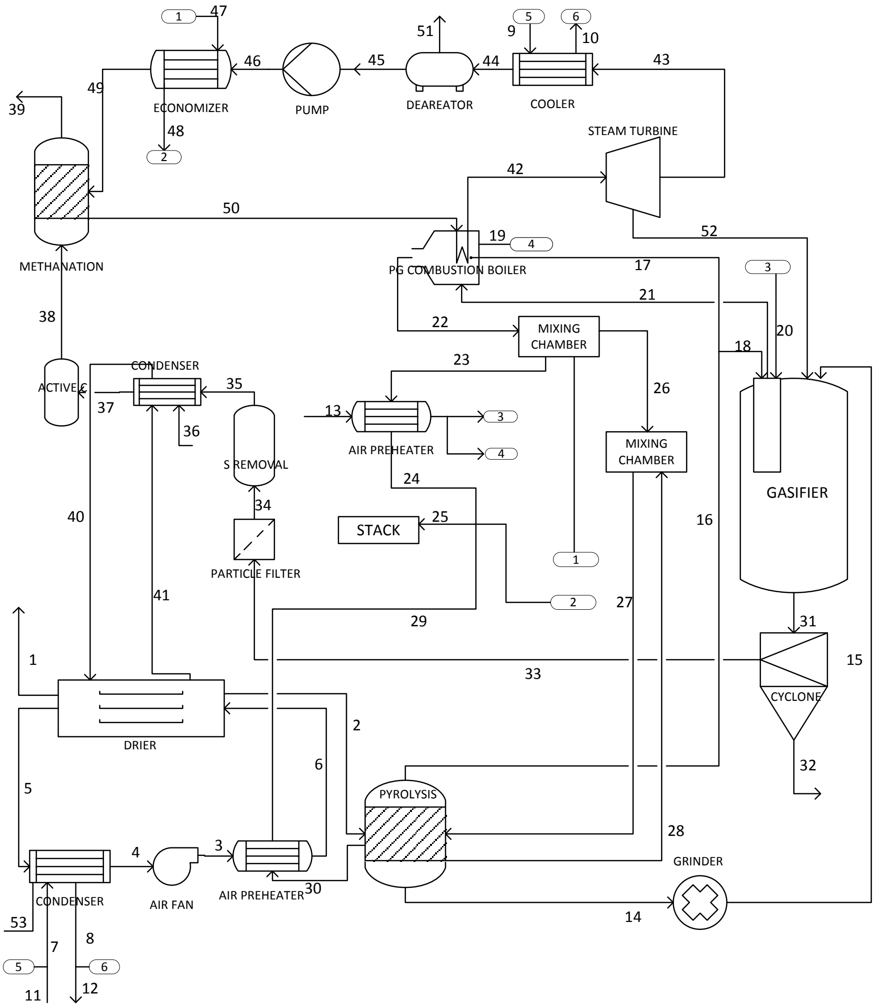
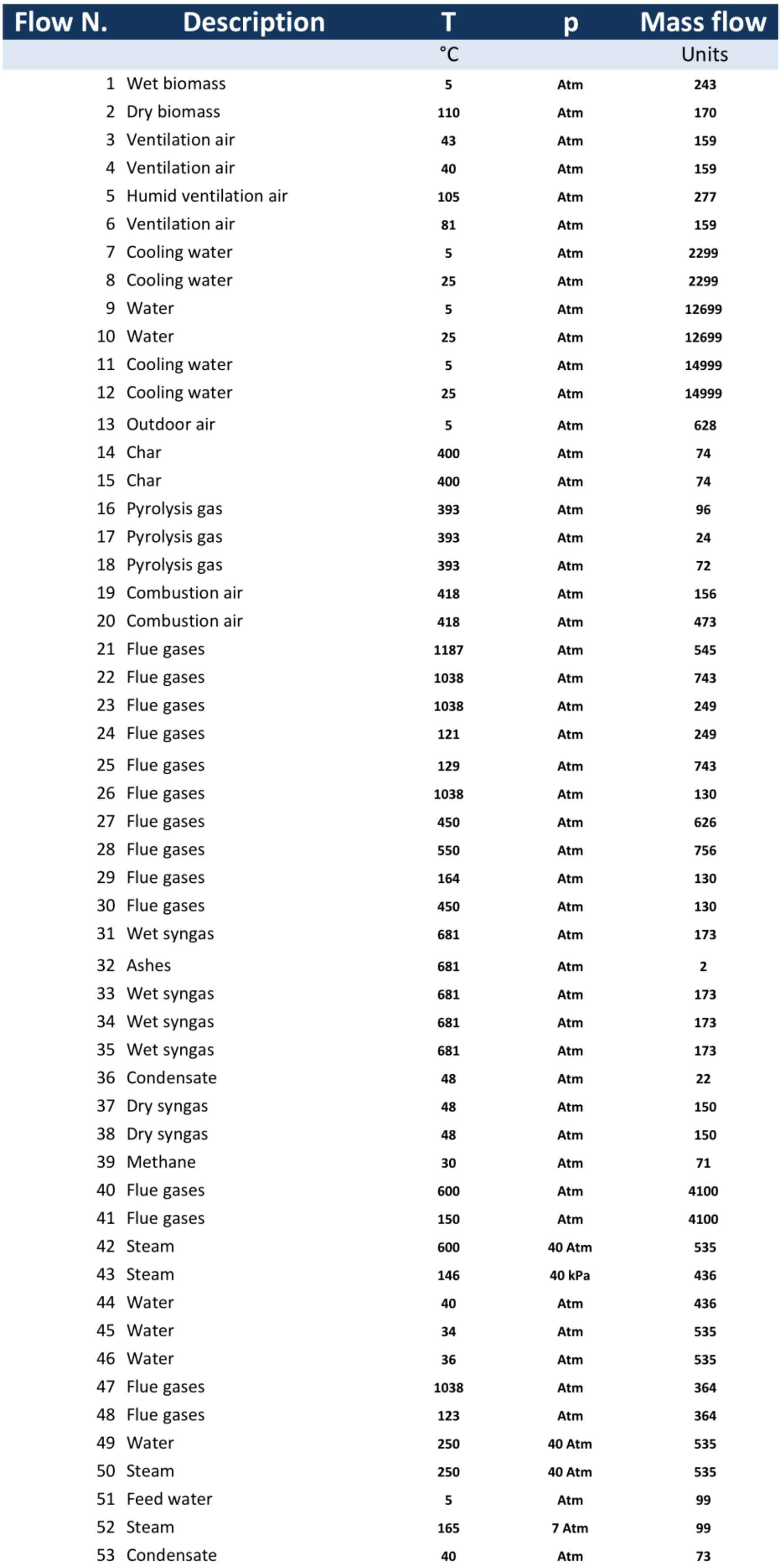


Figure 22 Flow diagram for the integration of WoodRoll® with methanation unit and steam cycle

Table 6 FlowTable for the integration of WoodRoll®, methanation unit and steam cycle



Flow N.	Description	T	p	Mass flow
		°C		Units
1	Wet biomass	5	Atm	243
2	Dry biomass	110	Atm	170
3	Ventilation air	43	Atm	159
4	Ventilation air	40	Atm	159
5	Humid ventilation air	105	Atm	277
6	Ventilation air	81	Atm	159
7	Cooling water	5	Atm	2299
8	Cooling water	25	Atm	2299
9	Water	5	Atm	12699
10	Water	25	Atm	12699
11	Cooling water	5	Atm	14999
12	Cooling water	25	Atm	14999
13	Outdoor air	5	Atm	628
14	Char	400	Atm	74
15	Char	400	Atm	74
16	Pyrolysis gas	393	Atm	96
17	Pyrolysis gas	393	Atm	24
18	Pyrolysis gas	393	Atm	72
19	Combustion air	418	Atm	156
20	Combustion air	418	Atm	473
21	Flue gases	1187	Atm	545
22	Flue gases	1038	Atm	743
23	Flue gases	1038	Atm	249
24	Flue gases	121	Atm	249
25	Flue gases	129	Atm	743
26	Flue gases	1038	Atm	130
27	Flue gases	450	Atm	626
28	Flue gases	550	Atm	756
29	Flue gases	164	Atm	130
30	Flue gases	450	Atm	130
31	Wet syngas	681	Atm	173
32	Ashes	681	Atm	2
33	Wet syngas	681	Atm	173
34	Wet syngas	681	Atm	173
35	Wet syngas	681	Atm	173
36	Condensate	48	Atm	22
37	Dry syngas	48	Atm	150
38	Dry syngas	48	Atm	150
39	Methane	30	Atm	71
40	Flue gases	600	Atm	4100
41	Flue gases	150	Atm	4100
42	Steam	600	40 Atm	535
43	Steam	146	40 kPa	436
44	Water	40	Atm	436
45	Water	34	Atm	535
46	Water	36	Atm	535
47	Flue gases	1038	Atm	364
48	Flue gases	123	Atm	364
49	Water	250	40 Atm	535
50	Steam	250	40 Atm	535
51	Feed water	5	Atm	99
52	Steam	165	7 Atm	99
53	Condensate	40	Atm	73

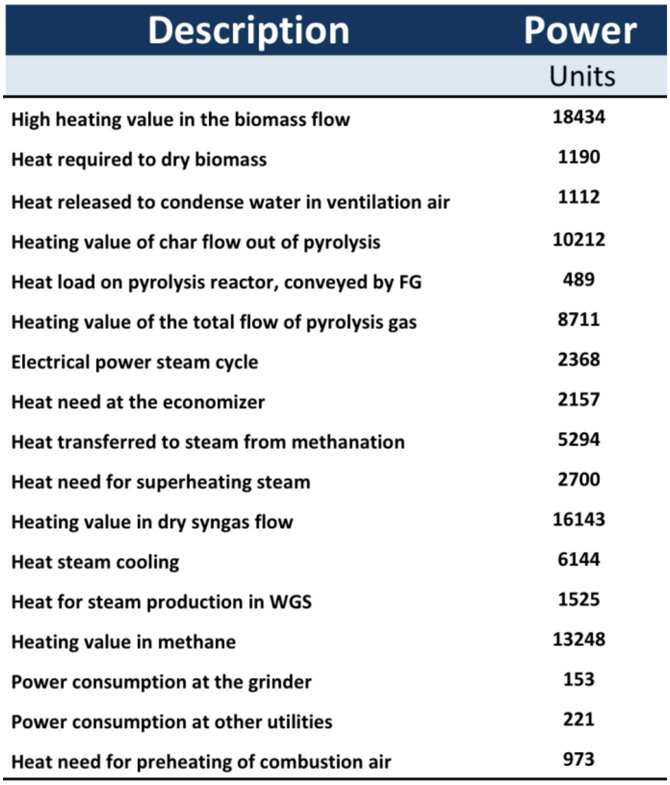
The performance of this setting is evaluated as:

$$\eta_{BM\ to\ Syn} = \frac{\dot{E}_{Output\ fuel}}{\sum \dot{E}_{Inputs}} = \frac{\dot{m}_{Syngas} \cdot LHV_{Syngas}}{\dot{m}_{Dry\ BM} \cdot LHV_{Dry\ BM} + P_{El\ engines}} = 86{,}0\% \tag{32}$$

$$\eta_{BM\ to\ CH4} = \frac{\dot{E}_{Methane}}{\dot{E}_{BM} + P_{El\ engines} + \dot{E}_{Steam\ WGS}} = 65{,}2\% \tag{33}$$

Where $\dot{E}_{Steam\ WGS}$ is the electrical power supplied by the renewable sources connected to the integrated system, producing steam for WGS reactor.

Table 7 Power Table for integration of WoodRoll®, methanation unit and steam cycle



Description	Power
	Units
High heating value in the biomass flow	18434
Heat required to dry biomass	1190
Heat released to condense water in ventilation air	1112
Heating value of char flow out of pyrolysis	10212
Heat load on pyrolysis reactor, conveyed by FG	489
Heating value of the total flow of pyrolysis gas	8711
Electrical power steam cycle	2368
Heat need at the economizer	2157
Heat transferred to steam from methanation	5294
Heat need for superheating steam	2700
Heating value in dry syngas flow	16143
Heat steam cooling	6144
Heat for steam production in WGS	1525
Heating value in methane	13248
Power consumption at the grinder	153
Power consumption at other utilities	221
Heat need for preheating of combustion air	973

The steam cycle takes heat inputs from the methanation reactor, as for the evaporative phase, from the flue gases, as for the preheating of process water and from the combustion of part of pyrolysis gas for the superheating of steam. The electrical efficiency of the steam cycle can be calculated as:

$$\eta_{El} = \frac{P_{El}}{\dot{Q}_{Eco} + \dot{Q}_{Methanation} + \dot{Q}_{Superheating}} = 23{,}3\% \tag{34}$$

Where, $\dot{Q}_{Eco}$ is the heat supplied to the economizer, $\dot{Q}_{Methanation}$ the waste heat from the methanation reactor supplied for the evaporation of water in the steam cycle and $\dot{Q}_{Superheating}$ is the heat required by the steam to reach 600°C at 40 atm, which is supplied by the PG burner.

Then, the electrical efficiency considering the entire biomass energy input is:

$$\eta_{BM\ to\ El} = \frac{P_{El}}{\dot{E}_{BM}} = 12{,}8\% \tag{35}$$

As said above, this configuration is designed to be applied to isolated system that have no connection to gas and energy grid. Therefore, its value lies on the possibility of providing both electricity and methane in the same supply point, using the same feedstock. However, both electricity and methane are produced online, with no intermediate storage buffer. In the occurrence of a programmed stop of the plant for maintenance or technical failure, the supply is immediately interrupted. If this configuration were ever implemented, the storage question should be carefully addressed. A possible way to avoid power shortage would be installing a methane buffer and a backup diesel engine for methane combustion, connected to an electricity generator. This arrangement should only operate during occasional stops, hence it should be cheap and not necessarily very efficient.

4.2. Case III: Syngas production with wet fuel

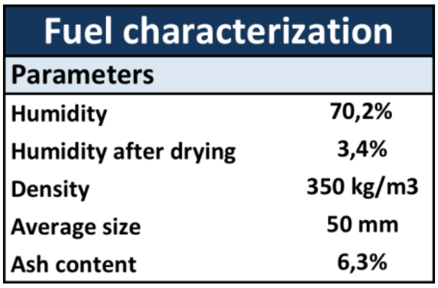
4.2.1. Description Case III

In the case of using 70,2% moist fibre sludge from paper mills, the heat from methanation can be recovered to the drier. The heat exchange is arranged with flue gases as heat carrier, because they ease the design of the drier. The pyrolysis gas produced is entirely burnt into the gasifier. Here the flow splits into a main stream, leading to a mixing chamber and a smaller flow, leading to a heat exchanger for preheating of combustion air. The purpose of the chamber is to provide a temperature control on the external jacket of the pyrolysis reactor. A recirculation flow is extracted by the outlet of the jacket and reintroduced to the mixing chamber to decrease the temperature of the incoming flow to the jacket, to 550°C. The target temperature for the outlet of the jacket is 400°C. After going through the jacket, this flow is flowing to a heat exchanger for preheating of water. The chimney temperature of the flue gases is set at 130°C to minimize the heat discharged to the atmosphere but also avoid condensation at the chimney. The wet syngas leaves the cyclone at 700°C and goes through the boiler to evaporate the steam for the gasification reactions. The gasification and pyrolysis reactor are modelled in the same way as in Case I.

Case III arrangement is designed to handle a very wet fuel in an efficient way. The elemental analysis in Table 9 shows 13,1 MJ/kg increase in heating value after drying. However, the sludge is richer in chloride, which can be cause for corrosion problems in steel pipes; to adopt feedstocks with Cl% > 0,025% for permanent operations, all stainless steel components in contact with the fuel should be modified to a corrosion-resistant steel alloy.

The only cooling utility in this setting is on the drier ventilation loop, where moisture is condensed. The cooling is arranged with a water flow from a natural source, assuming inlet temperature of water at 5°C and imposing an outlet temperature at 25°C.

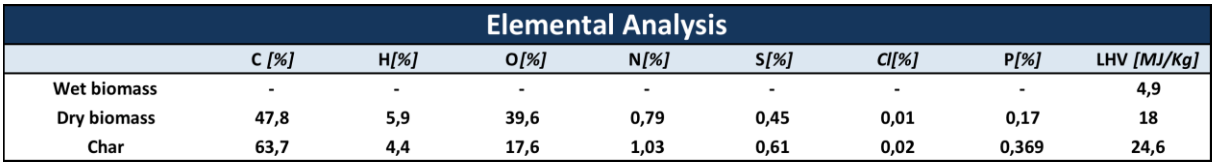
Table 8 Physical characteristics of fibre sludge from paper mills



Fuel characterization	
Parameters	
Humidity	70,2%
Humidity after drying	3,4%
Density	350 kg/m3
Average size	50 mm
Ash content	6,3%

Paper mill sludge was characterized on the base of its physical properties as humidity, density, average size as received and ash content.

Table 9 Elemental analysis of fibre sludge from paper mills



Elemental Analysis

	C *[%]*	H*[%]*	O*[%]*	N*[%]*	S*[%]*	Cl*[%]*	P*[%]*	LHV *[MJ/Kg]*
Wet biomass	-	-	-	-	-	-	-	4,9
Dry biomass	47,8	5,9	39,6	0,79	0,45	0,01	0,17	18
Char	63,7	4,4	17,6	1,03	0,61	0,02	0,369	24,6

The elemental analysis at different steps of the conversion shows an increase in concentration for the C, N, S, Cl and P content, once dried biomass is converted into char; the heating value is higher due to lower O content and higher C content.

4.2.2. Results Case III

Here follows a P&ID of the modelled integrated system; all mass flows and energy flows are shown in the Table 10 and 11 below.

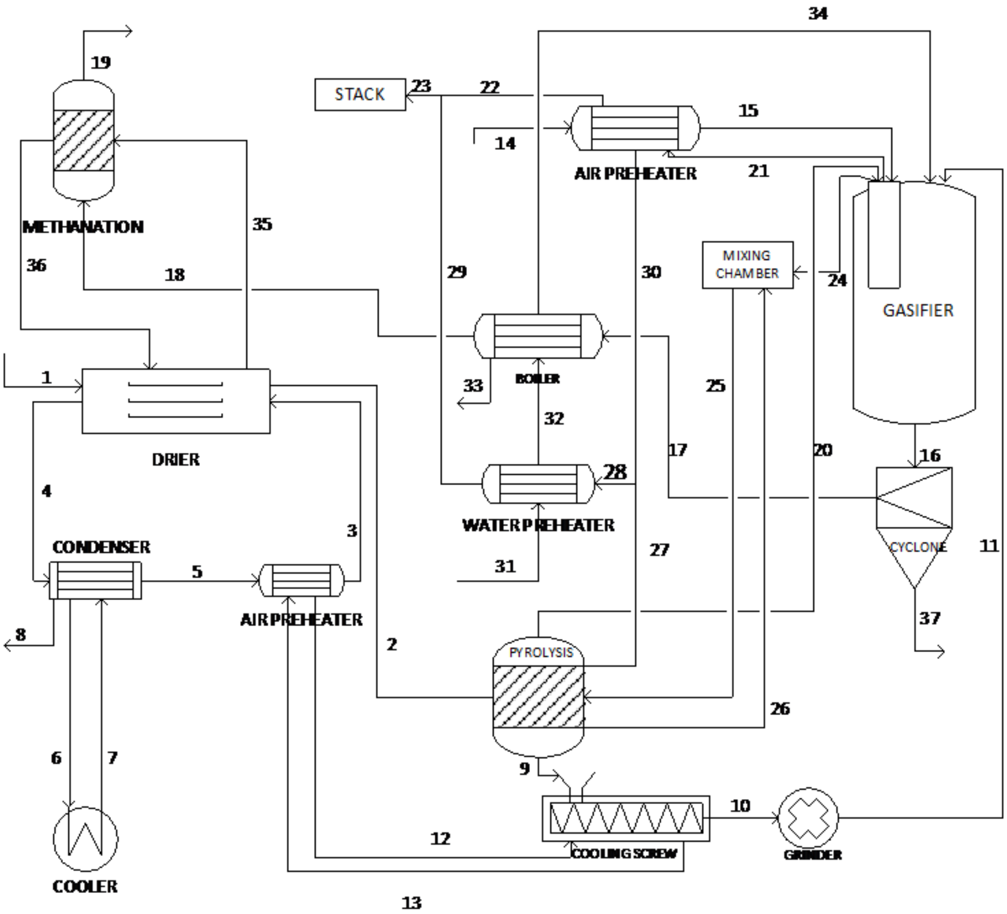


Figure 23 Flow diagram for integration of the WoodRoll® with methanation unit, with 70% moist feedstock

The model was tested with the same dry biomass input as for Case I and II. As the water in the biomass increases, the system tends to produce less pyrolysis gas and more char. In fact, in order to supply as much heat as it is required at the drier, the syngas flow has to increase: the wet syngas mass flow is directly proportional to the char mass flow. The fuel conversion efficiency is calculated as:

$$\eta_{BM\ to\ Syn} = \frac{\dot{E}_{Syngas}}{\dot{E}_{BM} + P_{El}} = 93{,}2\% \qquad (36)$$

$$\eta_{BM\ to\ CH4} = \frac{\dot{E}_{Methane}}{\dot{E}_{BM} + P_{El} + \dot{E}_{Steam\ WGS}} = 66{,}0\% \qquad (37)$$

Table 10 Flow Table for integration of the WoodRoll® with methanation unit, with 70% moist feedstock

Flow N.	Description	Compounds	T	p	Mass flow
			°C		Units
1	Wet biomass into drier	-	5	Atm	567
2	Dry biomass after drier	-	100	Atm	170
3	Dry ventilation air	N2, O2	130	Atm	209
4	Humid ventilation air	N2, O2, H2O	110	Atm	606
5	Dry ventilation air	N2, O2	40	Atm	209
6	Cooling water	H2O	5	Atm	10854
7	Cooling water	H2O	25	Atm	10854
8	Condensate	H2O + pollutants	40	Atm	397
9	Char	Mainly C, also O and H	400	Atm	80
10	Char	Mainly C, also O and H	30	Atm	80
11	Char	Mainly C, also O and H	30	Atm	80
12	Thermal oil	-	360	Atm	56
13	Thermal oil	-	35	Atm	56
14	Air	N2, O2	5	Atm	578
15	Air	N2, O2	610	Atm	578
16	Wet syngas	H2, CO, CO2, CH4, H2O	700	Atm	187
17	Wet syngas	H2, CO, CO2, CH4, H2O	700	Atm	187
18	Dry syngas	H2, CO, CO2, CH4	49	Atm	163
19	Methane	CH4	30	Atm	77
20	Pyrolysis gas	H2, CO, CO2, CH4, H2O,Tars	341	Atm	90
21	Flue gases	N2, CO2, H2O, O2	764	Atm	542
22	Flue gases	N2, CO2, H2O, O2	130	Atm	416
23	Flue gases	N2, CO2, H2O, O2	130	Atm	772
24	Flue gases	N2, CO2, H2O, O2	764	Atm	126
25	Flue gases to pyrolysis	N2, CO2, H2O, O2	400	Atm	733
26	Flue gases back from pyrolysis	N2, CO2, H2O, O2	550	Atm	607
27	Flue gases	N2, CO2, H2O, O2	400	Atm	232
28	Flue gases	N2, CO2, H2O, O2	450	Atm	358
29	Flue gases	N2, CO2, H2O, O2	130	Atm	358
30	Flue gases to water preheater	N2, CO2, H2O, O2	450	Atm	126
31	Water	H2O	5	7 bar	107
32	Water	H2O	165	7 bar	107
33	Condensate	H2O + pollutants	49	Atm	24
34	Steam	H2O	165	7 bar	107
35	Flue gases	N2, CO2, H2O, O2	120	-	6358
36	Flue gases	N2, CO2, H2O, O2	250	-	6358
37	Ashes	-	500	Atm	2

Table 11 Power Table for integration of the WoodRoll® with methanation unit, with 70% moist feedstock

Description	Power
	Units
High heating value in the biomass flow	18434
Heat required to dry biomass, from methanation	5738
Heat released to condense water in ventilation air	5252
Heating value of char flow out of pyrolysis	6065
Heat load on pyrolysis reactor, conveyed by FG	474
Heating value of the total flow of pyrolysis gas	12369
Heat removed from char	141
Heat need at the water preheater	533
Heat transferred to steam from syngas	1832
Heating value in dry syngas flow	17454
Heat for steam production in WGS	1104
Heating value in methane	13091
Power consumption at the grinder	165
Power consumption at other utilities	221
Heat need for preheating of combustion air	2018

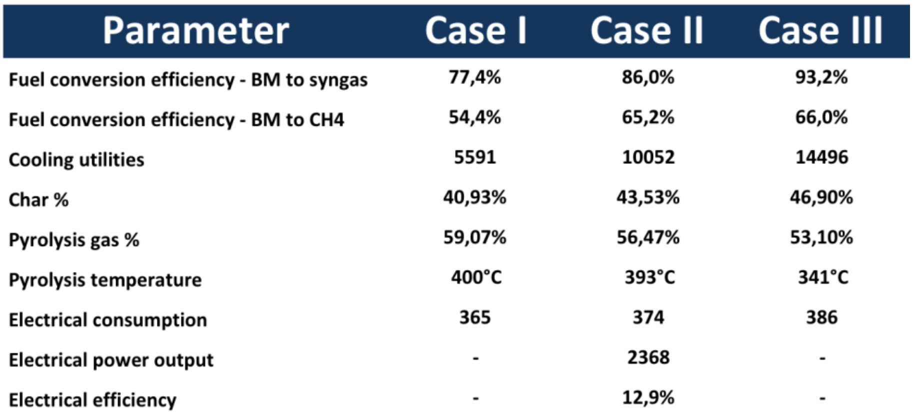
It has not been easy to achieve the convergence of the results while fulfilling the process requirements (e.g. dry syngas temperature below 100°C to allow condensation, stack temperature above 100°C to avoid flue gases condensation, etc). Eventually, the outlet temperature in the preheating of combustion air was adopted as the free parameter to balance the energy flows in the system. Most of the efforts were spent trying to detect a configuration for heat exchangers allowing this high level on fuel moisture and acceptable pyrolysis temperature (not lower than 320°C).

4.3. Discussion

The three calculation models were run with equal dry biomass input, so that direct comparison of thermodynamic values is possible. Comparing Case I to Case II and III, BM-to-Syn efficiency is lower. The reason for this is because PG has to supply heat to gasifier, pyrolysis and drying steps, while in Case II and III the drying step takes heat from, respectively, syngas cooling and methanation. In Case II, air is preheated and steam is produced from cooling flue gases and burning part of pyrolysis gas, so the increase in efficiency is inferior to Case III. However, in Case III, the entire drying heat load is provided by the waste heat from methanation, so pyrolysis temperature can be lowered in order to reduce production of PG, maximizing char and syngas yields.

Compared to the standard WoodRoll®, Case II and Case III present an advantage: the air for combustion of PG is preheated. This allows reducing the consumption of PG per unit volume of syngas produced. In Table 12, the three cases are compared among themselves with key parameters of the process.

Table 12 Comparison of key parameters for all cases. Power values are expressed in P.U.



Parameter	Case I	Case II	Case III
Fuel conversion efficiency - BM to syngas	77,4%	86,0%	93,2%
Fuel conversion efficiency - BM to CH4	54,4%	65,2%	66,0%
Cooling utilities	5591	10052	14496
Char %	40,93%	43,53%	46,90%
Pyrolysis gas %	59,07%	56,47%	53,10%
Pyrolysis temperature	400°C	393°C	341°C
Electrical consumption	365	374	386
Electrical power output	-	2368	-
Electrical efficiency	-	12,9%	-

With regards to the cooling utilities, Case II presents nearly twice the load discharged by Case I because of the cooler positioned in the steam cycle; the cooling effect on the drier is the same. Looking at Case III, the cooling need is almost threefold the Case I need: this is due to a very large moisture content in the lower-grade fuel.

The electrical consumption at each case is calculated as sum of the contribution from the grinder, which is proportional to the char flow, and all other electrical equipment, which are assumed to be the same for the three cases. In fact, the rest of the equipment consists mainly of fans for gas circulation or heating cables: as the energy input is the same for the three systems, it seems reasonable to consider equal electrical equipment for all cases.

5. Conclusions

The literature review of this thesis work has the objective of presenting the different alternatives for fuel synthesis, starting from syngas with high hydrogen content (H_2/CO=2). Each fuel conversion process has been outlined with a description of the thermodynamic conditions to adopt in order to achieve the required output fuel. Out of these alternatives, only methanation has been explored more in depth, as closer focus of the present activity of Cortus Energy AB. In fact, at the moment, the company is developing a commercial version of the gasification plant and a partnership with KIC InnoEnergy is aiming at converting methane from syngas. The objective of the modelling section of this thesis work is, hence, exploring how could Cortus integrate the WoodRoll® technology with the methanation unit developed by KIC InnoEnergy in Karlsruhe Institute of Technology, making good use of the waste heat available from the methanation process. In this section, the commercial version of the WoodRoll® gasification plant is modelled on Simulink in order to be able to verify the coherence of the model with the already-existing model produced by the company on VBA code. The analysis revealed a close match between the set of data. Consequently, several alternatives for the integration are shown, out of which only two are modelled. The first configuration allows conversion of syngas to methane plus conversion of electricity through a steam cycle, using waste heat from flue gases and methanation as thermal input. This configuration can be suitable for isolated systems having both electricity and methane grid, with abundance of wood or agricultural residues. This setting can yield 65,2% BM-to-CH_4 conversion efficiency and 12,9% electrical efficiency. The last configuration targets the utilization of very wet biomass waste streams, such as paper mill sludge, characterised by moisture levels about 70%; paper mills have to get rid of this feedstock, so they pay to have it withdrawn. The configuration is designed to shift a large thermal load on the drier, so the efficiency of the process is obviously reduced, as the heat supplied to the biomass for water evaporation cannot be further recovered: BM-to- CH_4 efficiency is 66,0%. The lower conversion efficiency is compensated by a negative cost on the feedstock supply. To further implement one of these models, a preliminary economical assessment should be carried out, together with a Life Cycle Analysis, in order to assess global emissions, consumption of natural resources and waste streams.

6. References

Supermethanol.eu, (2015), (accessed February 2015), Retrieved from: http://www.supermethanol.eu/index.php?id=21&rid=12&r=methanol_synthesis

Anderson, J. R., & Boudart, M. (1981). Dry M. E. in catalysis science and technology. New York: Springer-Verlag.

Anderson, R. B. (1984). The Fischer-Tropsch Synthesis. Orlando, FL: Academic Press.

Axens.net. (2015), (accessed March 2015). Retrieved from http://www.axens.net/document/19/conversion-of-syngas-to-diesel---article-ptq/english.html

Basu, P. (2010). *Gasification and pyrolysis of biomass - Practical design.* Elvesier Inc.

Bauen, A. (2004). In Encyclopedia of Energy. Cleveland: C.J. Ed. Elvesier: Amsterdam.

BiofuelSTP.eu. (2015), (accessed March 15), Retrieved from http://biofuelstp.eu/bio-sng.html

Buchholz, D. (2015, March 2). *Innovative processes for thermochemical SNG production from biomass.* Retrieved from www.edgar-program.com/.../680ddb25-d751-4501-be45-a97ee3e959e8

Chinchen, G. C., Denny, P. J., Jennings, J. R., Spencer, M. S., & Waugh, K. C. (1988). Synthesis of Methanol: Part 1. Catalysts and Kinetics. *Applied Catalysis*, pp. 1-65.

Coalspot.com. (2015), (accessed March 2015), Retrieved from http://coalspot.com/technical/file/Calorific%20value.pdf

Dacheng Hu, J. G. (2012). Enhanced Investigation of CO Methanation over Ni/Al2O3 Catalsyt for Synthetic Natural Gas Production. *Ind. Eng. Chem. Res.*, 51 (13), pp. 4875-4886.

Dybkjaer, I., & Christensen, T. S. (2001). Studies in Surface Science and Catalysis. 6. *6*, pp. 435-440.

Engvall, K. (2015), (accessed March 2015), Retrieved from http://conference.sgc.se/ckfinder/userfiles/files/4_3_Engvall_GGROS2015_pdf.pdf

Fischer Tropsch Synthesis. (2015), (accessed March 2015), Retrieved from TUM University: http://www.tc2.ch.tum.de/fileadmin/tuchtc2/www/ICP1/ICP1_1314/9-FT_synthesis-2013_PW.pdf

Ge, Q., Huang, Y., Qiu, F., & Li, S. (1998). Applied Catalysis A. 167(1), pp. 23-30.

Harms, H. G., Höhlein, B., Jørn, E. & Skov, A. (1980). *Oil & Gas J. 78, p.120.*

Huber, G. W., & Dumestic, J. A. (2006). Catalysis Today 111. pp. pp. 119-132.

IEA - Bioenergy. (2015), (accessed March 2015), Retrieved from http://www.iea.org/topics/renewables/subtopics/bioenergy/

IEA *Task 33*. (2015), (accessed March 2015), Retrieved from http://www.ieatask33.org/content/thermal_gasification.

Jensen, Poulsen, Andersen. (2011, April). From coal to clean energy. *Nitrogen + syngas*.

Jiao Liu, Dianmiao Cui, Jian Yu, Fabing Sua and Guangwen Xu. (2015). Attrition-resistant Ni-Mg/Al2O3 catalyst for fluidized bed syngas methanation. *Catal. Sci. Technol., 5*, 3119-312.

K. Klier, V. C. (1982). Catalytic synthesis of methanol from COH2: IV. The effects of carbon dioxide. *J. Catalysis*, pp. 343-360.

K.EU-25, B. (2005). *Oilseeds and Products Biofuels Situation in the European Union 2005; GAIN Report No E35058.* USDA Foreign Agricultural Service: Washington DC.

Kirkels, A. F. (2011). Biomass gasification. Still promising? A 30 year global overview. *Renewable & Sustainable Energy Reviews, 15*(1), 471,481.

Klass, D. L. (2004). In Encyclopedia of Energy. Cleveland: Elvesier.

Klier, K. et al. (1982). Catalysis.

Lee. (2015), (accessed March 2015). *Ohio University*. Retrieved from http://www.ohio.edu/people/lees1/DME.html

Lee, S., & Sardesai, A. (2005). Topics in Catalysis. Springer.

Liu Ke, S. C. (2009). *Hydrogen and syngas production and purification technologies.* American institute of chemical engineers.

Mills, G. A., & Steffgen, F. W. (1974). Catalytic Methanation. *Catalysis Reviews and Engineering 8 (1)*, pp. 159-210.

Muhler, M.; Tornqvist, E:; Nielsen, L. P.; Clausen, B. S.; Topsoe, H. et al. (1994). On the role of adsorbed atomic oxygen and CO2 in Copper-based methanol synthesis catalysts. *Catalysis Letters, 25(1-2)*, pp. 1-10.

NER300-SWD-224. (2012). *Moving towards a low carbon economy and boosting innovation, growth and employment across the EU.*

Ojeda M., R. S. (n.d.). *Energy science, Engineering and Technology: Biofuels from Fischer Tropsch synthesis.* Nova Science Publisher, Inc.

Peng, X. D., Wang, A. W., Toseland, B. A., & Tijm, P. J. (1999). Single-Step Syngas-to-Dimethyl Ether Processes for Optimal Productivity, Minimal Emissions, and Natural Gas-Derived Syngas. *Industrial & Engineering Chemistry Research, 28*, pp. 4381-4388.

Rostrup-Nielsen. (2011). *Concepts of syngas manufature: Catalytic science series.*

Rostrup-Nielsen, J. R. (2002). Syngas in perspective. *Catalysis Today, 71(3)*, pp. 243-247.

Rostrup-Nielsen, J., & Winter-Madsen, S. (2008). *Steam reforming and chemical recuperation.* American Chemical Society.

Sardesai, A., & Lee, S. (1998). Liquid phase dimethyl ether (DME) synthesis: a review. *Reviews in Process Chemistry and Engineering, 1(2)*, pp. 141-178.

Stöcker, M. (1999). Methanol-to-hydrocarbons: catalytic materials and their behavior. *Microporous Mesoporous Materials, 29 (1)*, pp. pp. 3-48.

Zwart, R. (2015), (accessed March 2015), Retrieved from http://www.biosng.com/fileadmin/biosng/user/documents/presentations/070402_-_Petten_-_Zwart.pdf