

Substitute Natural Gas from Biomass Gasification

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Worldwide demand for fossil fuels is increasing rapidly and at the same time known resources are diminishing. Especially energy sources such as oil and natural gas in Western Europe are almost depleted. This, and the fact that climate changes are more severe than before, has increased the demand for renewable, clean and sustainable energy. In Europe, natural gas accounts for about 25% of the total energy distribution and more energy is distributed as gas than as electricity [1]. It is therefore important to build up a sustainable gas supply for current and future needs. In this master thesis, twelve different systems for production of substitute natural gas, SNG, are evaluated. The systems consists of three gasifiers; entrained-flow, fluidised-bed and indirect and methanation is evaluated using isothermal and adiabatic methanation. Gas cleanup were performed using both conventional zinc oxide desulphurisation with PSA upgrade and a Rectisol® wash. The evaluations were performed through simulations accomplished in Aspen Plus™.

Introduction

Thermal gasification of biomass is one of many techniques that can supply the energy needed when modern society breaks its oil-dependency. The gas produced from thermal gasification, also known as syngas, contains too little methane to be of any interest and further processing is necessary. Gas upgrading also needs to be applied in order to increase the energy density of the gas.

There are a few routes to choose; utilise methanation reactors to produce methane from the syngas, produce Fischer-Tropsch (FT) liquids and methane in FT-reactors or a combination of both. The H_2/CO ratio needs to be set according to upgrade path with a water-gas shift reactor. Sulphur is a strong catalyst poison for both methanation and Fischer-Tropsch catalysts and must be removed. Regardless of the choice of gas upgrade process, the syngas must first be cleaned from sulphur, alkali and other impurities.

Among the gas conditioning techniques available, a zinc oxide bed for desulphurisation and pressure swing adsorption, PSA, for gas upgrading was chosen. To evaluate wet gas conditioning systems Rectisol® was chosen. The Rectisol® system handles both desulphurisation and gas upgrading.

To evaluate all system configurations a simulation model of the systems will be investigated. The models are made to evaluate any differences between the systems, and to some extent, how different parameters affect the SNG efficiency of the systems. The systems will comprise water-gas shift reactor, methanation reactor(s) heat recovery, desulphurisation, steam generation, drying and gas

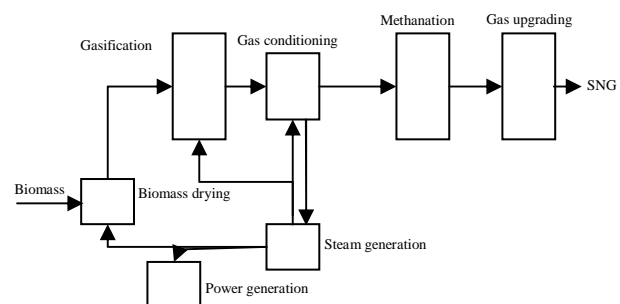


Figure 1: Simple flow-diagram of the systems.

upgrading. Figure 1 displays a simple flow-sheet of the systems.

Several parameters of the system are investigated by to what extent the effect SNG efficiency including: PSA methane recovery, isothermal methanation temperature and system pressure.

Gasification

There are several different gasification techniques commercially available and they are usually sorted into two groups; direct and indirect. In direct gasification the energy required for gasification is supplied in the same reactor by oxidising part of the feedstock. Indirect gasifiers supply energy to the reactions from an external source such as a burner. Indirect gasifiers are known to produce gases with higher methane content than direct gasifiers.

Most gasifiers were however engineered to gasify coal and as a result not all techniques have a commercially available full-scale solution for biomass. Prior to gasification the feedstock needs to be pre-treated with drying and grinding. The extent of the pre-treatment depends on the gasifier in use.

The gasification process is endothermic and thus requires external heat. Gasification is divided into two steps; pyrolysis, which is a low temperature process that operates without any oxidation and gasification that needs a gasification agent that contains oxygen such as steam or air [2].

If biomass is heated to about 400°C pyrolysis will start to occur. The pyrolysis does not require any oxygen, only the volatile compounds in the biomass will be gasified. Biomass contains ca 60 % volatile compounds compared to coal which contains < 40% volatile compounds. This makes biomass more reactive than coal. After thermal decomposition the volatile compounds are released as H₂, CO, CO₂, H₂O, CH₄ etc which is also known as pyrolysis gas. The remains after the pyrolysis is char coal [2].

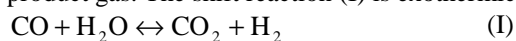
The pyrolysis can not convert all of the biomass into volatile compounds and therefore gasification is required. The gasification requires much higher temperatures than pyrolysis, usually in the range of 800-900°C and with a gasification agent present. The gasification includes partial oxidation and it breaks down most of the feedstock into volatile compounds and the remaining nutrients like alkaline earth metals etc. end up as ash. The produced gas from the gasification contains synthesis gas or syngas which consists of carbon monoxide, CO and hydrogen, H₂. The gas also contains methane, higher hydrocarbons like ethene, tars and inorganic impurities like HCL, NH₃, H₂S and CO₂.

There are many types of gasification reactors including fixed-bed, fluidised-bed and entrained-flow. The choice of gasifier lies in the gas composition of the synthesis gas and in the complexity of system.

Gas conditioning

Production of methane requires carbon monoxide and hydrogen in the presence of a catalyst. The H₂/CO ratio prior to methanation should be at 3 for stoichiometric methanation [2]. Of the gasifiers evaluated in this thesis none produced a gas with a H₂/CO ratio of 3 and a water-gas shift reactor is necessary.

The water-gas shift reaction is used to shift the H₂/CO ratio of the syngas. The reactors are operated at either high temperature, HT, or low temperature LT. There is also a stabilised LT-catalyst that can operate at temperatures of up to 320°C that is referred to as medium-temperature shift catalyst. There are different catalysts for each operating condition as well as the sulphur contents in the product gas. The shift reaction (I) is exothermic.



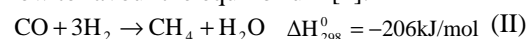
There are numerous processes for desulphurisation and for systems that require a cleaner gas, the zinc oxide (ZnO) bed can be utilised. This process operates at 250-300°C and can

remove sulphur down to levels of 100 ppb or even lower. However, zinc can react with halogens and form volatile compounds. These must be captured by a secondary guard bed, which normally consists of activated aluminium oxide (alumina) [3].

An alternative to zinc oxide beds are wet gas scrubbing processes. One such system is Rectisol, developed by Linde and Lurgi, it is able to capture both sulphur and carbon dioxide. The main advantage with this process for desulphurisation compared to zinc oxide is that it can generate a pure hydrogen sulphide (H₂S) stream suitable for a Claus-plant. The Rectisol process uses sub-cooled methanol as absorbent and several absorption columns.

Methanation

Methanation or methane synthesis occurs with reaction (II) which is very exothermic. Due to the high amount of heat that is released and to the high concentrations of the reactants, measures have to be taken to avoid hot-spots and to limit a rise in temperature. The temperature should also be kept low to favour the equilibrium [2].



There are several methanation reactor designs available and this thesis has evaluated isothermal methanation and adiabatic methanation with recycled gas. The adiabatic system in use is based on Haldor Topsoe's methanation process called TREMP™ (figure 2), Topsoe's Recycle Energy-efficient Methanation Process. The system uses three adiabatic reactors that utilises product recycle and intermediate cooling.

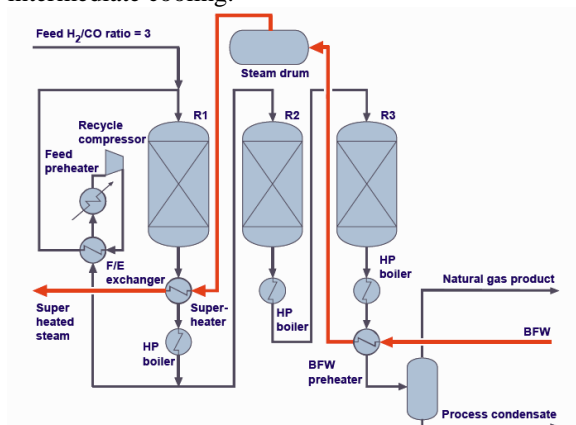


Figure 2: TREMP™ methanation process by Haldor Topsoe [4].

Gas upgrading

For systems using a zinc oxide bed for sulphur capture a gas upgrade systems needs to be applied to reach sufficient methane purity in the product gas. As for sulphur capture, there are numerous systems available for gas separation and one such system is pressure swing adsorption or PSA.

PSA, is based on molecular size separation. Feeding to the PSA occurs under high pressure and large molecules such as carbon monoxide are adsorbed to the packing material of the PSA, smaller passes through the packing. Then the pressure drops, thus releasing the adsorbed molecules. A minimum of two adsorber beds are required for continuous operation but PSA units are often composed of four to ten adsorber beds. For PSA's with clay as packing material, water must be kept below the dew point prior to the PSA as it will destroy the packing material [2]. Hydrogen sulphide adsorbs irreversibly on the packing and must be removed from the gas prior to injection [3].

Simulation systems

The systems all start after the gasifier, which was not possible to simulate in Aspen Plus™, and comprise a water-gas shift reactor, heat recovery, desulphurisation, methanation followed by gas upgrading. Biomass drying and steam/oxygen required for gasification have been included in all systems. All reactions are assumed to reach equilibrium. The target production of the plant is 100 MW SNG, based on LHV of methane, which is approximately 2 kg methane per second. The pressure for all steam streams is set to 90 bar. All heat generated in the methanation reactors are used to generated high pressure steam which is utilised to produce electricity by means of a steam turbine. The heat that has to low temperature for high pressure steam, is utilised as district heating along with condensing steam from the turbines.

The simulations were performed for the twelve base cases, table 1, with additional simulations to evaluate if system pressure, isothermal methanation temperature or PSA methane recovery affects the efficiency to SNG. Additional simulations were performed to evaluate the impact of methane losses in condensed water. The pressure and temperature simulations where, due to time constraints, only evaluated for the system containing entrained-flow gasifier, zinc oxide desulphurisation and isothermal methanation.

Table 1: The twelve base cases between gasifiers and methanation/gas cleanup.

Gasifier	Entrained-flow	Fluidised-bed	Indirect
Isothermal methanation/PSA	X	X	X
Isothermal methanation/Rectisol	X	X	X
Adiabatic methanation/PSA	X	X	X
Adiabatic methanation/Rectisol	X	X	X

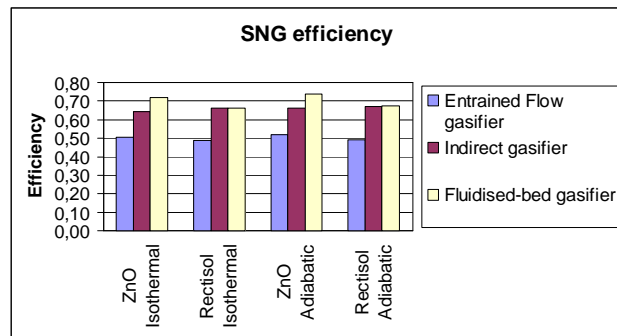


Figure 3: Comparison of SNG efficiencies for the test systems

Results

Figure 3 shows that both the fluidised-bed gasifier and the indirect gasifier perform better for SNG production than the entrained-flow gasifier. Furthermore there are only small differences when comparing gas upgrading and desulphurisation systems. But the results would look different if overall system efficiency were evaluated instead of SNG efficiency. The Rectisol system has a much higher power need and lower waste-heat utilisation.

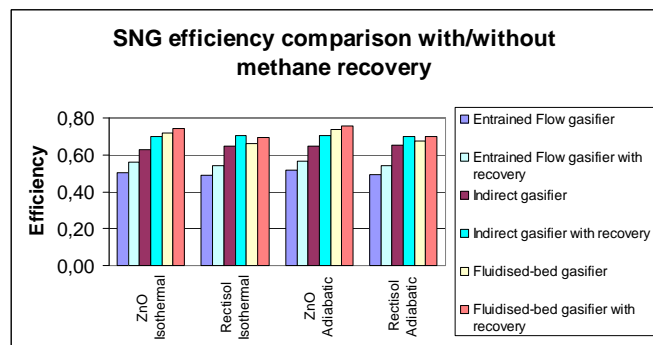


Figure 4: Methane recovery impact on SNG efficiency.

Recovering methane that is dissolved in water, by adiabatic flashing in atmospheric pressure, increases the SNG efficiency by 5-10 % depending on the configuration.

For the following evaluations only the system using an entrained-flow gasifier with zinc oxide desulphurisation and PSA gas upgrade were used due to time constraints. But as the results do not differ between desulphurisation and gas upgrade systems in the above figures, it should be representative for all systems.

Figure 5 show that increasing the system pressure has a negative impact on the SNG efficiency. The reason for the decreased efficiency probably lies in the solubility of methane and to some extent, carbon monoxide in water at elevated pressures.

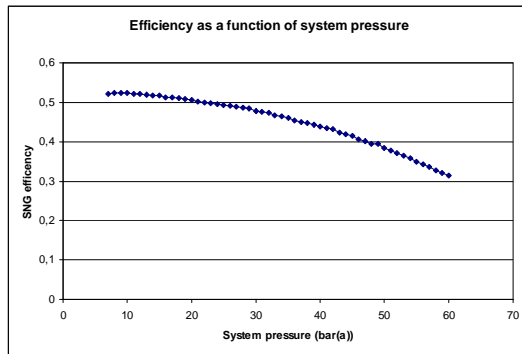


Figure 5: SNG efficiency as a function of system pressure.

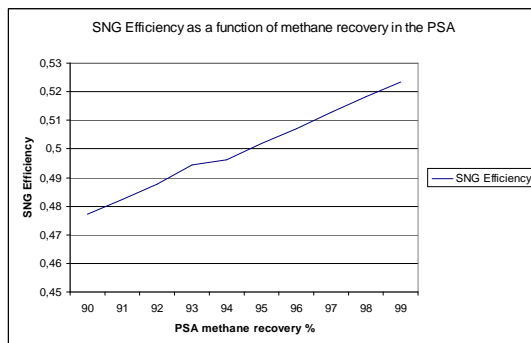


Figure 6: SNG efficiency as a function of PSA methane recovery.

Increasing the recovery of methane from 90 to 99 %, according to Volker Eichenlaub [5], increases the SNG efficiency by almost 10 % as can be seen in figure 6. If a high recovery of methane is possible then it should be implemented as it affects SNG efficiency by a significant amount. The only drawback of a higher recovery is the purity of the produced gas as it decreases with increased recovery.

The isothermal methanation temperature has no impact on the SNG efficiency as can be seen in figure 7.

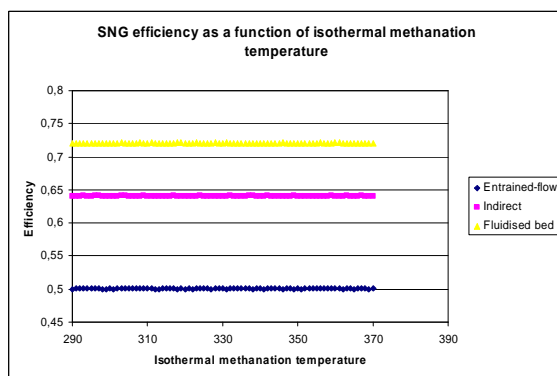


Figure 7: SNG efficiency as a function of isothermal methanation temperature.

Conclusions

Natural gas is a fossil fuel and as such, will be depleted some time in the future. Currently there is a good infrastructure for natural gas in Europe and the gas grid is expanding. In Sweden the grid is limited to the west coast but expansion to Stockholm is being evaluated. Therefore, a biomass based substitute for natural gas would already have the necessary infrastructure and could phase out natural gas over time. Future phase out of SNG in favour of hydrogen is also possible and is planned by E.ON.

The simulations of the systems based on different gasification techniques showed that not all of them are appropriate for SNG production. Indirect gasification has the advantage of higher methane content in the gas leaving the gasifier. The results clearly show the advantage of higher methane output from the gasifier that both the fluidised-bed and the indirect gasifier have. Both gasifiers have significantly higher efficiencies than the entrained-flow gasifier.

The choice in gasifier is the most important factor as can be seen from the results. Comparing results of different systems using the same gasifier, reveals only small differences, at least when evaluating SNG efficiency.

The simulations show that SNG efficiencies from biomass to methane of 50 % are possible with either gasifier. The fluidised-bed and indirect gasifiers were able to produce SNG with an efficiency around 67 %, which coincide with other studies [6]. Furthermore, utilising a Rectisol gas cleanup system does not have a significant negative impact on SNG efficiency, but it affects overall efficiency.

The simplest system; zinc oxide desulphurisation and PSA gas cleanup coupled with either methanation system is the best choice. It is based on well established, widely used equipment and it offers better efficiency than a wet-gas cleanup such as Rectisol. The only reason for using a Rectisol wash is if there is significant amount of sulphur in the gas stream for use in a Claus plant or to capture carbon dioxide. Carbon dioxide capture is not necessary for biomass based plants as the carbon emissions are considered neutral.

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