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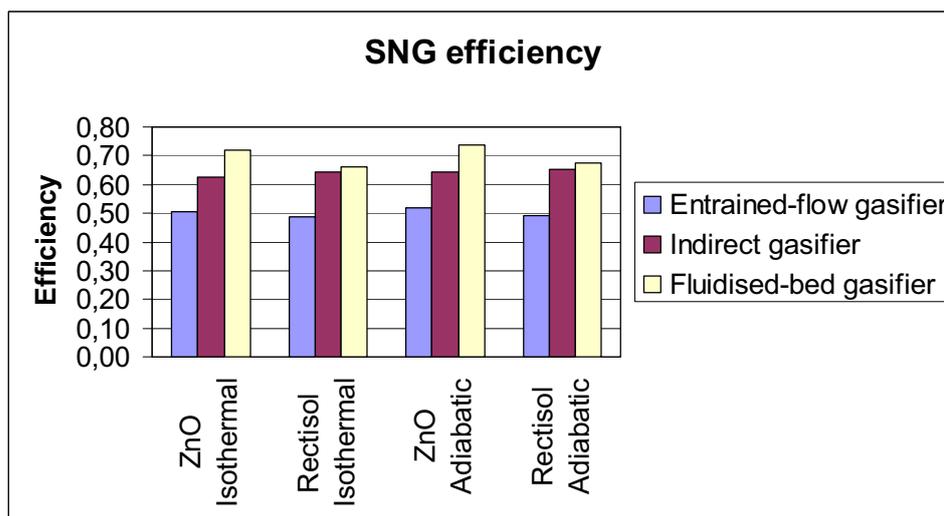
## Abstract

Biomass is by many considered as the only alternative to phase-out the usage of fossil fuels such as natural gas and oil especially for the transportation sector where alternative solutions, such as hydrogen fuel cells and batteries, are not yet fully developed. Thermal gasification or other methods such as pyrolysis of the biomass must be applied in order to produce an intermediate product suitable for further upgrading to either gaseous or liquid products.

This thesis will evaluate the possibilities of producing, substitute natural gas, (SNG) from biomass gasification by using computer simulation. Three different gasification techniques were evaluated; entrained-flow, fluidised-bed and indirect gasification coupled with two different desulphurisation systems and two methanation processes. The desulphurisation systems were a zinc oxide bed and a Rectisol® wash system. Methanation were performed by a series of adiabatic reactors with gas recycling and by an isothermal reactor.

The impact on SNG efficiency from system pressure, isothermal methanation temperature and PSA methane recovery were evaluated as well.

The results show that the fluidised-bed and the indirect gasifier have the highest SNG efficiency. Furthermore there are little to no difference between the methanation processes and small differences for the gas cleanup systems. SNG efficiencies in excess of 50 % were possible for all gasifiers, figure below. SNG efficiency is defined as the energy in the SNG product divided by the total input to the system from biomass, drying and oxygen.



**Figure: SNG efficiency for the systems.**

Increasing system pressure has a negative impact on SNG efficiency as well as increasing operating costs due to increased power for compression. Isothermal methanation

temperature has no significant impact on SNG efficiency. Recovering as much methane as possible in the PSA is the most important parameter.

Recovering methane that has been dissolved in condensed process water increases the SNG efficiency by 2-10% depending on system.

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# 1 Introduction

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.

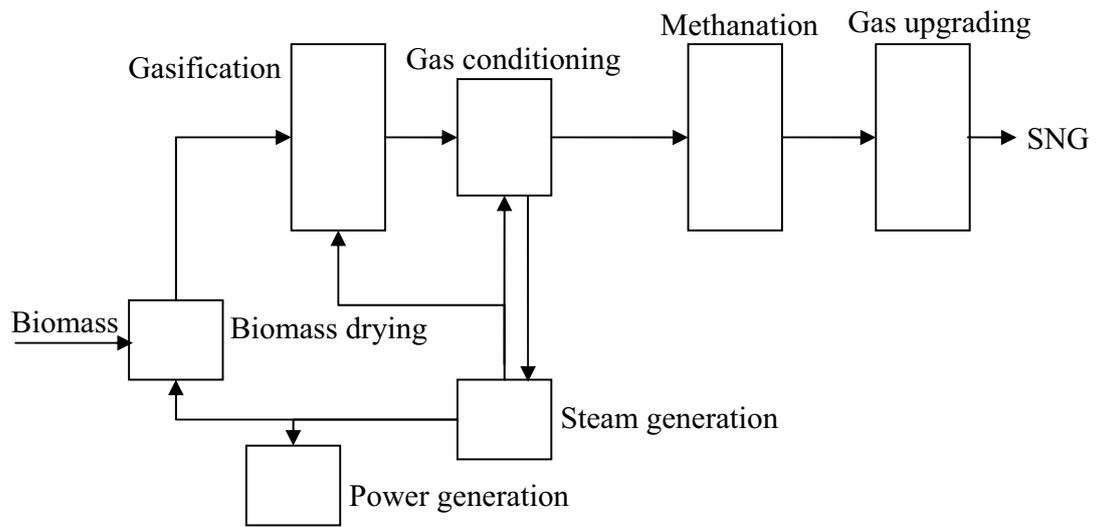
Gasification of biomass is the technology that is currently the most attractive to produce energy from renewable resources. The technology is well established, has a good efficiency and if complemented with methanation or Fischer-Tropsch synthesis, has very wide product range.

The produced gas has to meet the required quality for H-gas or high quality gas (approximately  $11.1 \text{ kWh/Nm}^3$  [2]) in Germany according to project specifications [1]. The quality concerns Wobbe Index and relative density. There are other requirements as well such as sulphur and water, but these will be met automatically due to process constraints.

This thesis will cover the process from biomass to a finished product. The product will be substitute natural gas, SNG, and the objective is to have a process with as high efficiency to SNG as possible.

The methanation reactions are highly exothermic, and as a result, large amounts of energy are released in the reactors as heat. This is the biggest concern when designing the process because the waste heat needs to be utilised as efficiently as possible. The heat is released at a relatively high temperature which allows for the production of high pressure steam with additional super-heating. The steam will be used in the process but can also be used to produce electricity which will increase the plants operating profits.

Figure 1 shows a basic process flow-diagram for the methanation plant with the important operations. All operations will be described in further detail in this thesis.



**Figure 1: Schematic over the SNG process.**

## 2 Gas Quality

Currently, there is no legislation concerning natural gas and the composition it must have. However the gas distributors have an agreement towards their clients concerning the gas quality, such as Wobbe Index (WI), dew point, etc. but that is not government legislated. Therefore, as long as the quality is not compromised regarding the aforementioned parameters, any gas mixes that have met the required quality can be outputted on the gas network [3]. This however, only applies in Sweden; internationally this is controlled by the EASEE-gas, European Association for the Streamlining of Energy Exchange-gas, in the Common Business Practice, which states a table of allowable composition in natural gas, table 1 [4]. This means that the gas can meet Swedish gas consumer's demand on quality but may not meet the EASEE-gas's quality. This can introduce problems if the gas is to be exported to other European countries.

**Table 1: EASEE regulation of natural gas quality.**

Parameter	Unit	Min	Max	Recommended implementation date
Wobbe Index, WI	kWh/m <sup>3</sup>	[13.60]	15.81	1/10/2010
Relative density, d	m <sup>3</sup> /m <sup>3</sup>	0.555	0.700	1/10/2010
Total sulphur	mg/m <sup>3</sup>	-	30	1/10/2006
H <sub>2</sub> S + COS (as S)	mg/m <sup>3</sup>	-	5	1/10/2006
RSH (as S)	mg/m <sup>3</sup>	-	6	1/10/2006
O <sub>2</sub>	mol %	-	[0.01]	1/10/2010
CO <sub>2</sub>	mol %	-	2.5	1/10/2006
H <sub>2</sub> O dew point	°C at 70 bar(a)	-	- 8	-
Hydro carbon dew point	°C at 1- 70 bar(a)	-	- 2	1/10/2006

In the Common Business Practice, it is assumed that natural gas does not contain any hydrogen. Furthermore it states that, if future gas usages include manufactured gases the recommendations may need to be re-evaluated. Finally it concludes that it is the common understanding that stability of the natural gas quality is of the outmost importance.

For businesses that have specific requirements such as flame properties, the Wobbe Index alone is not adequate. For example, a mixture of 60% propane and 40% air has the same Wobbe Index as natural gas, but because of the pre-mixing of the air and the propane, the flame will be different. If the substitute for natural gas contained much CO there would almost certainly be a mismatch in WI unless the gas could be mixed with a high volumetric heating value gas (propane, butane, etc.). If the gas, after WI upgrade, contains high amounts of H<sub>2</sub> and CO, variations in flame height and flashback tendency can make the substitution unsatisfactory even if the WI is met [5].

The target quality of the gas shall meet the German H-Gas considering Wobbe Index (9.7-13.1 kWh) and relative density (0.555-0.700 kg/kg) according to project

specification. With these restrictions, the gas can contain a maximum of 1.75 % hydrogen per volume, methane accounts for the remainder.

The product gas should be delivered at 16 bar to the transmission network according to project specification.

### 3 Gas Production

Producing energy-rich gases such as SNG from biomass is a difficult process and there are not yet many full-scale plants in the world. This thesis will cover the entire process starting with pre-treatment to upgrading the produced gas. Figure 2 shows a basic process flow-sheet with alternative products; SNG and Fischer-Tropsch liquids. The processes have similar in achillary equipment but differ in required gas composition, system pressures etc. All steps from drying to finished product will be explained in this chapter.

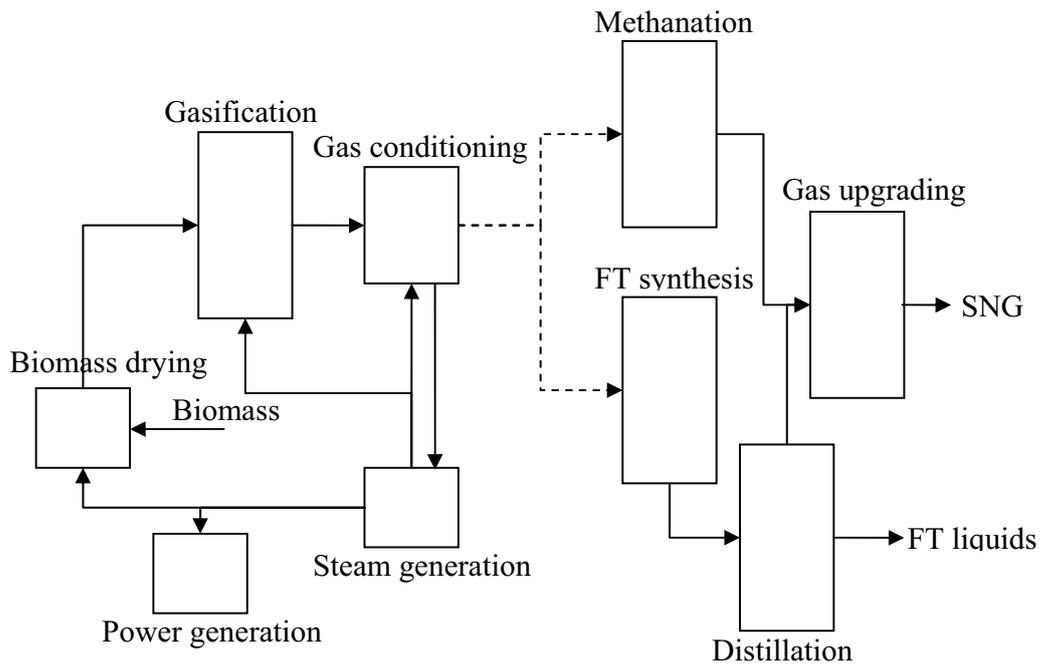
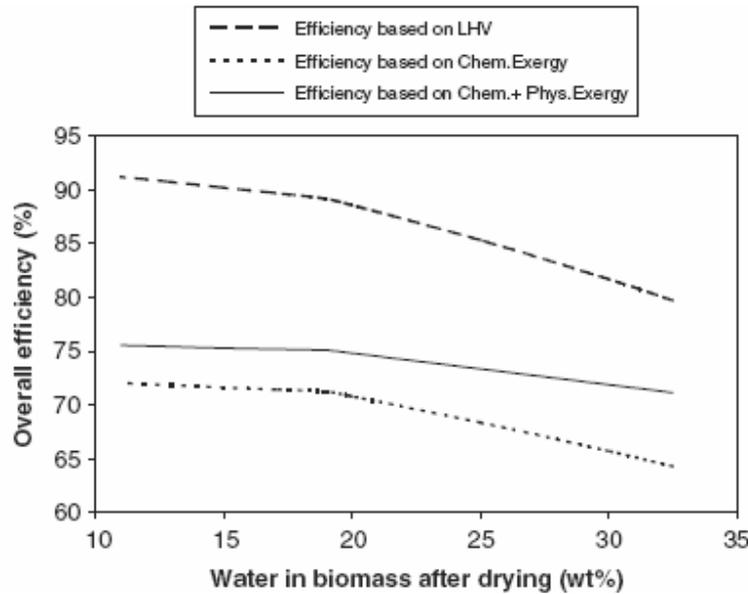


Figure 2: Schematic of the SNG process with co-production of FT-liquids.

#### 3.1 Biomass Drying

The biomass needs to be dried prior to gasification to improve efficiency. Figure 3 shows the efficiency of gasification as a result of biomass drying. There are several different types of dryers to choose from and the choice depends on a number of parameters.



**Figure 3: Improvement of gasification efficiency by drying using enthalpy of product gas [7].**

The dryer can be either direct heated by hot air or steam or indirectly heated where the heat source is separated from the wet material. The advantage with the indirect dryer is that it is possible to recover the latent heat of the evaporated water in the material. Drying is achieved by heating the material, thus evaporating the water in the feed. During the drying, the material's temperature is the same as the boiling point of water at the drying pressure. When the material is dried, the temperature rises as a result of the hot surroundings. If the material is heated above 260°C in the presence of air it could ignite. It is therefore important to keep the temperature under control [7]. The biomass contains approximately 50 wt-% water when taken from storage [6].

### 3.1.1 Rotary Dryers

Rotary dryers are the most common type of biomass dryer and the most widely-used is the direct heated single-pass dryer. In the rotary dryer, the biomass is passed through a rotating drum where it comes in contact with hot gases. On the inside of the drum there are flights that move the biomass through the hot gases, thus increasing the mass and heat transfer. The rotary dryer can handle large as well as small particles. Rotary dryers can operate at inlet temperatures of ca 230-1100°C and outlet temperatures of 70-110°C. The residence time depends on the particle size and is less than a minute for small particles to 10-30 minutes for larger particles.

### 3.1.2 Flash Dryers

In the flash dryer, a high velocity hot air stream is mixed with the wet material. The close contact between the material and the air results in very rapid drying. After the dryer, the air and solids are separated in a cyclone. Depending on the scenario, the air may need to be scrubbed of particulate matter that follows the gas stream.

The temperature in the flash dryer is lower than in the rotary dryer, but above the combustion temperature of the biomass.

### **3.1.3 Superheated Steam Dryers, SSD**

The superheated steam dryers are similar to flash dryers but instead of air they use superheated steam to dry the biomass. Under normal operating conditions, enough superheated steam is mixed with wet material to allow complete drying while maintaining superheating. Typically 90% of the steam leaving the dryer is recirculated and the other 10% that represents the evaporated water from the material is removed.

The main advantage with the SSD is that the steam that is leaving the dryer can be used directly in other processes [8].

## **3.2 Gasification**

Gasification is a thermal process that breaks down the chemical bonds in the fuel in order to produce an energy rich gas. The process is an endothermic process which 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 [9].

During gasification, it is important to maintain the optimum oxygen input. The maximum efficiency of the gasification is achieved when just enough oxygen is added to allow complete gasification. If more oxygen is added, energy is released as sensible heat in the product stream.

The isotherms at 823°C and 600°C in figure 4, indicates the solid carbon-boundary lines. Above the carbon-boundary line, solid carbon exists in heterogeneous equilibrium with gaseous components; and below, only gaseous components are present in homogeneous phase equilibrium. This implies that oxygen should be added until the solid carbon-boundary is reached. For coal, oxygen should be added (the arrow in figure 4) until point A is reached and complete gasification is achieved [7].

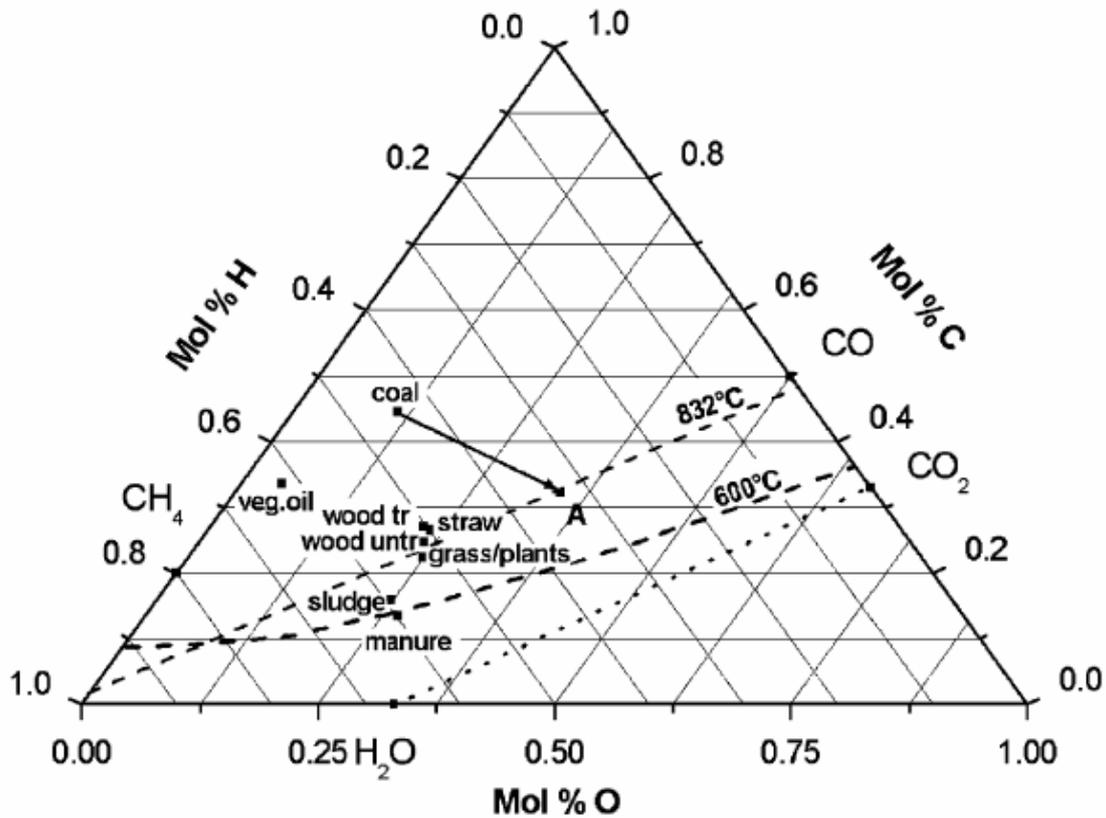


Figure 4: Location of biofuels in ternary C–H–O diagram.

### 3.2.1 Pyrolysis

If biomass is heated to about 400°C pyrolysis will start to occur. The pyrolysis does not require any oxygen but 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 H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub> etc which is also known as pyrolysis gas. The remains after the pyrolysis is char coal [9].

### 3.2.2 Gasification

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, H<sub>2</sub>. The gas also contains methane, higher hydrocarbons like ethane, tars and inorganic impurities like HCL, NH<sub>3</sub>, H<sub>2</sub>S and CO<sub>2</sub>.



The product gas from the gasifier contains the volatile components from the pyrolysis as well as the syngas. The composition of the gas depends on a number of parameters such as gasification temperature and pressure, feedstock, reactor type and gasification agent. Generally higher temperature favours syngas production while lower temperature yields higher tar and methane rich gases. Increased pressure will increase the methane yield due to the equilibrium of reaction (1) [9].

Because of the endothermic reactions in gasification heat must be added. This can be achieved either direct, with partial oxidation and/or combustion as in the case with air or pure oxygen as gasification medium or indirect.

When air is used as gasification medium in direct gasification, the product gas is nitrogen diluted. This will decrease the lower heating value, LHV, of the gas and increase the cost of the down stream processes as more gas needs to be processed.

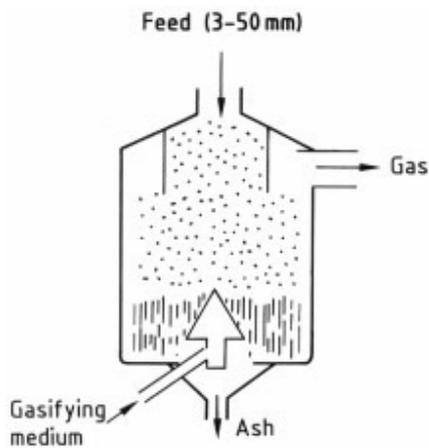
An alternative is to use pure oxygen as gasification medium. This will eliminate the nitrogen dilution problem but it increases the costs significantly.

### **3.2.3 Reactor Types**

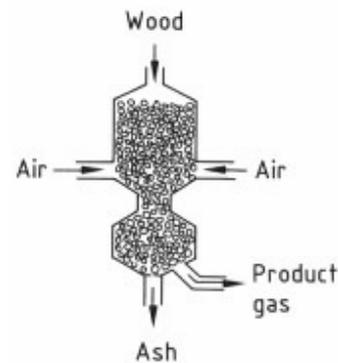
There are a number of different reactor types that can be utilised for gasification. Most of the reactors have been developed for coal gasification and may not be suitable for biomass feedstocks. Among the available reactors are the fixed-bed also called moving-bed, fluidised-bed and entrained-flow gasifier. A summarising table of typical gas composition for the relevant gasifiers can be found after their descriptions.

#### **3.2.3.1 Moving-bed Gasifiers**

In the moving-bed gasifier, the feedstock is slowly moving down in the reactor and the ash is taken out in the bottom. Figure 5 shows a countercurrent moving-bed gasifier where the gasifying medium is blown in from the bottom. The advantage with this type of gasifier is excellent thermal efficiency because the gasifying medium is pre-heated by the outgoing ashes and the outgoing gases pre-heats the incoming feedstock [9].



**Figure 5: Countercurrent moving-bed gasifier.**



**Figure 6: Downdraft moving-bed gasifier.**

The residence time of a moving-bed gasifier is typically in the region of 1-2 h and the carbon conversion is high.

When wood is used in moving-bed gasifiers, most processes apply the co-current or downdraft configuration. The advantage of this is that the product gas flows through the combustion zone where tars are cracked. Figure 6 shows a schematic of a downdraft wood gasifier.

Moving bed gasifiers are suited for small-scale application, typically 200 kg wood per hour [9].

### 3.2.3.2 Fluidised-bed Gasifiers

In the fluidised-bed gasifier the feedstock is mixed with a bed material and the gasification medium has a sufficiently high velocity to allow the solid particles to lift. This requires smaller particles typically 3-10 mm which puts higher demand on the grinding. Because of the fluidisation, the particles move more randomly and mix with the bed material which causes a uniform temperature in the reactor. The maximum temperature is determined by the ash softening and sticking behaviour [9].

Fluidising-beds with gas velocities that are exceeding the minimum required (3-10 m/s) are called circulating or fast fluidised beds. The fluidised-bed gasifiers are especially suited for biomass gasification as it allows for good flexibility regarding particle sizes and easier scale-up than moving-bed gasifiers [9].

### 3.2.3.3 Entrained-flow Gasifiers

In entrained-flow reactors, the particles are carried by the reacting gases. Therefore the particles must be smaller than in the other systems. About 70 per cent of the particles must be smaller than 0.1 mm. The small particles together with a high temperature allow for good carbon conversion and very low tar content in the product gas. The residence time in an entrained-flow reactor is a few seconds. The reactants (e.g. biomass, oxygen,

steam) are feed through burners in the reactor at a high velocity and the feedstock is instantly gasified due to the high temperature of about 2000°C. The only drawback with entrained-flow gasifiers for SNG production is that the methane content in the product gas is close to zero [9].

### 3.2.3.4 Indirect Gasification

With indirect gasification, heat is supplied from an external source. The source can be any heat source such as a burner or even a nuclear reactor. The goal is to transfer the heat generated in the external device to the gasification reactor. There is a number of different ways to accomplish this, for example to simply heat the external walls of the gasifier. This is however not the best way as it results in an uneven temperature profile in the reactor. An alternative is to use the fluidising medium as a heat transfer medium and circulate it through both the gasifier and the heat source. However, this approach will only work for fluidising reactors and, due to air compression expenditures, operates at atmospheric pressure [9].

An example of this type of system is the twin-bed gasifier. This gasifier uses two fluidised reactors that can be either bubbling or circulated [10].

The main reason for using indirect gasification is to circumvent nitrogen dilution when using air as gasification medium. Indirect gasification has also shown the highest methane content in the product gas [9].

### 3.2.3.5 Supercritical Gasification

A new gasification method that is considerably different from conventional gasification has emerged. The gasification is achieved in supercritical water at pressures of 30-50 MPa and temperatures in excess of 500°C. This gasification technique is based on gasification of feed stocks with very high water content > 90%.

The gasification yields hydrogen, carbon dioxide and small amounts of methane and carbon monoxide. The supercritical water gasification can be regarded as a high pressure steam reforming of biomass and among the benefits are low char and tar formation as a result of organic solubility in supercritical water. The technique is not yet fully developed and is not an alternative for drier biomass < 90 % water [11].

**Table 2: Typical raw gas composition for biomass gasification, vol-% for dry gas.**

<b>Gas component</b>	<b>CFB [12]</b>	<b>Indirect [12]</b>	<b>Entrained-flow [13]</b>
H <sub>2</sub> , hydrogen	30-40	17.5	21-32
CO, carbon monoxide	20-30	50	27-47
CO <sub>2</sub> , carbon dioxide	15-25	9.4	13-31
CH <sub>4</sub> , methane	8-12	15.5	0-0.5
C <sub>2</sub> H <sub>4</sub> , ethylene	-	1.1	-
C <sub>2</sub> H <sub>6</sub> , ethane	-	6	-
N <sub>2</sub> , nitrogen	1-5	-	9-17

## 3.3 Gas Conditioning

After gasification, the product gas contains organic and inorganic contaminants and particles. These contaminants need to be removed to avoid damage on downstream processes.

### 3.3.1 Particle Removal

A cyclone after the gasifier removes the largest particles and returns them to the gasifier. However the cyclone can not remove the finest particles, the limit depends on the design of the cyclone, but particles smaller than 5  $\mu\text{m}$  can not be captured by a cyclone [14].

Cyclones are often used in series, where the first captures the largest particles and the following cyclones capture increasingly smaller particles.

In order to capture particles smaller than 5  $\mu\text{m}$ , a particulate filter must be utilised. The filter can be ceramic, porous metal or granular bed filters. The ceramic filter can be based on a SiC with a thin coating of fine-ground aluminosilicate. The ceramic filters have high collection efficiency, approaching 100 %. However ceramic filters may have reliability concerns when operated at temperatures above 815°C as well as the possibility of chemical degradation and creep.

The porous metal filters have, like the ceramic filters, high collection efficiency but, unlike ceramic filters, they can be operated at temperatures approaching 1000°C depending on the alloy. Unlike the ceramic filters, the porous metal filters have a high resistance to thermal shock which occurs during periodic cleanup of the filters.

The granular bed filters are a bed filled with a granular material which can be either static or moving bed. In the static case, the bed adsorbs the particles and when the bed becomes full it needs to be cleaned. The cleaning is achieved by reversing the gas flow over the bed. Moving bed filters alleviate the need for periodic cleaning by flowing the media downwards and the gas upwards thus allowing for continuous use. A moving bed filter developed by Combustion Power Company claimed to have a collection efficiency of 93 % for particles < 4  $\mu\text{m}$  and greater than 99 % for particles > 4  $\mu\text{m}$  [14].

### 3.3.2 Tar Removal

#### 3.3.2.1 Tars

Tars can be classified into four categories: primary products, secondary products, alkyl tertiary products and condensed tertiary products. The primary products are derivatives of cellulose, hemicellulose and lignin and comprise relatively simple organic compounds. The secondary products are phenolics, which are aromatic alcohols, and olefins. Alkyl tertiary products are mainly methyl derivatives of aromatic compounds. Condensed tertiary products include benzene, naphthalene, anthracene and pyrene.

The main reason to remove the tars is that, when the temperature decreases in downstream processes, the tars will condense and damage heat exchangers and other equipment. The tar dew point is the determining parameter when the tars condense. The dew point is the temperature of the gas at which the partial pressure of the tars equals the saturation pressure. The dew point is also dependant of the composition of the tars. By decreasing the tar concentration, thus decreasing the tar dew point, condensation of the tars can be avoided [12].

Tar removal is one of the greatest technical challenges of gasification systems. The existing processes for tar removal can be divided into three categories; physical processes which is a separation process, thermal processes and chemical processes.

Physical processes include wet scrubbing, demisters and other processes. However, they are only effective at tar removal when the gas has been cooled to less than 100°C which is thermodynamically inefficient.

In the thermal process, the gas is passed through a reactor at high temperature. The high temperature decomposes the tars into carbon monoxide, hydrogen and other light gases. The primary tars are the easiest to decompose but the condensed tertiary products requires significantly higher temperatures in excess of 1000°C and high residence times. This results in higher material costs due to the use of expensive alloys that can withstand the high temperature. The high temperature cracking of the tars decrease the methane yield of the gasification.

### **3.3.2.2 Chemical Processes**

#### **Steam**

Adding steam and/or oxygen, increases the cracking rate of the tars in the temperature range 950-1250°C. Oxygen is effective in the range 600-700°C and primarily at cracking the primary products and to inhibit the formation of the aromatic compounds. However once benzene, the primary aromatic compound, has been formed, oxygen can not crack it. The addition of steam has been reported to produce tars that are more easily reformed catalytically. Steam also facilitates the water gas shift reaction and due to the equilibrium, adding more steam the reaction will produce more hydrogen and carbon dioxide [14].

#### **Catalytic cracking**

The catalytic cracking works just like thermal cracking only at a lower temperature. This has several advantages: the cracking can take place in the gasification reactor or in a downstream reactor. If the catalyst is used in the gasifier it can be mixed with the fluidising medium. The lower temperature also decreases equipment costs for the reactors.

The catalyst may be either metallic, such as nickel or aluminium, or a metal-oxide, such as dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ) or limestone ( $\text{CaCO}_3$ ). It has been reported that dolomite beds have cut tar production in half at 820°C. The addition of limestone in the reactor bed can also lower the sulphur contents according to the reactions (3) and (4).



However the calcium sulphate can be regenerated with carbon monoxide or hydrogen to form calcium oxide and sulphur dioxide. There is also the probability of forming calcium sulphide.

In research at Battelle Laboratories, the combination of DN-34, a proprietary catalyst made of “essentially alumina”, has shown a tar reduction of almost 100 %. It also shows potential to reduce polynuclear aromatic hydrocarbons (PAH) which are the most difficult tars to control. Other studies have shown tar reduction in excess of 95 % but at the cost of severe catalyst deactivation [14].

Catalytic cracking has been studied intensively in recent years but there are currently a limited number of commercially available systems.

### 3.3.3 Alkali

Alkali and alkaline earth metals, especially potassium, are prevalent in many biomass feed stocks. Alkali metals vaporise at the high temperature in the gasifier. When the temperature decreases, to around 600°C, in downstream processes, the alkali metal condenses. The alkali deposits on metal surfaces where it can cause corrosion and, if present in a gas stream, can cause erosion to turbine machinery. The alkali deposits on metal surfaces causes degradation in thermal transfer.

Alkali can be removed either by adsorption or by leaching. Adsorption can be categorised as physi-sorption and chemi-sorption. In physi-sorption the alkali are attracted by van der Waal’s forces. These bonds are weak and as a result the alkali can desorb easily.

In chemi-sorption, the bonding is a chemical bond thus making it much stronger than a physic-sorption. The stronger bond in chemi-sorption can classify it as irreversible. This is often preferred as it is less likely that the alkali is desorbed in inappropriate locations in the system.

When adsorption is used to capture alkali, the sorbent is known as an alkali getter and process is often referred to as “getting”. Bauxite has shown great potential as an alkali getter, with a removal efficiency of 99 % at a residence time of 0.2 s.

Leaching is accomplished by washing the biomass prior to gasification. Because of the solubility of alkali metals in water, more than 80 % of the potassium and sodium and more than 90 % of the chlorine can be removed [14].

### 3.3.4 Sulphur Capture

There are numerous processes for desulphurisation, but there are two methods that are commonly used to remove sulphur from biosyngas. Both methods use adsorption to remove sulphur from the gas stream and both methods requires rather clean syngas. The first method uses iron containing active carbon. With this process, sulphur contents of

1 mg/m<sup>3</sup> can be achieved. This is not sufficient for downstream catalysts such as the nickel-based catalyst used in the methanation process. 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) [15].

An alternative to zinc oxide beds is to use a wet process such as Rectisol®. The Rectisol® process can separate hydrogen sulphide from the stream with concentrations high enough to allow a Claus process. Rectisol® wash is also a very good process for carbon dioxide removal, see chapter 3.6.4, *Removal by absorption, scrubbing*.

Because of the low temperatures of the desulphurisation processes above and the higher temperatures upstream and downstream of the desulphurisation, other methods should be applied to increase the efficiency.

Zinc oxide beds has been operated at temperatures up to 650°C with good H<sub>2</sub>S and COS capture. The study showed that higher temperatures resulted in higher sulphur uptakes. Higher pressures also increase the efficiency of the zinc oxide bed. The sorbent was tested at temperature ranging between 250-650°C and pressures of 2-20 atm. Furthermore, the sorbent also showed great regenerability with air diluted with nitrogen at 823 K [16].

A problem with high temperature regeneration of zinc oxide beds is that volatile zinc compounds are formed. This can be avoided by using zinc titanate as sorbent. Zinc titanate has shown the same capability for sulphur removal as zinc oxide, but it is considerably more stable at elevated temperatures [17].

### **3.3.5 Water-Gas Shift**

The WGS reactors can be 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 (2) is exothermic.

The high temperature shift catalyst is typically iron oxide promoted with chromium. These catalysts are vulnerable to sulphur poisoning as in sulphur-rich systems; a cobalt-molybdenum catalyst must be utilised. The cobalt-molybdenum catalyst on the other hand requires elevated sulphur levels in the feed to maintain their activity. The high temperature shift occurs at a range of 300-500°C. When these catalysts are used, the reaction is often referred to as raw-gas shift or sulphided CO-shift. After the HT shift, the carbon monoxide content is approx. 3 vol %. The high temperature shift can occur without a catalyst depending on pressure at temperatures in excess of 900°C [5] [9].

Low temperature shift catalyst is based on copper-zinc oxide on an alumina support. These catalysts are extremely sensitive to sulphur poisoning. The sulphur content in the

feed is limited to < 0.1 ppm. The catalyst is active at a temperature range of 200-270°C which results in carbon monoxide content in the product gas to approx. 0.2-0.3 vol % [5]. The cobalt-molybdenum catalyst can reduce the carbon monoxide content to approx. 1.6 vol % (dry) which can be further reduced to 0.5-1.0 vol % (dry) in a two-stage system [5].

### 3.4 Synthesis Gas

Synthesis gas is the common name for gas containing carbon monoxide and hydrogen that is used in reactors to produce chemicals. There are a lot of products that can be manufactured from synthesis gas including methanol, FT-liquids, methane and ammonia. Synthesis gas is often obtained either from gasification or from reforming. A typical example steam reforming of natural gas followed by ammonia production. In ammonia production however, carbon monoxide is a catalyst poison and the synthesis gas is methanated after the water-gas shift reactor to eliminate carbon monoxide. Different syntheses require different ratio between hydrogen and carbon monoxide.

#### 3.4.1 Methanation

In order to increase the methane contents of the product gas, methanation is required. The reaction is highly exothermic and because of that it is important to remove the heat from the reactors. There are two main applications for methanation; methanation for the elimination of carbon monoxide in hydrogen production, such as the production of ammonia, and for SNG production. The two applications differ very much mainly because in the latter case, methanation is performed with the goal to have as high hydrogen conversion as possible [9].

Methanation or methane synthesis occurs with reaction (5) and (6) which are 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 [9].



The catalyst used in methanation reactors is a nickel-based catalyst supported on alumina, kaolin or calcium aluminate. Sulphur as well as arsenic are poisons which must be removed from the system. The catalyst contain < 15 wt % nickel and precaution must be taken to prevent the formation of the highly toxic nickel carbonyl Ni(CO)<sub>4</sub>. The formation is favoured by low temperatures < 200°C and high carbon monoxide partial pressures. It is therefore important to have proper procedures on start-up and shutdown [9].

Carbon monoxide also reacts with iron to form iron carbonyl which is poisonous and causes corrosion problems. Iron carbonyl also decomposes on the catalyst when the temperature is increased. Thus carbon monoxide must be heated in stainless steel heat exchangers. Years of plant operations have shown that with the right precautions, carbonyl formation can be suppressed successfully [9].

Carbon dioxide, in reaction (6), is first converted to carbon monoxide with the reverse shift reaction and then it is converted to methane according to reaction (5) [5]. The Boudouard reaction (7) will be thermodynamically favoured at elevated temperatures, as at the outlet of the reactor. Reaction (8) can also pose a problem if care is not taken. However if temperatures are kept moderately low and small residual hydrogen exists in the gas outlet, it can be avoided [9].

Typically the reaction is operated at inlet temperatures of 250-300°C and at pressures in excess of 30 bar. The high pressure favours the equilibrium and also improves the kinetics [9].

#### 3.4.1.1 H<sub>2</sub>/CO-ratio

Synthesis gas for methane production is often classified by their stoichiometric number (SN) which is the ratio between the reactable hydrogen and carbon oxides according to equation (A).

$$SN = \frac{\eta \cdot v_{H_2}}{3v_{CO} + 4v_{CO_2}} \quad (A)$$

where  $\eta$  represents the equivalent hydrogen consumption required for hydrogenation of unsaturated and higher hydrocarbons in methane production. The specifications for SNG requires < 10 vol % H<sub>2</sub> which result in a SN < 1.05, but due to the restriction of carbon dioxide in SNG, the gas should meet 0.98 < SN < 1.03.

For stoichiometric methanation, there is little risk for carbon formation according to the Boudouard reaction, even at elevated temperatures of up to 700°C. This becomes a problem at lower SN. Lower SN also requires carbon dioxide removal to a greater extent. This is the most commonly used process of the commercially available reactors.

#### 3.4.1.2 Reactor Designs

In order to control the heat of reaction in methanation there are several different reactors that have shown success.

There are a number of commercially available methanation systems in use. Most of them are designed for methanation of syngas produced from coal gasification at high pressures. Thus, the methanation reactors are designed for pressures of 40-60 bar [12].



The cooling method utilised in these types of reactors increases the difficulties of controlling the heat of reaction. As the methanation reactions are highly exothermic, the temperature control becomes increasingly difficult and thus, hot-spots can pose a problem in TWR reactors [9].

The main advantage with the plug-flow reactor is that only one reactor is necessary and this is because the reactor can contain any number tubes. This results in a lower investment and operating costs. The biggest disadvantage of the reactor is the problems involved in replacing depleted catalyst [9].

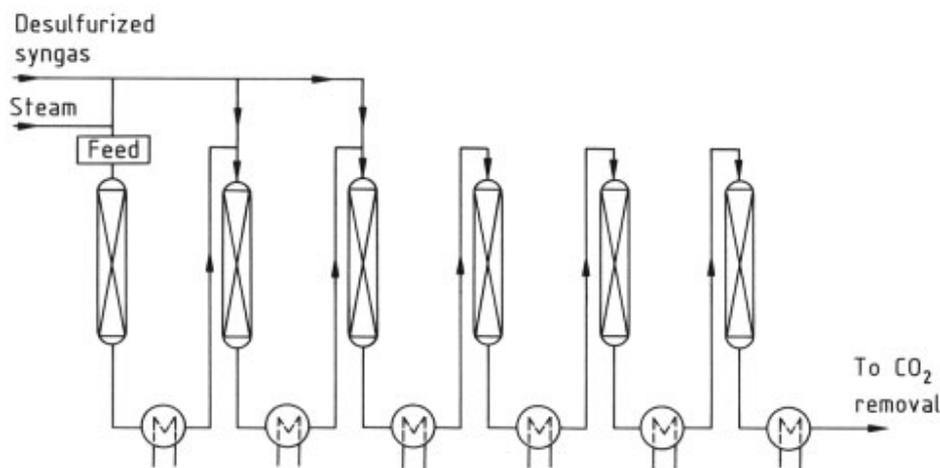


Figure 8: Single-pass throughwall cooled methanation process [9].

### 3.4.1.5 Fluidised-bed Reactor

Methanation as well as other highly exothermic processes can favourably be carried out in a fluidised reactor. The main advantages with fluidised bed reactors is; evenly dispersed catalyst and reactant gases, low thermal gradients thus better temperature control and easy catalyst replace.

Only one process found in the literature uses a fluidised-bed – the *Comflux* methanation. It was operated 1980-1985, for about 8000 h and was developed by Thyssengas. The process was run at 60 bar and with a H<sub>2</sub>/CO of 2.7-4, this has several advantages such as minimising the carbon dioxide formation from the water-gas shift reaction [19].

### 3.4.2 Fischer-Tropsch

Fischer-Tropsch, FT, synthesis is a non-selective synthesis that produces a wide range of hydrocarbons with 1 to > 100 carbon atoms. C<sub>1</sub> compounds however, can be produced with 100% selectivity and heavy waxes have high selectivity. The mechanism is assumed to be step-wise growth of the hydrocarbon, one carbon atom being added at a time. There are two processes that are generally used in FT synthesis; high temperature, HTFT and low temperature, LTFT.

The high temperature process operates at 330-350°C and uses a fused iron catalyst. The high temperature synthesis is favourable for petroleum and light olefin products. Low temperature synthesis is operated at 220-250°C over either an iron catalyst or a supported cobalt catalyst. The low temperature favours heavier products such as waxes and diesel products [9]. The catalysts above are rapidly poisoned by sulphur. Nickel and ruthenium can also be used as catalyst in LTFT synthesis [20].

The reactions may be represented by reactions 9A, 9B, 10A and 10B, where A denote reactions yielding water and B yielding carbon dioxide. The heat-of-reaction is very high, ranging from approx. -200 kJ/mole for methane to approx. -860 kJ/mole for toluene according to the reactions A. Reactions B are even more exothermic.



The water-gas shift reaction is thermodynamically favoured and any water vapour in the product gas is a result of slowness of the subsequent shift reaction [20].

The carbonyl formation mentioned in methanation above, also occurs in FT synthesis at low temperature. This is one of the factors limiting the FT synthesis to relatively low pressures [20].

### 3.4.2.1 Reactor Systems

Commercially there are two reactor types for LTFT synthesis that are operated. SASOL and Shell have operated a tubular fixed-bed reactor for several decades with success in South Africa and Bintulu, Malaysia respectively.

The SASOL reactor is catalysed by iron and Shell's reactor uses a cobalt catalyst. SASOL also operates a slurry bed reactor which has been successful. Both reactor types operate at pressure of 2.5 MPa. Advantages for the slurry reactor compared to the tubular fixed-bed include much higher capacity and a much smaller pressure drop over the reactor.

There is also a more significant advantage with the slurry bed; the mixing of the reactor allows almost isothermal operation. The advantage of this is that there will not be any temperature gradients, thus allowing much higher operating temperatures and increased reaction rates [9].

For HTFT synthesis, there are currently two reactor systems operated commercially. The circulated fluidised-bed reactor has been operated by SASOL since the 1950s and it uses fused iron catalyst. The catalyst and syngas is circulated in the reactor system. The reactor system is complex and it requires large amounts of catalyst. The amount of

catalyst results in relatively high pressure drops. This and other disadvantages are eliminated when using a SAS reactor. SAS or SASOL Advanced Synthol reactors are similar to bubble column reactors. The reactor vessel contains a fluidised bed consisting of fused and reduced iron catalyst. The syngas is bubbled through the bed by means of a distributor at the bottom. The vapour pressure is about 2.5 MPa and the temperature 340°C at the vapour phase. The advantage of the SAS reactor over the CFB reactor is its simplicity and better heat removal. The increased heat removal allows for higher loads and better scaling of the reactor [9].

## **3.5 Gas Upgrading**

After methanation or FT synthesis, the gas must be upgraded. For methanation, the upgrade basically consists of removing water, carbon dioxide and additional products from the gas stream. For FT synthesis, a distillation unit is required to separate the different fractions and an additional hydro-cracker may be necessary depending on operating conditions. After the hydrocarbon upgrade in the FT system, the gas exiting the distillation column has to be upgraded as in the case for methanation in order to recover the light hydrocarbons such as methane, ethane etc.

### **3.5.1 Carbon Dioxide Capture**

In order to meet the requirements for SNG, carbon dioxide contents must be lowered significantly from the gas stream. There are several commercially available processes to remove carbon dioxide; most of them operate at low temperature.

### **3.5.2 Membrane Separation**

In membrane separation, the gas is passed through a membrane which retains the methane and lets carbon monoxide and smaller molecules pass. The membranes can be organic liquids, ceramic or metallic material or polymers. The methane is retained on the high pressure side of the membrane, thus eliminating some of the necessary compression prior to output on the gas grid. Membrane separation operates at pressure range 25-40 bar [15].

### **3.5.3 Pressure Swing Adsorption**

Pressure Swing Adsorption, 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 adsorbers are required for continuous operation but PSA units are often composed of four to ten adsorbers. 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 [9]. Hydrogen sulphide adsorbs irreversibly on the packing and must be removed from the gas prior to injection [15].

### 3.5.4 Removal by Absorption, Scrubbing

Carbon dioxide is soluble in water and the solubility increases with the pressure. Methane is also soluble in water and a flash column is required to separate it from the water. The carbon dioxide is released when the pressure is lowered and the water can be recirculated.

Selexol® is a registered trademark for a polyglycol ether that is used as a scrubbing liquid. Carbon dioxide is soluble in the liquid but it also removes water and hydrogen sulphide. The gas enters the absorber at the bottom and the scrubbing liquid is injected at the top. As the gas moves up in the absorber, the gas is cleaned from carbon dioxide, water and other impurities. The regeneration is performed in a similar column but with air blown in from the bottom. Water-scrubbing, as mentioned above works in the same way [15].

The Rectisol® process (figure 9), developed by Linde and Lurgi, uses methanol cooled down to subzero temperatures. At this temperature both carbon dioxide and hydrogen sulphide are very soluble. The selectivity for hydrogen sulphide and carbon dioxide absorption in the Rectisol wash is very good and it allows for a sulphur-free carbon dioxide recovery. The Rectisol wash is a very flexible process which can be adapted to many specific requirements. It is possible to remove CO<sub>2</sub> and H<sub>2</sub>S down to levels of < 10 vppm and < 0.1 vppm respectively. The tail gas consists mainly of N<sub>2</sub> and CO<sub>2</sub> which means that the tail gas can be released, unprocessed, to the environment [21].

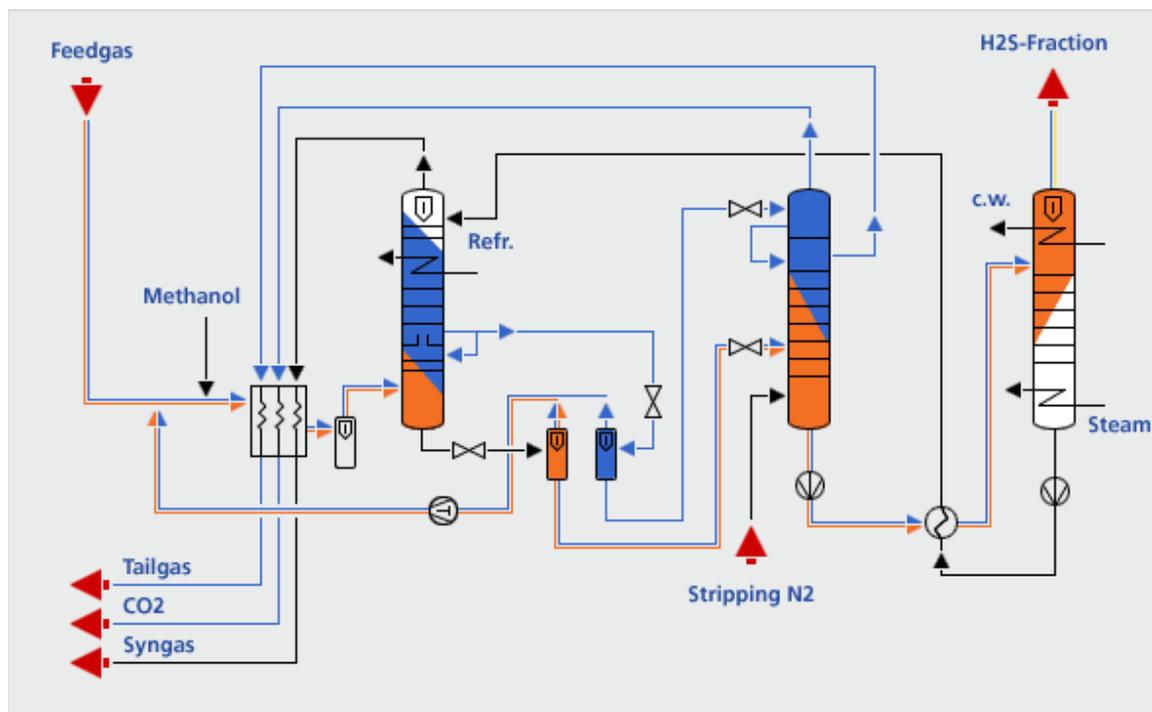


Figure 9: Rectisol® process by Linde and Lurgi [22].

Wet processes have good selectivity and also have the advantage of hydrogen sulphide and water removal. They are however operated at low temperature which is very disadvantageous for the overall energy efficiency.

### **3.5.5 Cryogenic Separation**

In cryogenic separation, the gas is cooled to very low temperatures, typically below  $-150^{\circ}\text{C}$ . The separation is based on different boiling temperatures of substances in the gas. As the gas is cooled, substances with higher boiling point condense and can be removed while the other substances remain in the gas [9]. The advantage with cryogenic separation in conjunction with gasification could be that it enables oxygen-blown gasification without too much added cost.

### **3.5.6 High Temperature Removal**

High temperature carbon dioxide removal techniques are under development. The advantage with high temperature capture is the elimination of cooling and heating of large gas streams that is thermodynamically inefficient. In a recent study, an eutectic salt promoted lithium zirconate sorbent has been tested. The results show a great potential for high temperature carbon dioxide capture at temperatures of  $600\text{-}700^{\circ}\text{C}$  [23].

## **3.6 Steam Generation**

Steam is produced in a boiler or a steam generator. When the heat source is nuclear power or fossil-fuel based boilers the term generator is often used. Boilers using hot gas as heat source are generally called heat recovery steam generators, HRSGs. All heat transfer in a HRSG takes place convectively [24].

## **3.7 Power Generation and Heat**

Any excess heat in the processes should be utilised to produce electricity which can be used on-site or provided to the power grid. The excess heat that has too low exergy to generate power should be used as district heating. There are many alternatives to produce electricity and most of them use a generator powered by an engine or a turbine, but there is also the possibility to use a fuel cell.

### **3.7.1 Turbines**

Plants that incorporate excess steam can generate on-site power by using a steam turbine. The steam turbine has been widely used in power generation for over a century and enables power output as well as district heat. For maximum power output, a condensing turbine should be used. However, the temperature after a condensing turbine is too low for district heating. In order to improve the overall efficiency of the plant, the steam should be outputted from the turbine at a higher pressure and then condensed in a heat exchanger to supply district heating.

Gas turbines or combustion turbines are widely used because they offer high power output yet being relatively compact. The efficiency of a gas turbine is not as high as that

of a steam turbine with a boiler. Gas turbines are used in the most modern power plants such as Integrated Gasification Combined-Cycle, IGCC, and combined-cycle power plant and in space-limited sites [25].

### **3.7.2 Combustion Engines**

Combustion engines for power generation such as diesel engine-powered generators offers high efficiency (up to 45 %) while still being compact and cheap. However, the emissions and the limited power output, results in a limited number of uses such as back-up power and peak-hour reserves [25].

### **3.7.3 SOFC, Solid Oxide Fuel Cells**

For electric power generation, as an alternative to using natural gas powered gas turbines, solid oxide fuel cells, SOFC, can be utilised. These fuel cells operate at a high temperature, typically in the range 900-1000°C and they have much higher efficiencies (55-70 %) than turbines. SOFC can be operated on a wide range of fuels from pure hydrogen to a mixture of carbon monoxide, methane and hydrogen. They have a high tolerance to sulphur contamination [10].

FuelCell Energy, FCE, has been selected by the U.S. Department of Energy, DOE, to develop a multi-MW coal based SOFC. The goal of the program is to develop 100 MW and larger systems with efficiencies over 50 % when converting coal to electric energy. The average efficiency of today's coal-based power plants is around 35 % [26].

## 4 Process Design

For mass and energy balance calculations, a flow-sheeting application was chosen. Aspen Plus was the application of choice due to availability. Simulation of gasification in Aspen Plus is not possible with the default unit operations and as a result, the gasification outlet streams are the starting point in these simulations.

The gasification techniques examined in this study requires different downstream equipment. The difference lies in the gas composition, temperature and pressure. The gasifiers that have been included in this thesis are; pressurised oxygen-blown entrained-flow gasifier, pressurised oxygen-blown fluidised-bed gasifier and an indirect gasifier. All gasifier data where supplied by E.ON Gas Sverige AB.

For sulphur removal, two processes has been examined; the Rectisol process and a zinc oxide bed. The Rectisol is expected to have a negative impact on the overall efficiency due to the subzero temperature but it has the advantage of removing CO<sub>2</sub> prior to methanation as well. Removing carbon dioxide before the methanation reactor(s) favours the equilibrium of both the water-gas shift and the methanation.

The target production of the plant is 100 MW SNG based on the lower heating value 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 gasifier data provided by E.ON Gas Sverige AB did not contain any tars or chars and thus, no tar-removal equipment was necessary.

For the methanation, two different approaches have been studied; adiabatic reactor, in the form of recycle-gas reactors and isothermal reactors. The recycle-gas processes are based on the TREMP™ process and the isothermal reactor approach is similar to a fluidised bed methanation process. The methanation reactors are fed with streams at 290°C. For the recycle gas reactors, the recycle ratio is set so that the temperature exiting the first reactor reaches 675°C. The isothermal reactor is operated at 310°C and the cooling is provided as boiling water without super-heating. The high temperatures allows for 200°C super-heated steam at 90 bar. The biomass drying is achieved by mixing a stream of liquid water with a hot gas stream. The temperature of the gas exiting the dryer is set to 10°C higher than the temperature of the exiting biomass.

Fischer-Tropsch synthesis has also been examined because of the advantages of producing a gas with higher hydrocarbons than methane such as propane. The addition of higher hydrocarbons in the producer gas increases the Wobbe Index of the biogas and thus, allows more impurities in the gas such as carbon dioxide.

Because of the choice of flow-sheeting application, Fischer-Tropsch synthesis was not possible. This is because of the limited number of unit operations supported by Aspen Plus in its base state. Modelling the Fischer-Tropsch synthesis may have been possible, but due to time limitations it was ruled out. The same applies for biomass related operations such as grinding, drying and, as previously mentioned, gasification.

For all processes water and impurities such as carbon dioxide, carbon monoxide and nitrogen need to be removed from the product stream. For this a PSA unit is used. The methanation process does not produce any carbon dioxide; however some carbon monoxide is shifted to carbon dioxide in the methanation reactors. But overall, the carbon dioxide levels are low.

The PSA unit is sensitive to condensing water and thus the water content in the gas stream must be kept below the dew point. This is achieved by first lowering the temperature prior to the PSA unit to allow some water to condense and then increasing the temperature.

Fresh air is assumed to have a temperature of 20°C.

Production of oxygen for gasification is assumed to consume 0.5 kWh<sub>el</sub> / Nm<sup>3</sup> [27].

The simulations were performed for the twelve base cases, table 3, with additional simulations to evaluate if system pressure or isothermal methanation temperature affects the efficiency to SNG. 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 3: The twelve base cases between gasifiers and methanation/gas cleanup.**

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

In order to evaluate the system thoroughly, all gasifiers have to be coupled with all different downstream processes. This results in a total of twelve process alternatives to evaluate. The results will also show the gasifier best suited for a specific process or for all processes, if that is the case.

As previously mentioned, the different gasification techniques require different downstream equipment. This affects the amount of power and district heating generated.

The Rectisol wash has a huge negative impact on the simulation time and the systems ability to converge. The added mass balance calculations that is necessary for the absorbers and stripper increases the simulation time by a significant amount. In addition



The zinc oxide desulphurisation system is described in figure 10. Starting at the gasifier, which depending on the gasifier used requires steam and/or oxygen. After the gasifier, heat is recovered by steam generation and/or superheating prior to the zinc oxide bed. The temperature of the syngas is cooled to 300 °C from the gasifier output temperature. After the desulphurisation the gas is cooled and compressed to the system pressure which is 30 bar(a) for all systems except for the pressure sensitivity analysis tests. The gas is cooled after the compressor and steam is added prior to the water-gas shift reactor. A part of the stream is bypassed the reactor. The bypass amount, the added steam and the reactor inlet temperature is controlled to achieve a H<sub>2</sub>/CO ratio of 3.

The gas is cooled again to the inlet temperature of 290 °C for the methanation reactor(s). Large amounts of heat is generated in the reactor(s) which either recovered directly in the reactor as for the isothermal reactor or by cooling the exiting gases. Heat is recovered by steam generation.

More heat is recovered and water is removed from the steam prior to the PSA. The PSA is set to a methane recovery of 99 %. Residual components such as carbon monoxide, hydrogen and methane in the PSA off-gas are catalytically combusted. The off-gas is mixed with heated air and used in the biomass drying. Heat recovery for district heating is applied where appropriate.

## 4.2 Rectisol Wash Flow-sheet

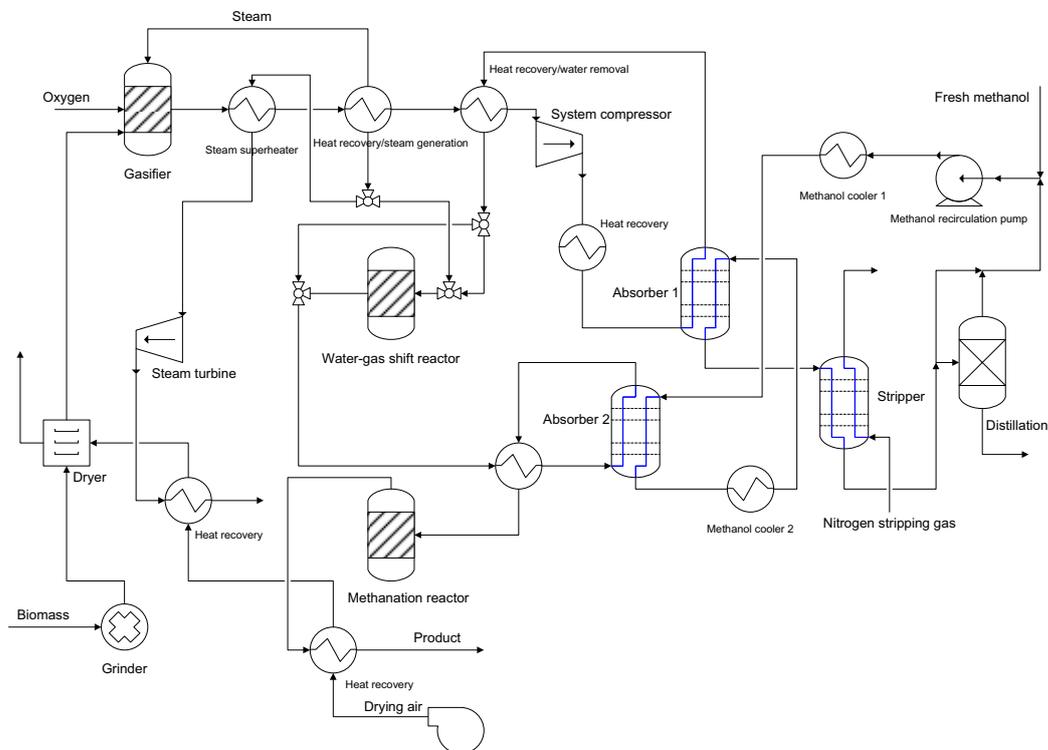


Figure 11: Process flow-sheet for the systems using a Rectisol wash.

The systems using the Rectisol wash follows the flow-sheet in figure 11. Starting at the gasifier, the gas is cooled and heat is recovered by superheating and steam generation. The cooled gas exiting the first absorber is heat exchanged with the hot gases from the gasifier, thus cooling the stream and removing water prior to compression in the system compressor. Heat is again recovered prior to the first absorption column where methanol is used to clean the gas from sulphur compounds.

The gas then exits the absorber and is heated prior to water-gas shift. Steam is added, the bypass ratio and the inlet temperature is controlled to shift the  $H_2/CO$  ratio to 3. The gas is then fed to the second absorber where carbon dioxide is removed along with additional water. Exiting the second absorber is a stream containing carbon monoxide, hydrogen, methane and residual components such as methanol, carbon dioxide and water. The purified stream is fed the methanation reactor(s). Heat is recovered as described in the previous chapter. Air to the drying is heated at a number of different locations depending on where the heat is available, this is system dependant.

Fresh methanol is mixed with regenerated methanol, cooled and then fed to the second absorber to absorb carbon dioxide. The exiting methanol is saturated with carbon dioxide and is cooled prior to injection in the first absorber. The exiting methanol is stripped in nitrogen and part of the stream is distillated.

### 4.3 Aspen Plus

Aspen Plus is a process modelling tool that allows for simulation of large and complex systems. Aspen Plus is one of many software packages in the Aspen family. Aspen stands for Advanced System for Process Engineering. The strength of Aspen Plus lies in its vast library of physical properties for substances. There are a few critical facts that need to be clarified though. Only components that have been specified in the program setup can exist in the system. This can result in simulation results that are inaccurate in comparison to experimental data. The components that were specified for all systems are;  $CO$ ,  $CO_2$ ,  $H_2$ ,  $CH_4$ ,  $H_2O$ ,  $O_2$ ,  $H_2S$ ,  $N_2$ ,  $NH_3$ ,  $SO_2$  and  $COS$ . Aspen also have difficulties with solids, and therefore solid carbon was not specified as a valid component. As a result, carbon formation in the methanation cannot be evaluated.

Aspen Plus simulates stationary systems and it calculates heat- and energy balances. There are additional tools for simulation such as dynamic systems but these were not used in this thesis. When the system changes, for example as a result of adding or removing equipment, the simulations need to be rerun. Aspen Plus does not calculate the affect of a specific change.

All changes to the system are handled by *design specifications* which are a means of varying variables based on a number of defined parameters.

Aspen Plus is developed and sold by AspenTech [28].

### 4.3.1.1 Aspen Specific Configuration

All reactors are based on *REquil* which is a reactor that allows all reactions to reach equilibrium unless specified to restrict the equilibrium. No restrictions were necessary for the simulations that were run and as a consequence, all reactions reach equilibrium. For the methanation only reaction (5) was specified due to the low shift activity for the methanation catalyst.

The property method and base method were both set to NRTL.

All compressors and turbines operate isentropic with an efficiency of 0.72 and all heat exchangers are operated with a heat-transfer coefficient of 0.85 kW/m<sup>2</sup>°C for all possible configurations, be it liquid-liquid or gas-gas. The heat exchangers are also assumed to have 100 per cent efficiency, meaning that all heat that is available is transferred between the streams without losses. Where cooling or heating a stream by heat exchanging with another stream, it is assumed that the temperatures of the streams can differ with a  $\Delta T$  of 10°C.

The heat losses for heat exchangers apply to all apparatus.

The drying is simulated by mixing a gas stream with a water stream. The amount of water that needs to be evaporated from the biomass is calculated using equation (B).

$$\dot{m}_{\text{H}_2\text{O}} = \frac{\dot{m}_{\text{biomass}} \cdot 0.85}{0.5} - \dot{m}_{\text{biomass}} \quad (\text{B})$$

where  $m_{\text{biomass}}$  is taken from appendix B. 0.85 is the percentage of dry substance after drying and 0.5 before drying. The drying does not take into account the heat necessary for heating the dry substance in the feed stock.

The oxygen production for the processes that require oxygen (entrained-flow and fluidised-bed gasifiers) has been included, by calculating the required energy demand.

Due to the complexity of the Rectisol process, the limited amount of time for simulation and some Aspen Plus constraints, a simplified process was developed that is fairly accurate. It does not however separate sulphur from carbon dioxide and the entire gas stream is left as a tail gas, figure 12.



The methanol is recirculated between the two absorbers, the stripper. The stripped methanol is cooled and injected at the top of the second absorber to remove carbon dioxide from the gas. After the column it is cooled again prior to injection in the second column where sulphurous compounds are removed from the gas. The methanol is then stripped in nitrogen in the stripper. Due to water accumulation in the system, part of the methanol stream is distilled.

The first simulations were performed by a simple recycle of methanol from the stripper with a partial distillation of the stream. This meant complications because of the way Aspen Plus handles its design specifications. The initial testing resulted in methanol flows in excess of 100 kg/s, in most cases the simulations could not be completed, so another approach was necessary.

The model that was developed is presented in figure 12. Instead of recirculating the methanol from the stripper and distillation column, it is a simulated recycle. No methanol is recycled for the system and thus Aspen Plus was able to complete the simulations. This is how the system works and what assumptions it is based on.

First and foremost, the only reason to simulate a recycle is to see the impact that the soluble impurities has on the system. This is accomplished by separating out the used methanol (box above distillation) and mixing the fresh methanol with the impurities. Using only this approach would result in a higher cooling need as the exiting methanol is cooler than the fresh. The temperature of the mixed stream of fresh and used methanol is another parameter that needed to be simulated.

The white box (top left of distillation) is a stream duplicator which takes one stream and outputs two or more identical streams. The first stream is the stream that the impurities are taken from and the second stream is used to mix the simulated fresh methanol (top right stream) with the used methanol. This stream will have the exact same physical properties as a recirculated stream would. The final manipulation was to take the temperature of this mixed stream and apply that to the actual methanol stream used in the system (heat exchanger before recirculation pump).

## 5 Results

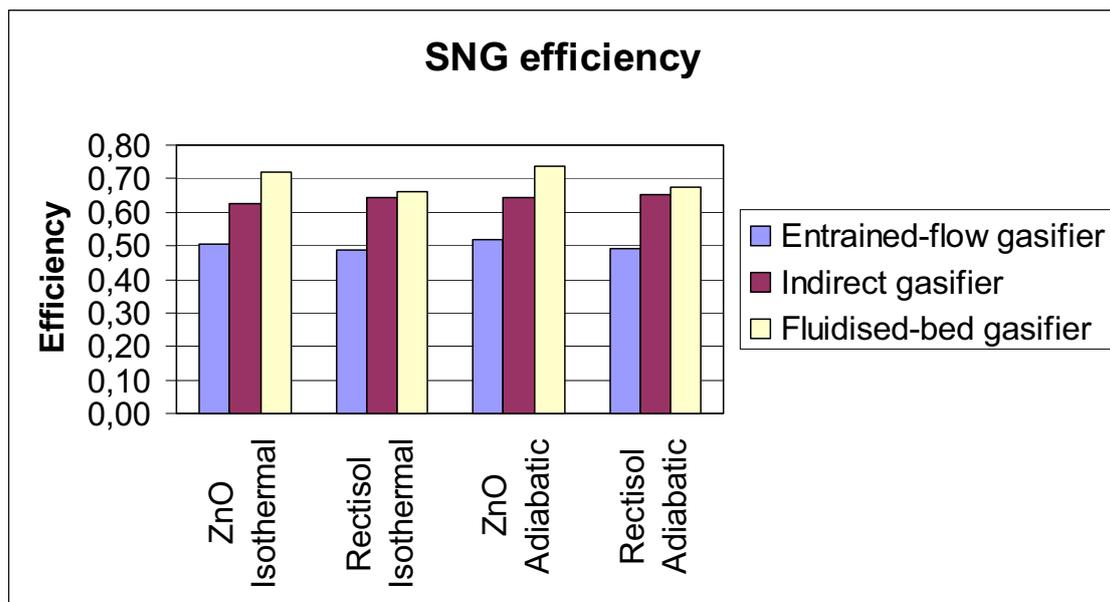
All systems are evaluated based on their efficiency to SNG. Efficiency is defined as in equation (C)

$$\eta = \frac{\text{Energy}_{\text{SNG}}}{\text{Energy}_{\text{Input}}} \quad (\text{C})$$

Input is the total input including biomass, oxygen and drying were necessary. Power is considered as input if there is a power deficiency. All system includes drying of the biomass. For the fluidised-bed, which has the highest demand on moist content, some external energy was required for drying. Recovery of methane in the PSA was set to 99 %, which is the highest that industrial systems can achieve. See chapter 5.2 for simulations results of methane recovery in the condensed water stream. Units are in MW for figures 14-25 below. The parameters in table 4 are set for all systems unless otherwise specified.

**Table 4: System parameters.**

System parameter	Value
System pressure	30 bar(a)
Target SNG production	100 MW
Steam pressure	90 bar(a)
H <sub>2</sub> /CO-ratio	3
PSA methane recovery	99 %



**Figure 13: The efficiency to SNG for the systems at 30 bar (a).**

The fluidised-bed and the indirect gasifier have the highest efficiency to SNG, figure 13. Table 5 below, lists the efficiencies in numbers.

The reason for the lower efficiency for the entrained-flow gasifier lies both in the efficiency of the gasifier but also in the methane output from the gasifier. A high methane output will increase the SNG efficiency as is seen for the other two gasifiers. The fluidised-bed has the highest efficiency and also the highest methane output from the gasifier.

It should be noted that for the zinc oxide systems, almost 10 % methane is lost in the condensed water prior to the PSA unit where additional methane is lost. If the methane in the condensed water could be used without too much additional cost the efficiency would increase even further.

There are only small differences between the fluidised-bed and indirect gasifiers for the Rectisol wash systems, figure 13, when comparing to zinc oxide systems. The reason for the similar results lies in the drying. There is not enough heat available in the Rectisol wash systems for the high requirement for moist content that the fluidised-bed gasifier has, figure 22-25. The drying impact is less evident for the fluidised-bed systems with zinc oxide desulphurisation.

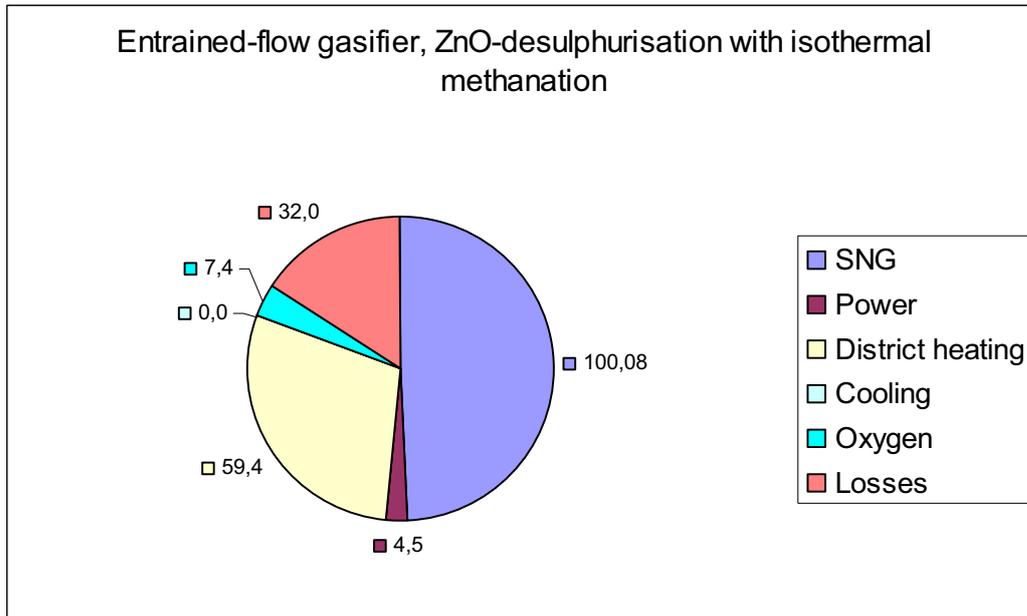
**Table 5: SNG efficiencies for the systems at 30 bar(a) in percentages.**

<b>Gasifier</b>	<b>Entrained-flow</b>	<b>Fluidised-bed</b>	<b>Indirect</b>
Isothermal methanation/PSA	50	72	63
Isothermal methanation/Rectisol	49	66	65
Adiabatic methanation/PSA	52	74	65
Adiabatic methanation/Rectisol	49	67	65

The efficiency for the Rectisol wash should be lower because of some methane loss due to absorption in the methanol. But as mentioned previously, this effect had to be removed due to Aspen Plus limitations. There is also a considerable cooling need in the Rectisol process, results in figure 16-17.

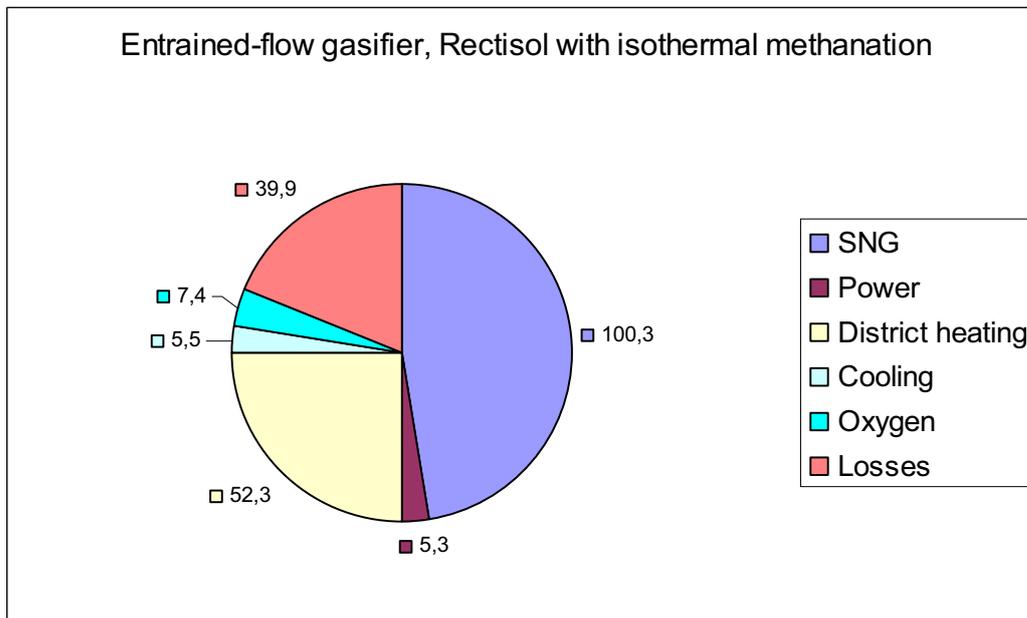
## **5.1 Entrained-flow Gasifier Results**

Figure 14-17 shows the results from the systems utilising an entrained-flow gasifier. Units are in MW.



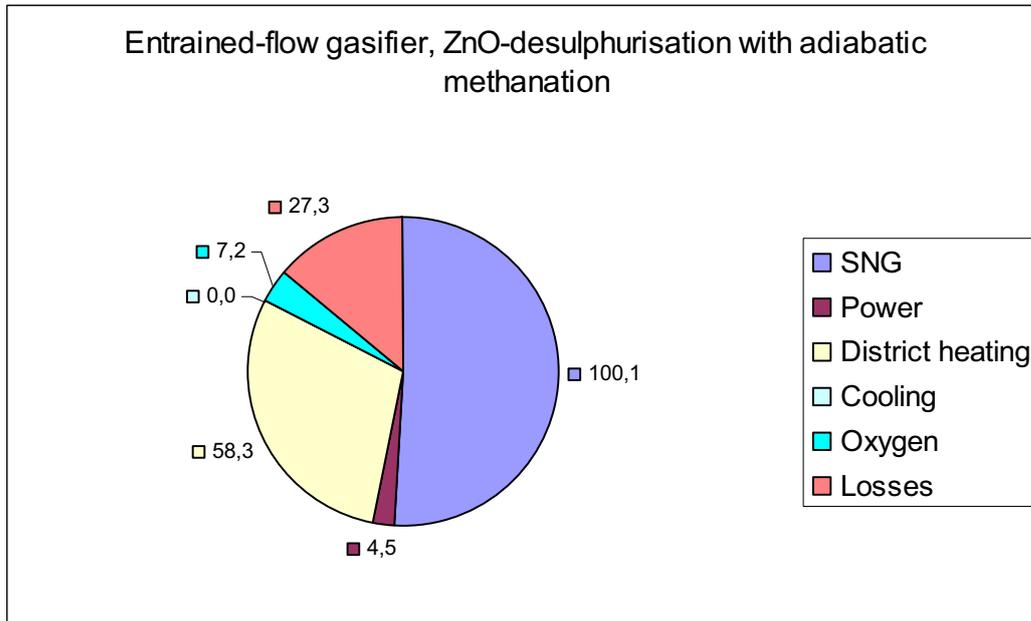
**Figure 14: ZnO-desulphurisation, PSA gas cleanup and isothermal methanation.**

Total input for the system in figure 14 was 199 MW.



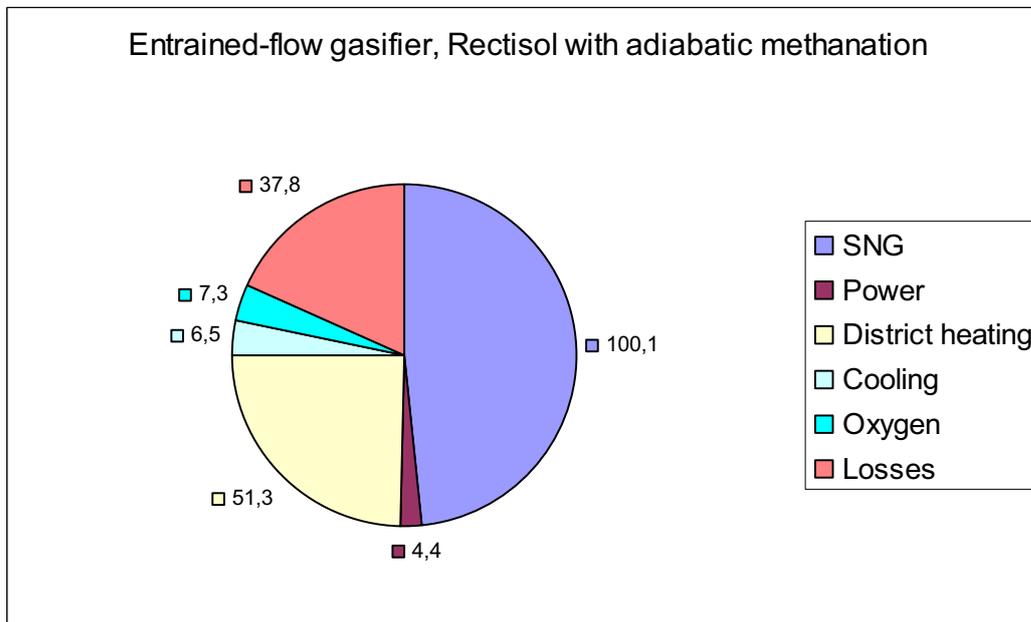
**Figure 15: Rectisol gas cleanup with isothermal methanation.**

Total input for the system in figure 15 was 205 MW.



**Figure 16: ZnO-desulphurisation, PSA cleanup and adiabatic methanation.**

Total input for the system in figure 16 was 193 MW.



**Figure 17: Rectisol gas cleanup with adiabatic methanation.**

Total input for the system in figure 17 was 203 MW. The results from the entrained-flow gasifier simulations show that the SNG efficiency is about the same, around 50 %. The Rectisol wash however, has more losses and requires more energy, typically for cooling. The adiabatic systems show higher SNG efficiency and lower losses than the isothermal systems.

## 5.2 Indirect Gasifier Results

Figure 18-21 shows the results from the systems utilising an indirect gasifier. Units are in MW. Negative values for power indicate a power need and that is included in the input.

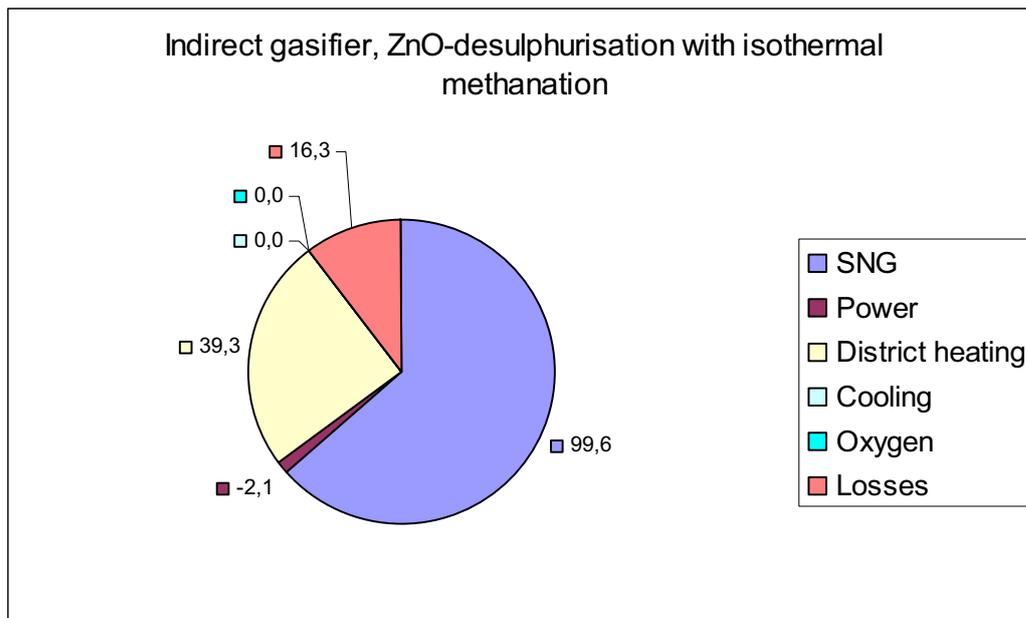


Figure 18: ZnO-desulphurisation, PSA cleanup and isothermal methanation.

Total input for the system in figure 18 was 161 MW.

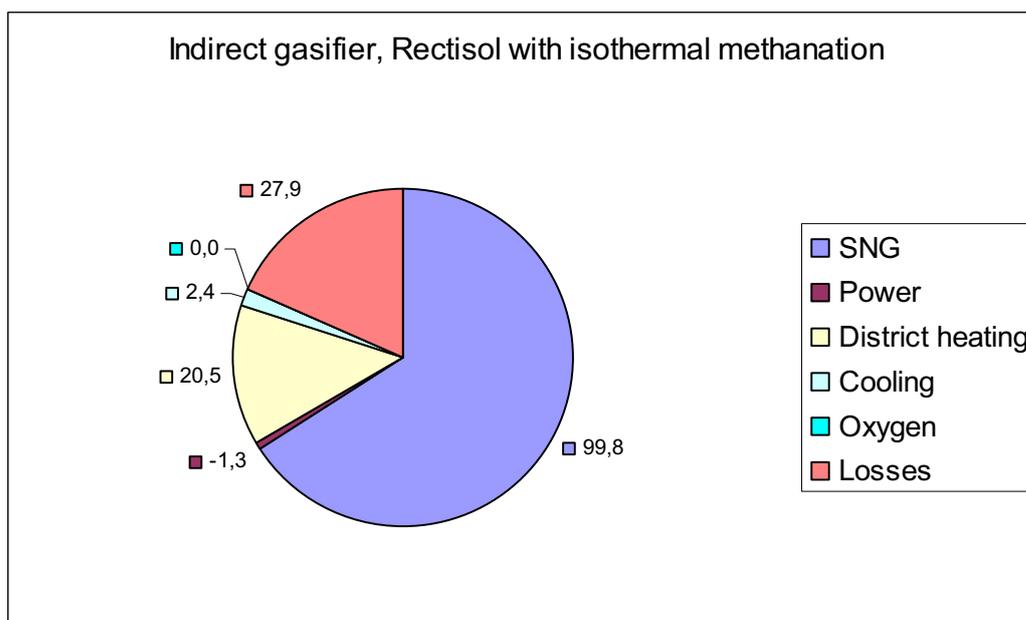
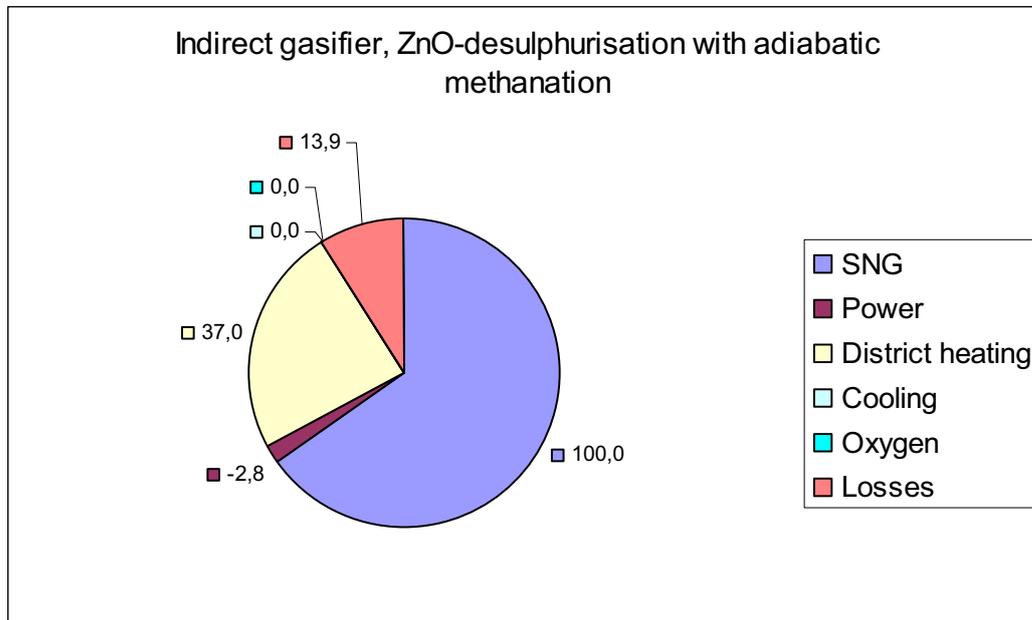


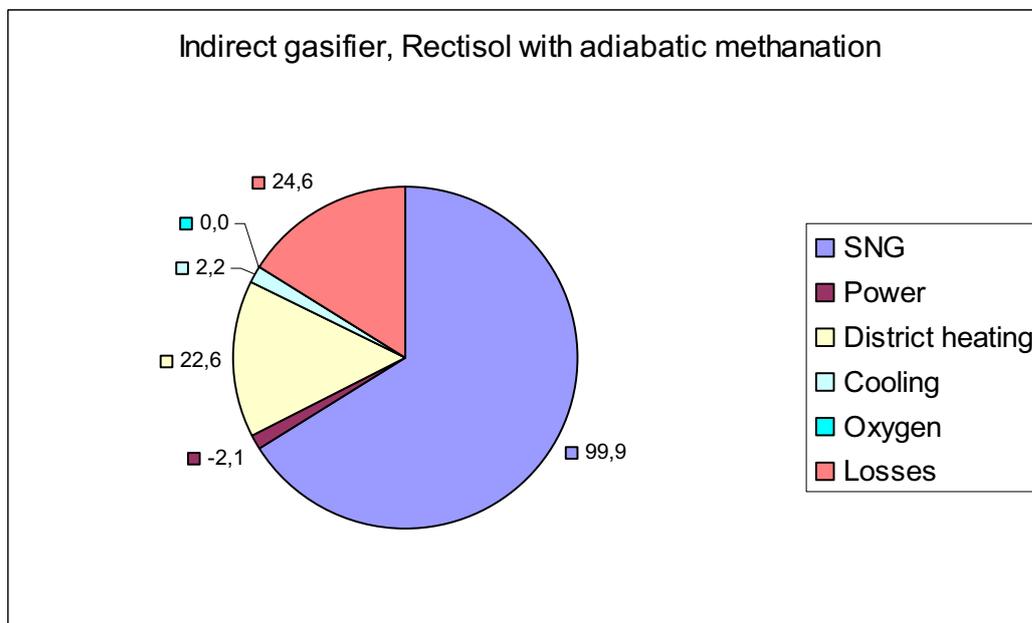
Figure 19: Rectisol gas cleanup with isothermal methanation.

Total input for the system in figure 19 was 156 MW.



**Figure 20: ZnO-desulphurisation, PSA gas cleanup and adiabatic methanation.**

Total input for the system in figure 20 was 158 MW.



**Figure 21: Rectisol gas cleanup, adiabatic methanation.**

Total input for the system in figure 21 was 155 MW. The indirect gasifier has an efficiency to SNG of about 66 %. But that comes at the expense of decreased district

heating and power compared to the entrained-flow gasifier. The indirect gasifier also has lower losses than the entrained-flow gasifier.

### 5.3 Fluidised-bed Gasifier Results

Figure 22-25 shows the results from the systems utilising an fluidised-bed gasifier. Units are in MW.

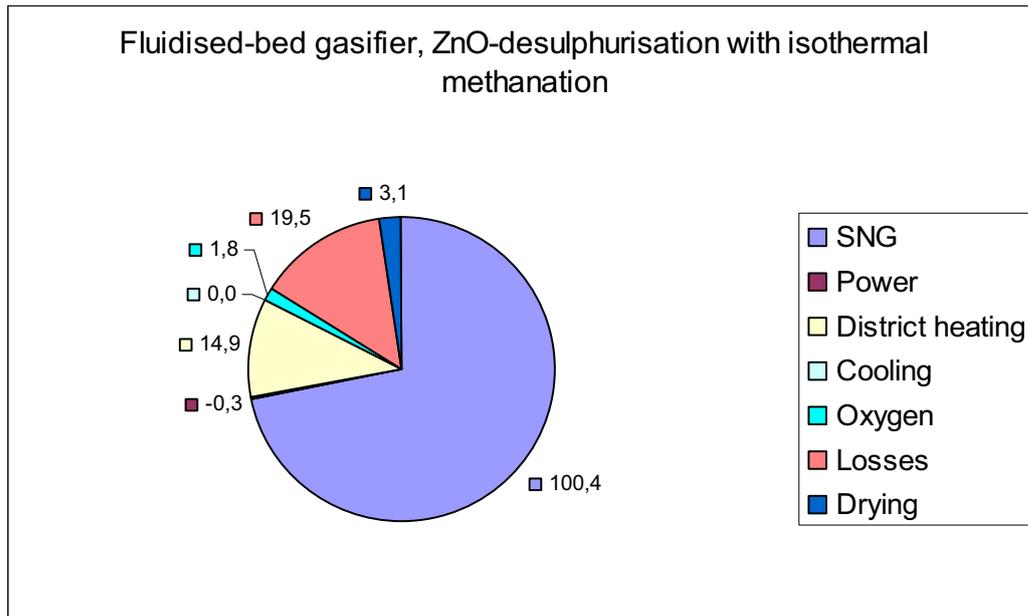
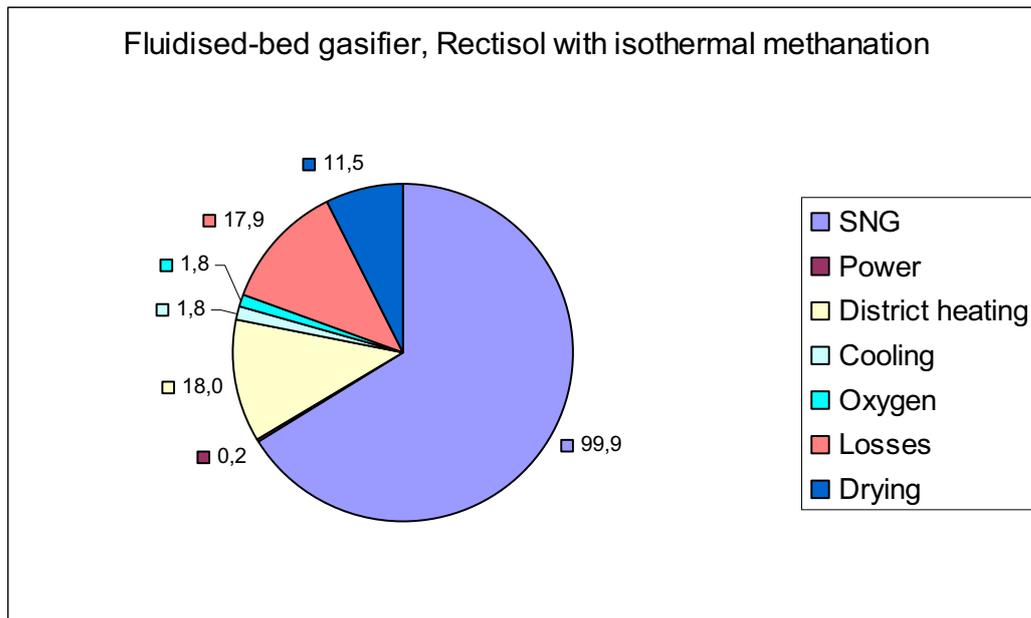


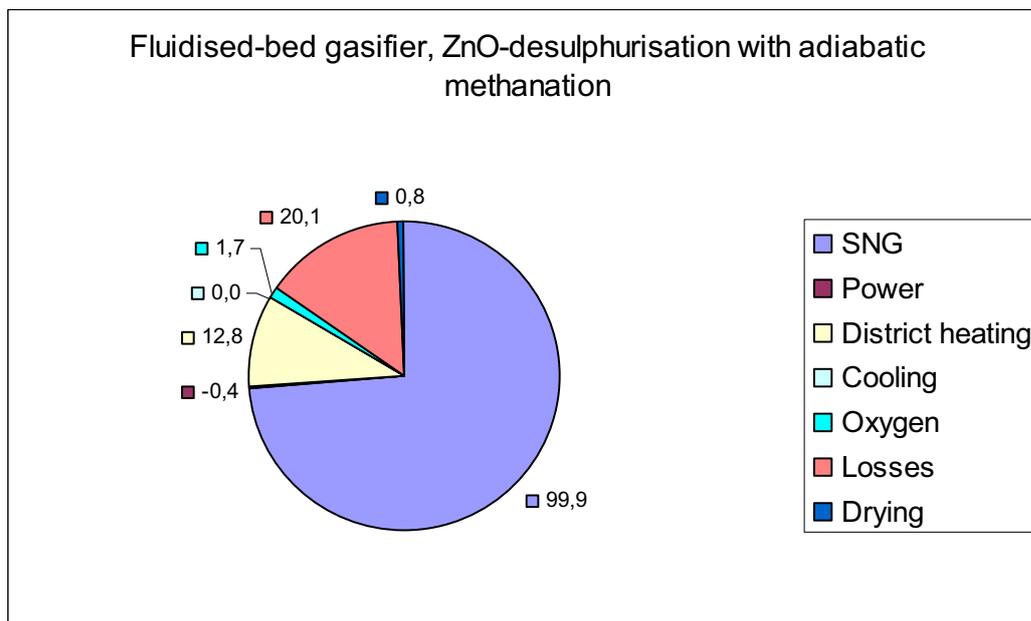
Figure 22: ZnO-desulphurisation, PSA gas cleanup and isothermal methanation.

Total input for the system in figure 22 was 140 MW.



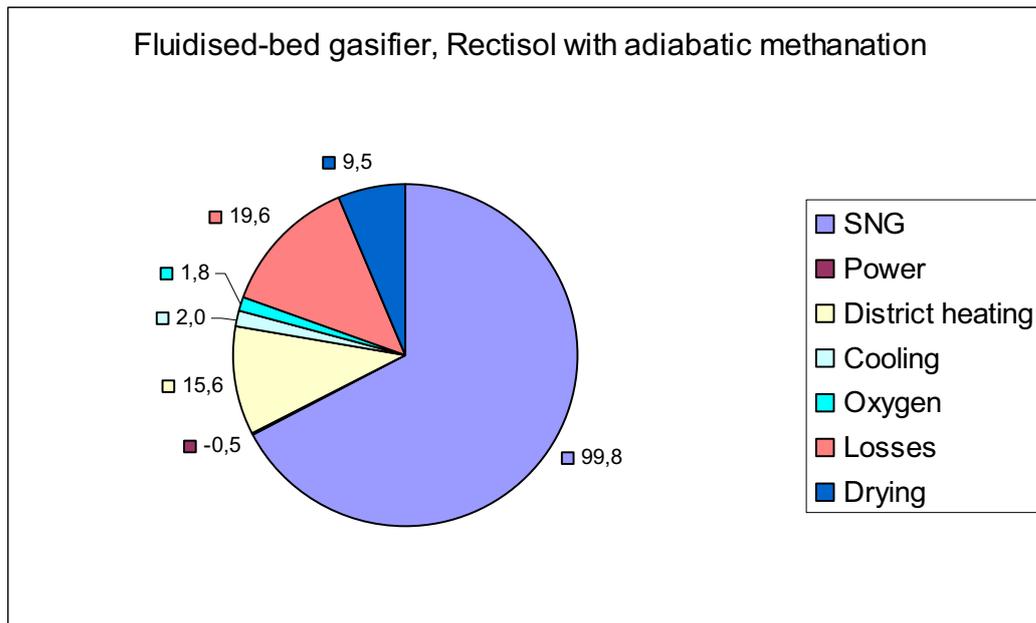
**Figure 23: Rectisol gas cleanup, with isothermal methanation.**

Total input for the system in figure 23 was 151 MW.



**Figure 24: ZnO-desulphurisation, PSA gas cleanup and adiabatic methanation.**

Total input for the system in figure 24 was 136 MW.



**Figure 25: Rectisol gas cleanup with adiabatic methanation.**

Total input for the system in figure 25 was 149 MW. The fluidised-bed gasifier has the highest efficiency to SNG of all systems evaluated in this thesis. The gasifier also has the highest requirement on moisture content in the biomass and as a result there is not enough heat available in the system for drying.

## 5.4 Recovery of Condensed Methane

To evaluate the impact on SNG efficiency that the methane in the condensed water has all simulations were run again but with a second flash column after the water removal. The flash column was an adiabatic column operating at atmospheric pressure and methane is assumed to be in equilibrium between vapour and methane dissolved in water.

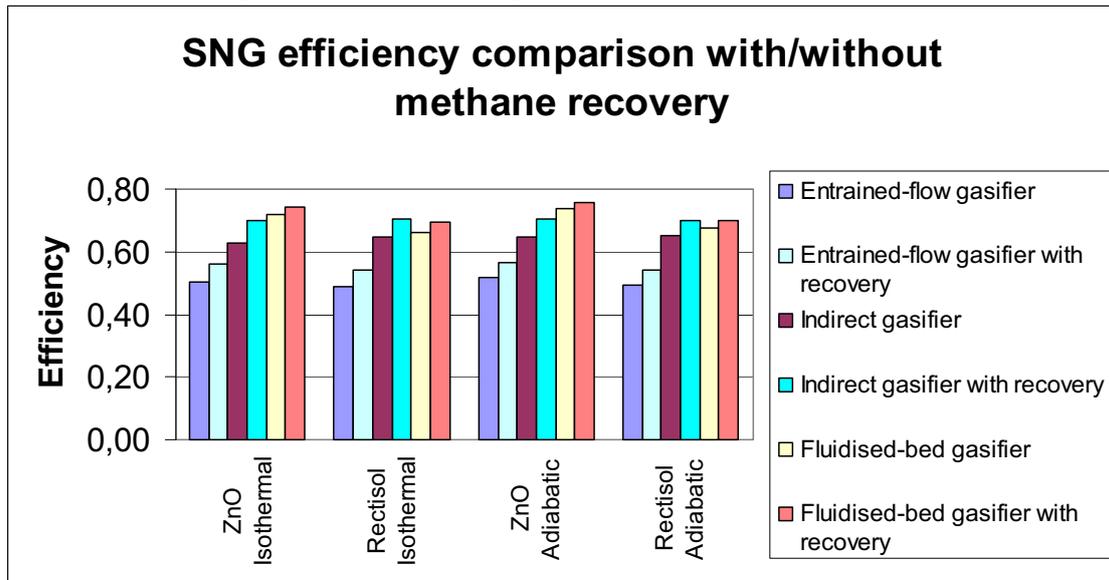
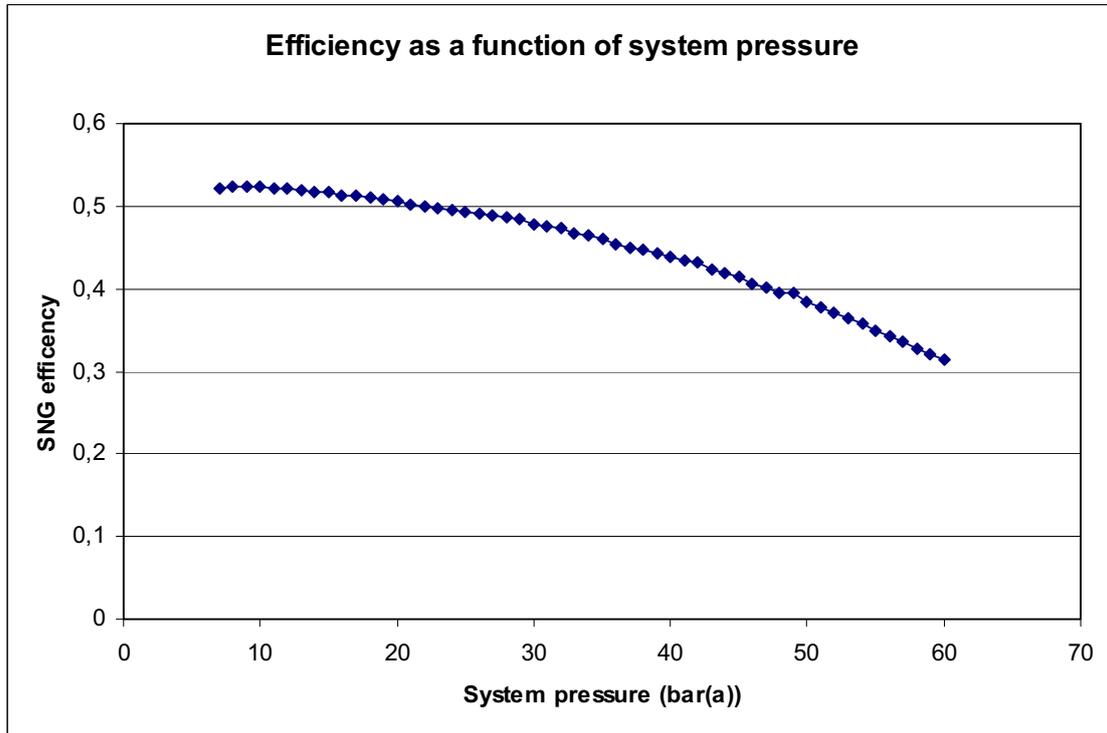


Figure 26: Comparison of SNG efficiency for zinc oxide systems with and without recovery of methane in condensed water.

Figure 26 show that, with recovery of the condensed methane, the efficiency increases by 2-10 %. It may not be practically possible to recover all methane that this theoretical study has shown, but it definitely has a considerable impact on system efficiency.

## 5.5 Pressure Effect

The system pressure was a variable that where examined and a second set of simulations where executed. According to the stoichiometry of the methanation reactions, there are more mol being consumed than formed and thus, the reactions should be favoured by an increased system pressure. A  $H_2/CO$  ratio of 3 was maintained for the simulations at 60 bar(a). Due to time constraints, only simulations for entrained-flow gasifier with zinc oxide desulphurisation simulations were run. The choice was made based on the fact that the gasifier and the desulphurisation technique had the highest overall efficiency.

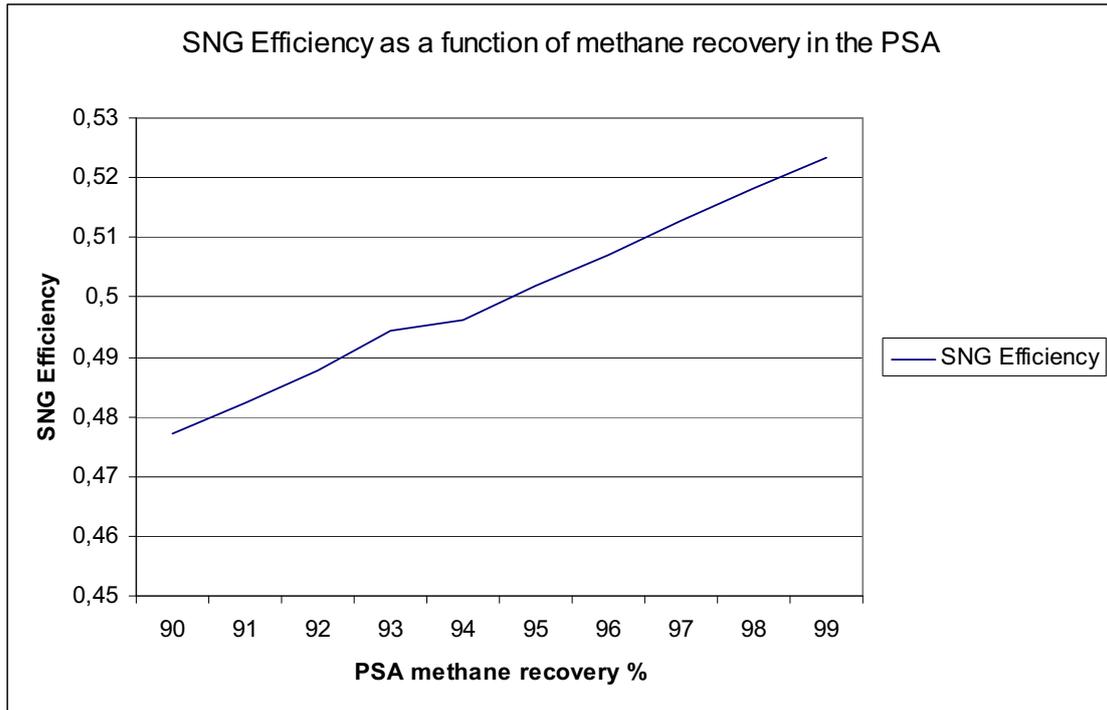


**Figure 27: SNG efficiency for entrained-flow gasifier with zinc oxide desulphurisation and isothermal methanation at 7-60 bar(a).**

However, the results showed otherwise, figure 27. Increasing the system pressure decreased the efficiency to SNG. Increasing the system pressure increases the amount of methane that is soluble in water and thus more methane needs to be produced to reach the specified 100 MW.

## 5.6 PSA Recovery

The initial simulations were conducted at a methane recovery of 90 per cent. This was deemed to be low and an e-mail from Volker Eichenlaub [29] confirmed this. All simulations were re-run with a methane recovery of 99 % and a sensitivity analysis was performed for PSA methane recovery.

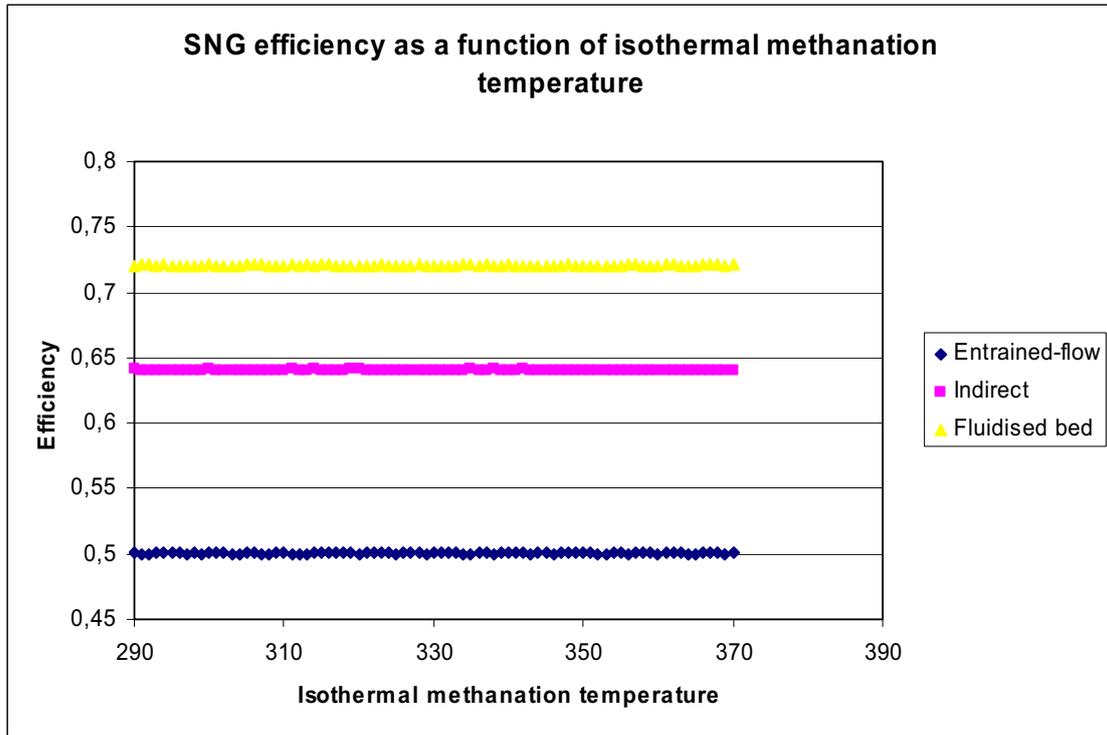


**Figure 28: Sensitivity analysis for PSA recovery of methane. The system is entrained-flow gasifier with isothermal methanation and zinc oxide desulphurisation. System pressure where 30 bar(a).**

Figure 28 shows that there is almost a linear dependency between methane recovery and SNG efficiency. The deviation from the straight line at 93-94 % recovery probably lies in the simulation model.

## 5.7 Isothermal Methanation Temperature

The temperature for the methanation was also a parameter that was evaluated as the reaction is highly exothermic.



**Figure 29: The effect on SNG efficiency as a function of isothermal methanation temperature.**

Figure 29 shows that there is no response in SNG efficiency when isothermal methanation temperature changes. Any effect seen is probably an effect of simulation model accuracy.

## 6 Discussion and Conclusions

Most people agree that the modern societies excessive use of fossil fuels has to come to an end sooner rather than later. However, what most people do not agree on is how to change a cheap, abundant and energy-rich resource such as oil into a clean, sustainable and renewable resource such as biomass. This is one, if not the largest, question that our modern society needs to solve.

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 showed a clear advantage for both the indirect and fluidised-bed gasifier when comparing efficiency to the entrained-flow gasifier. The advantage is a direct result of the methane output from the gasifier.

However, the entrained-flow gasifier has the advantage when it comes to tars as both the indirect and the fluidised-bed gasifier has a considerable amount of tars in real-world systems that must be removed. Tar removal should not affect the efficiency to SNG for the affected systems but it will increase plant operating and investment costs.

There are certainly some major drawbacks with SNG, one being the fact that its overall efficiency from raw material to end product is rather low, especially when the end product is electricity. If the end product is electricity, then a biomass-fired power plant has a higher efficiency from biomass to electricity.

The alternative to producing SNG using methanation reactors, Fischer-Tropsch synthesis, may be a more attractive solution. Fischer-Tropsch synthesis offers a much wider product range which could have some advantages such as financial benefits. There is also the possibility for co-production of SNG as well as FT-liquids. This approach would utilise both methanation process and Fischer-Tropsch synthesis. The results gained were unfortunately too deviant from the products gained in industrial synthesis. One of the reasons that the results differed from the industrial processes where due to insufficient kinetic data for the FT reactions and therefore only equilibrium constrained reactions where run [27].

Fischer-Tropsch and methanation in co-production is also a possibility with the combined advantage of both a high methane output and possibly FT-liquids, such as bio-diesel.

The simulations show that SNG efficiencies from biomass to methane of 50 % are possible for all systems but the indirect and fluidised bed gasifier has considerably high efficiencies. Furthermore, utilising a Rectisol gas cleanup system does not have a significant negative impact on SNG efficiency, but on overall efficiency. The decrease in overall efficiency is a result of increased electricity usage in the cooling systems but it is also a result of less utilisation of available heat due to cooling needs.

The gasifier choice lies between the indirect gasifier and the fluidised-bed gasifier. They have both shown good capability to SNG production and the choice may be affected by factors not included in this thesis such as feed stock preparation, equipment cost but also tars.

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.

What is certain is that no one knows how future energy distribution is going to transpire and SNG could be one of many routes that become successful. Future energy politics will determine what technologies that are sustainable, but there are many advantages with bio-SNG. Most importantly, a short term phase-out of fossil based energy is necessary and bio-SNG is a means to achieve that.

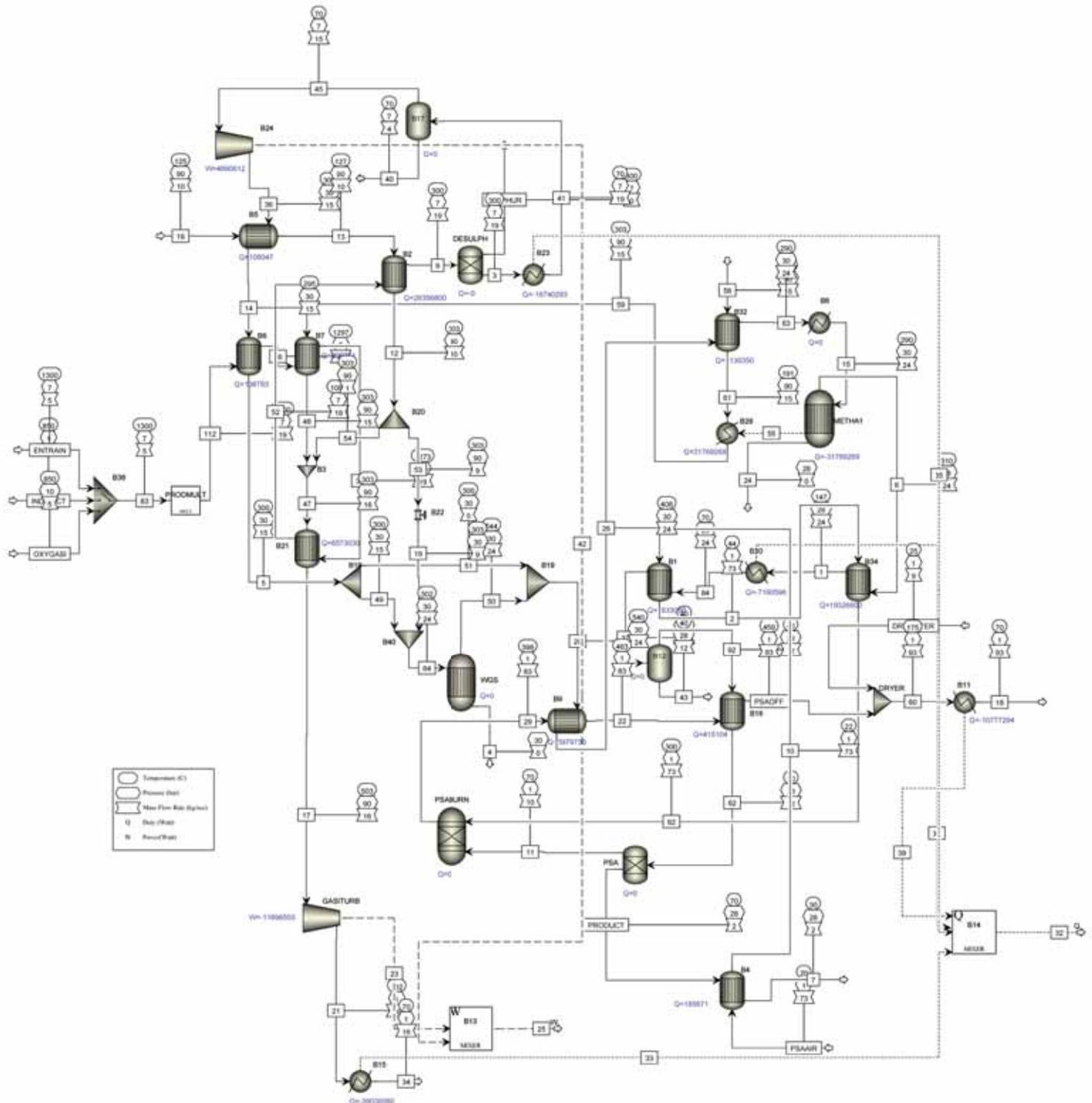
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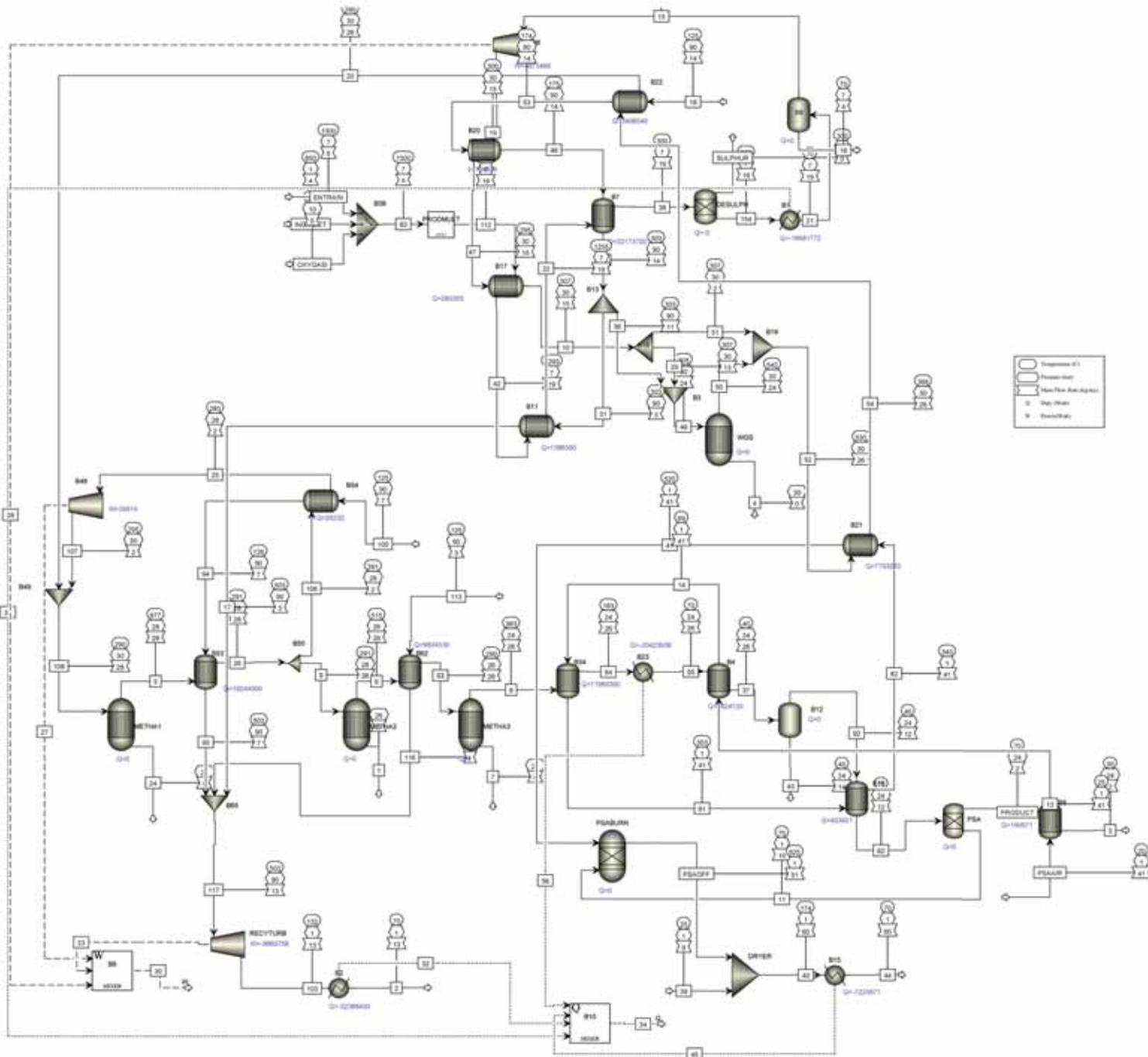
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# Appendix A, Process Flow-sheets

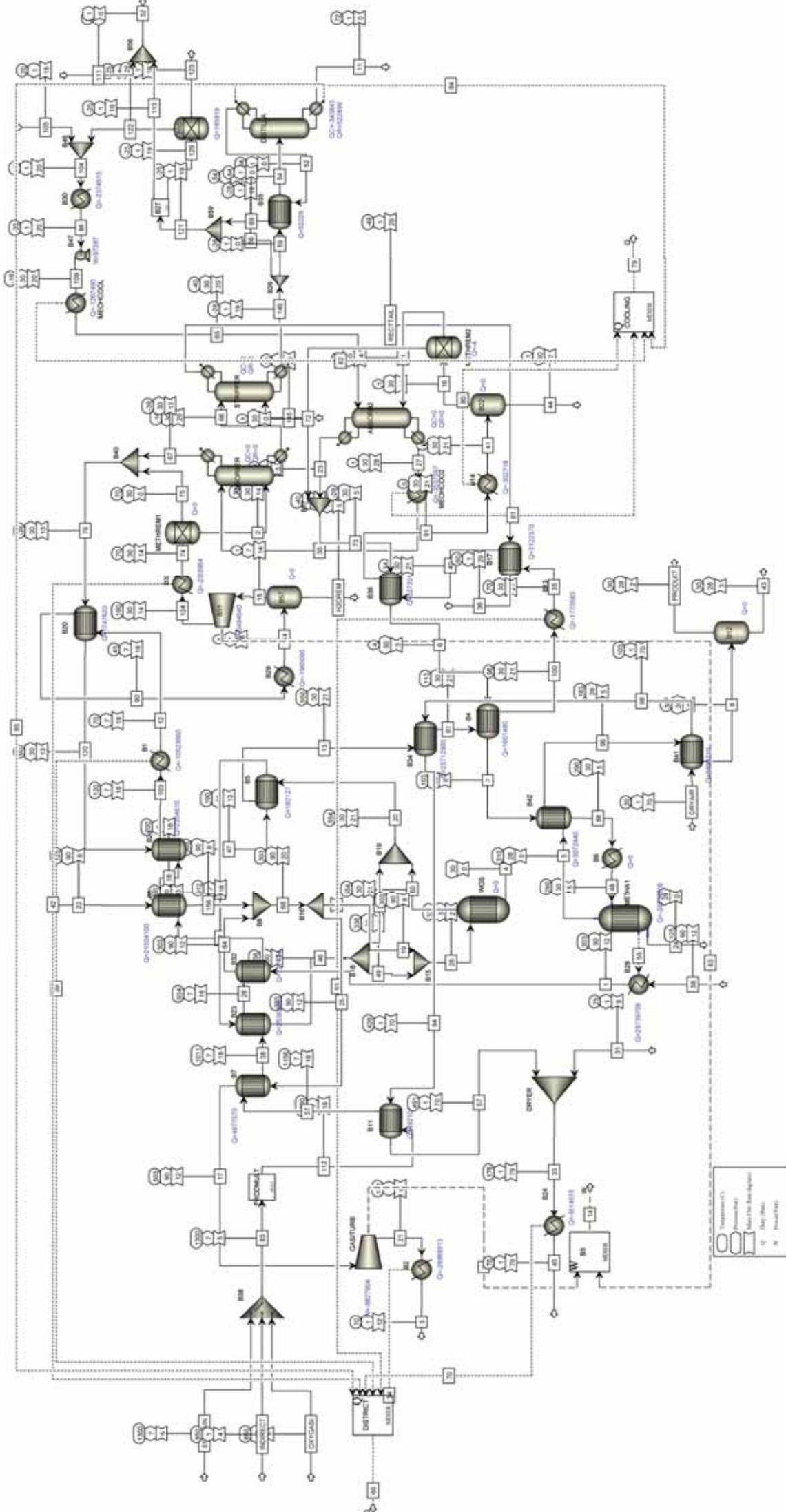
## Entrained-flow Gasifier, ZnO Desulphurisation, Isothermal Methanation



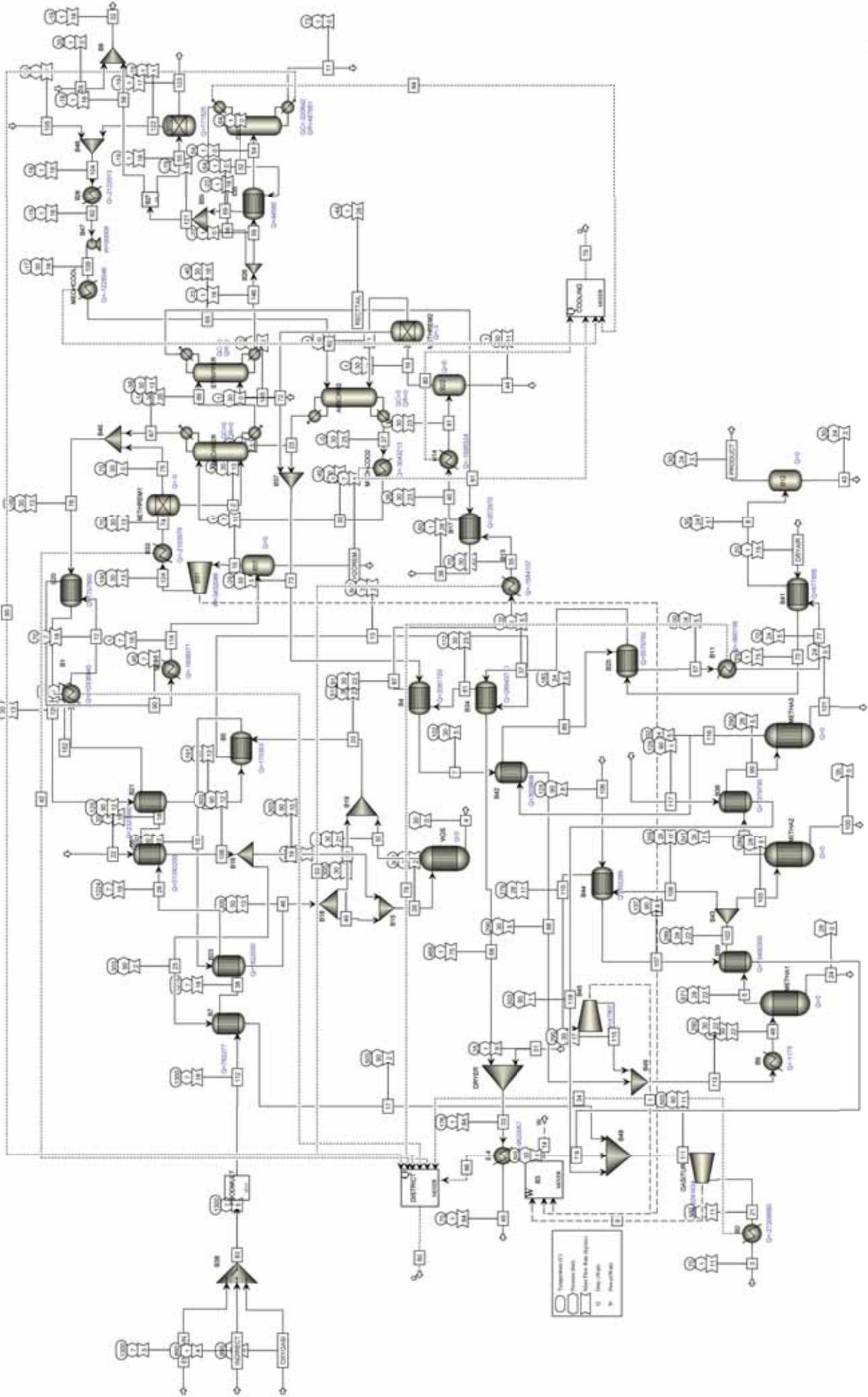
# Entrained-flow Gasifier, ZnO Desulphurisation, Adiabatic Methanation



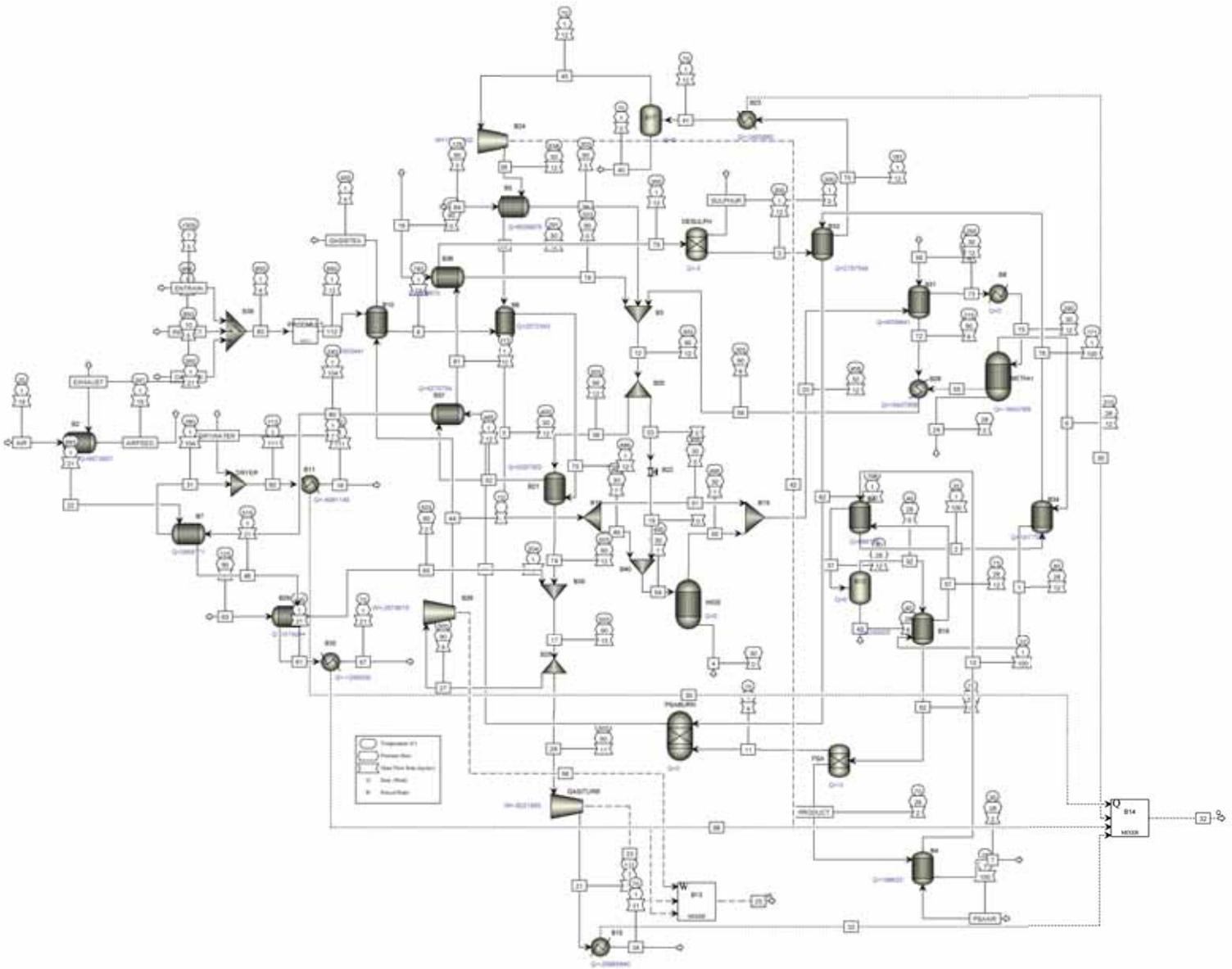
# Entrained-flow Gasifier, Rectisol Desulphurisation, Isothermal Methanation



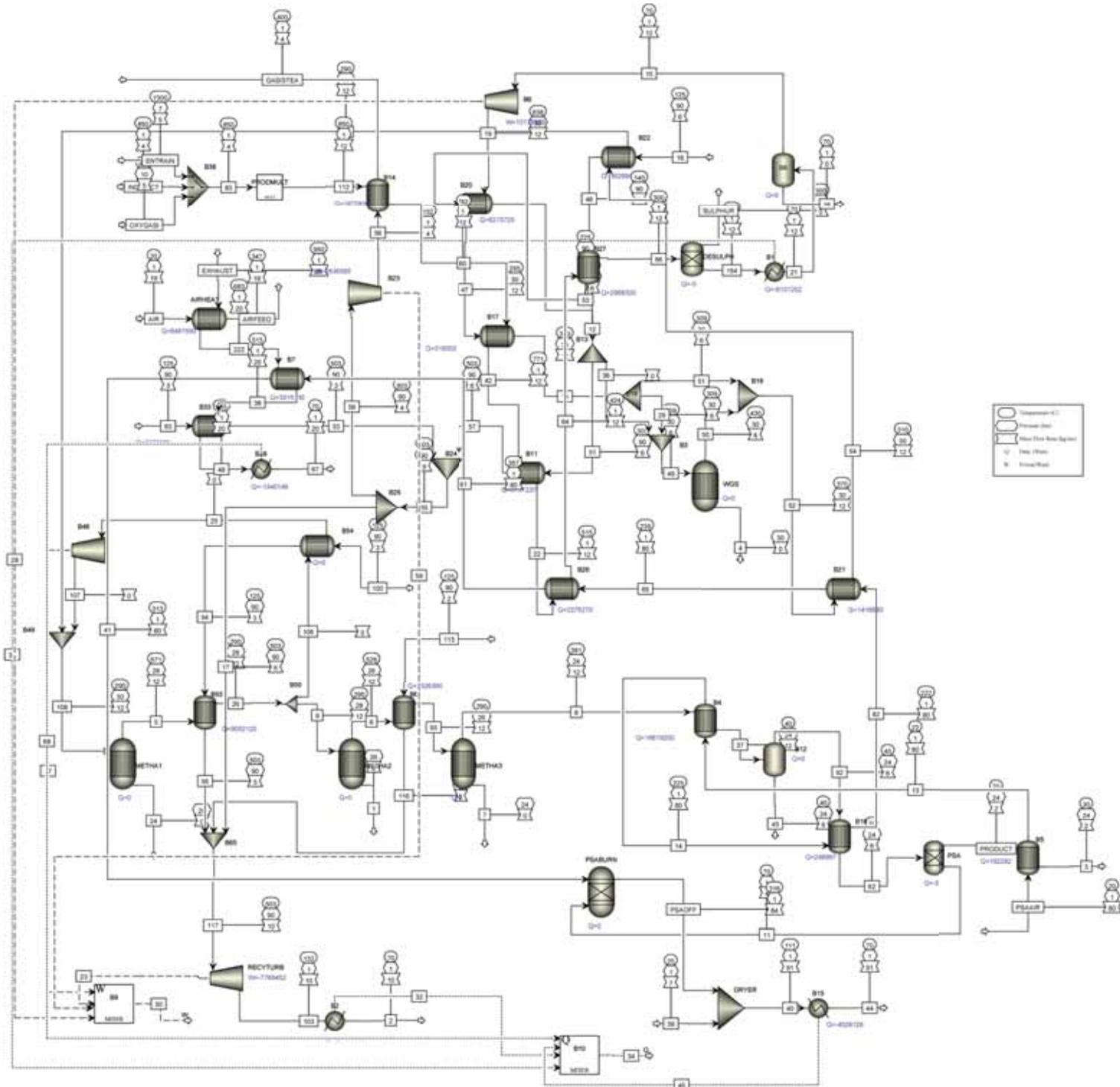
# Entrained-flow Gasifier, Rectisol Desulphurisation, Adiabatic Methanation



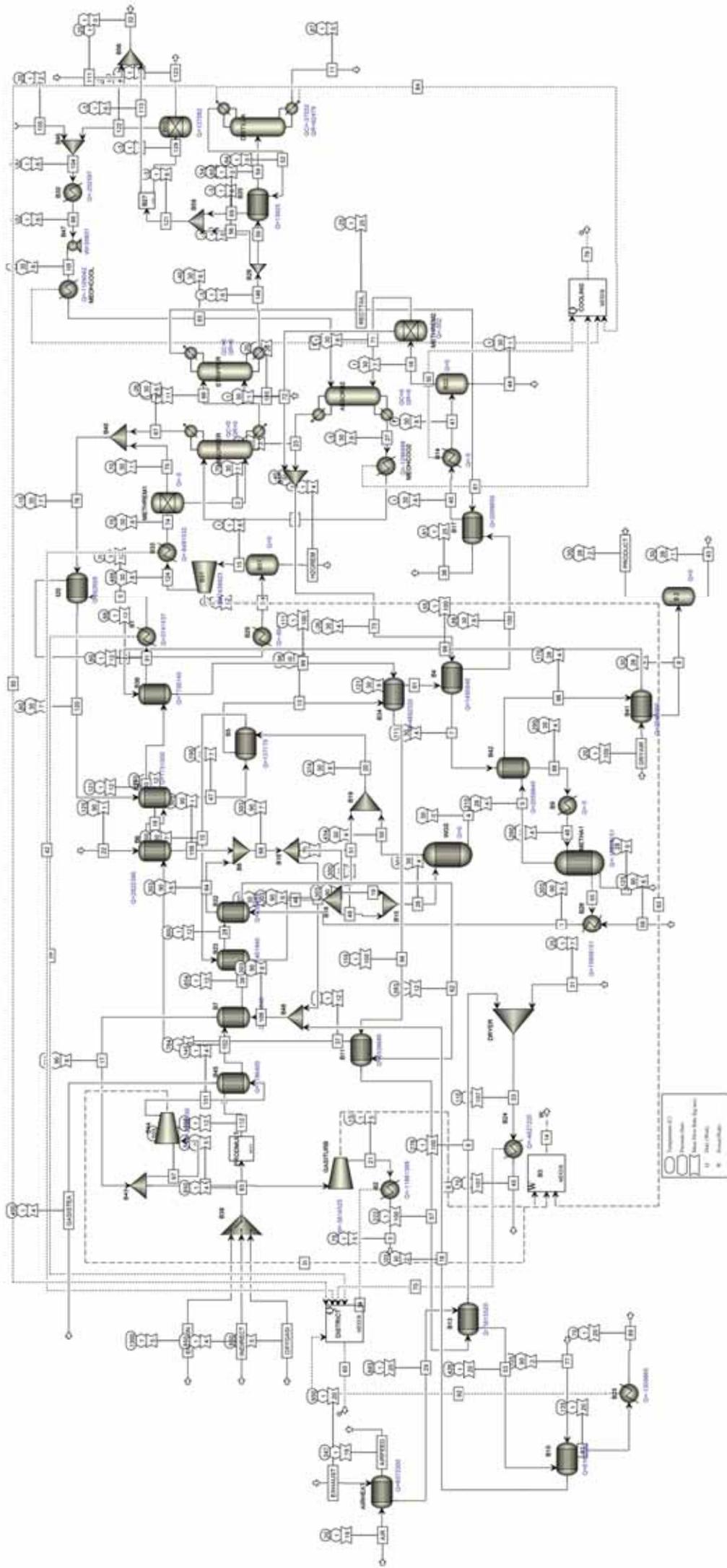
# Indirect Gasifier, ZnO Desulphurisation, Isothermal Methanation



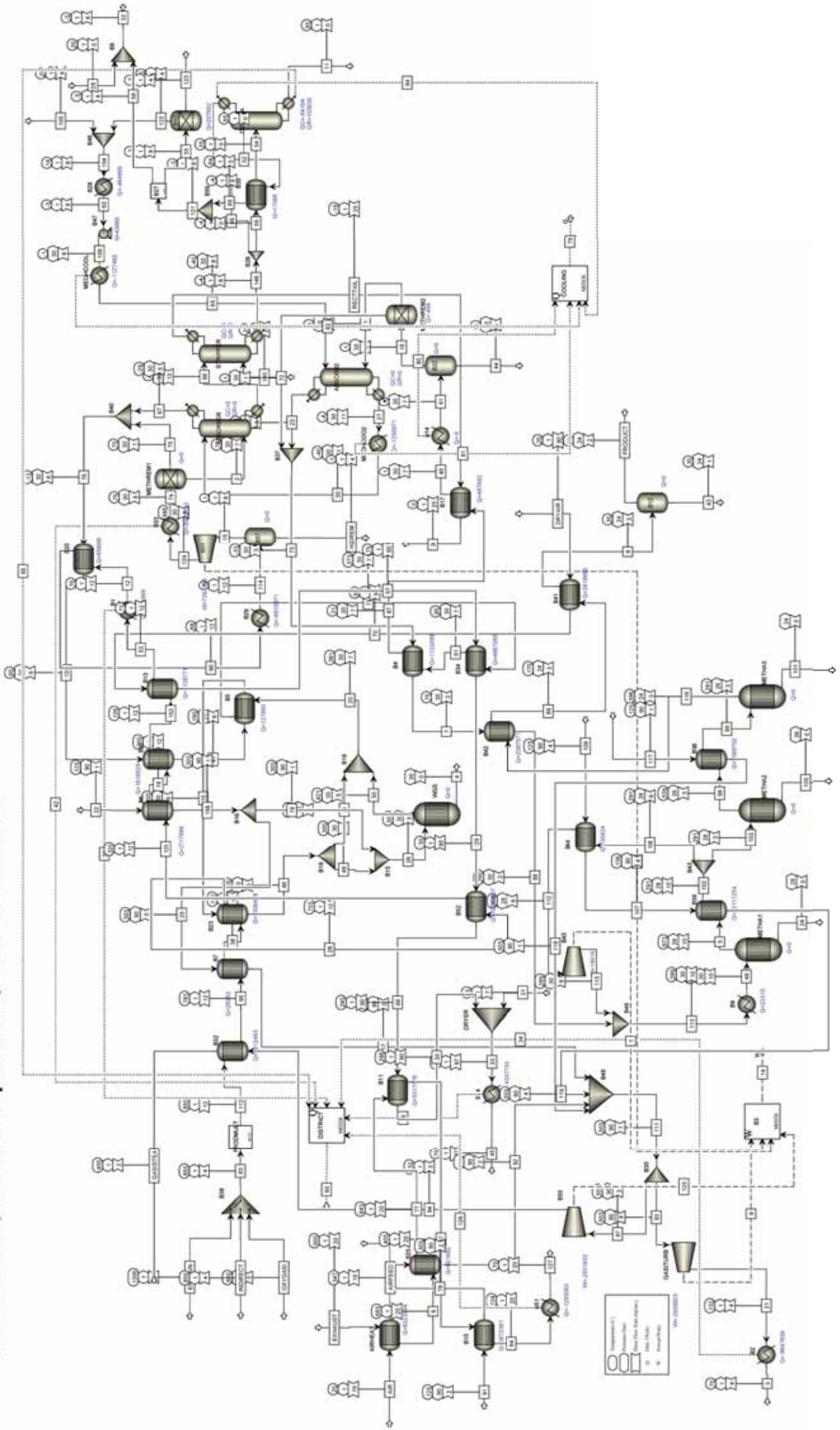
# Indirect Gasifier, ZnO Desulphurisation, Adiabatic Methanation



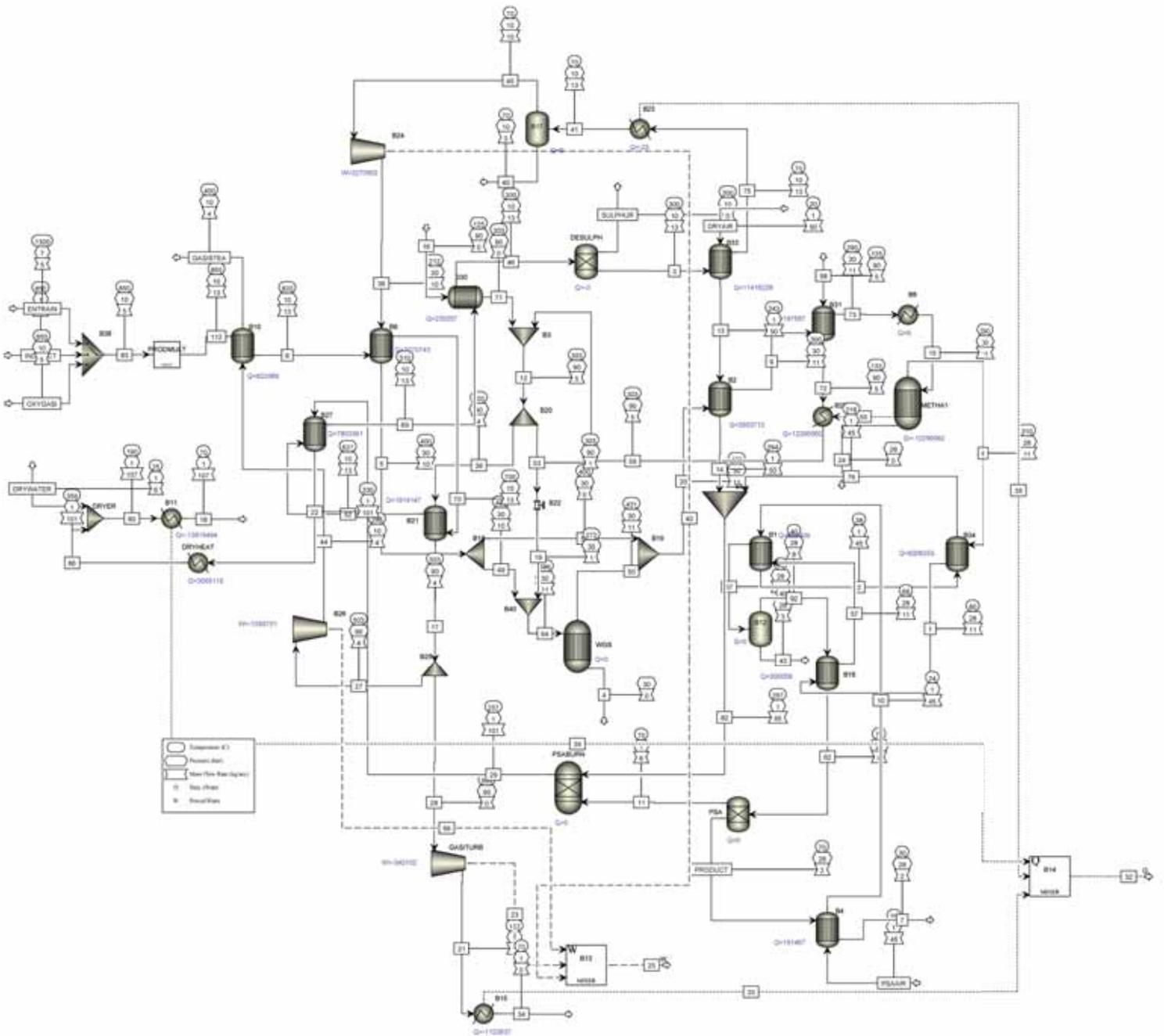
# Indirect Gasifier, Rectisol Desulphurisation, Isothermal Methanation



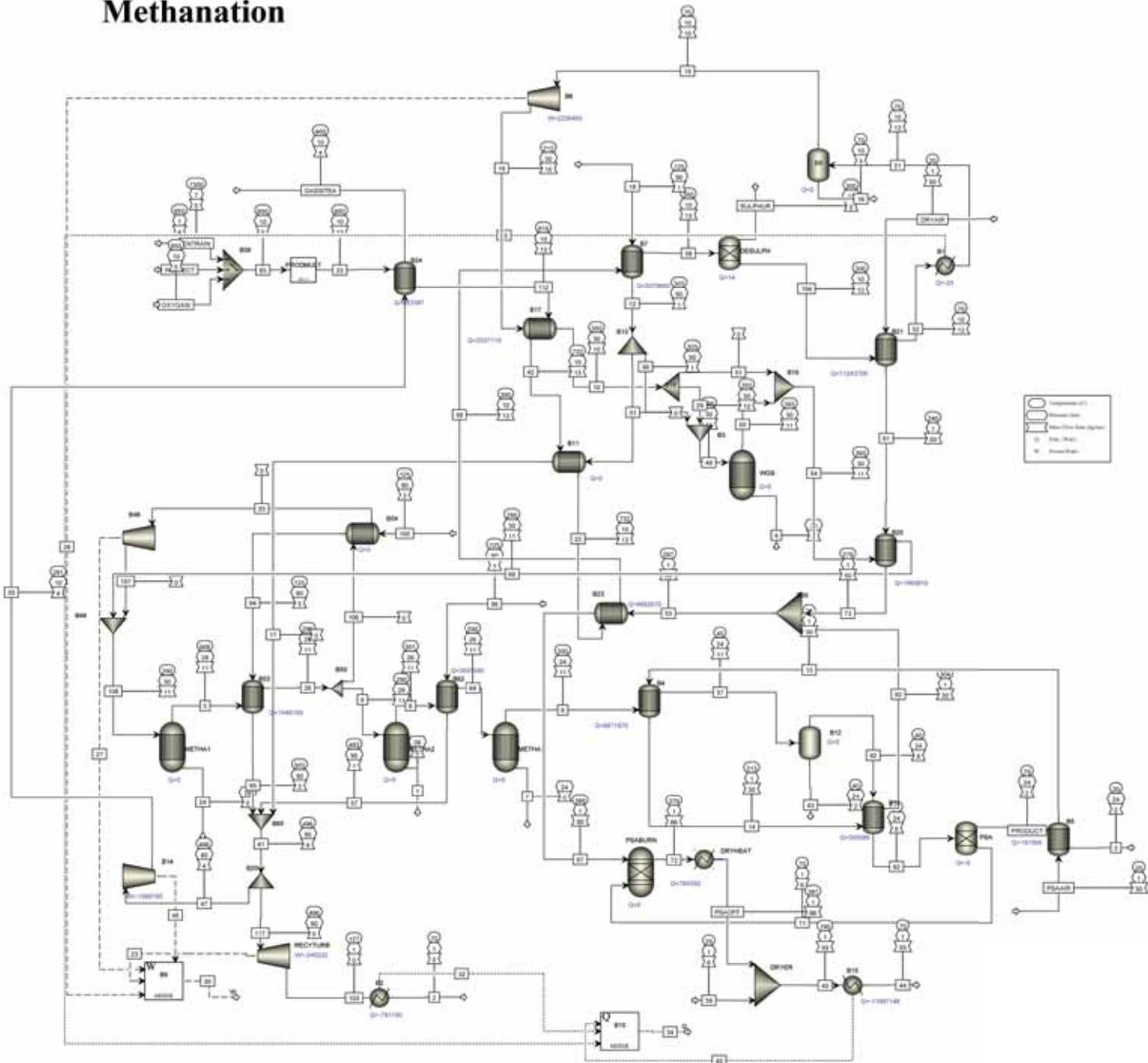
# Indirect Gasifier, Rectisol Desulphurisation, Adiabatic Methanation



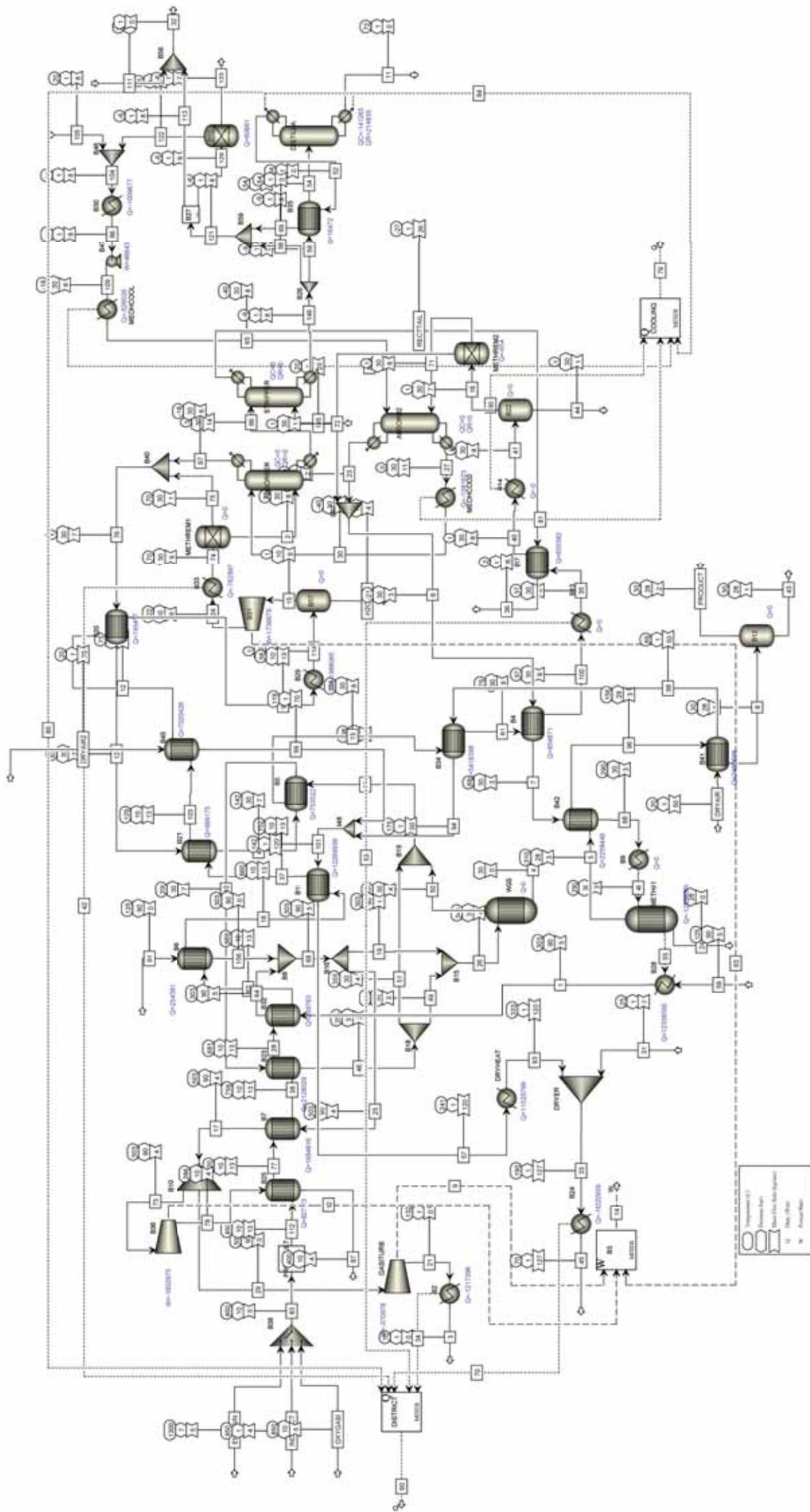
# Fluidised-bed Gasifier, ZnO Desulphurisation, Isothermal Methanation



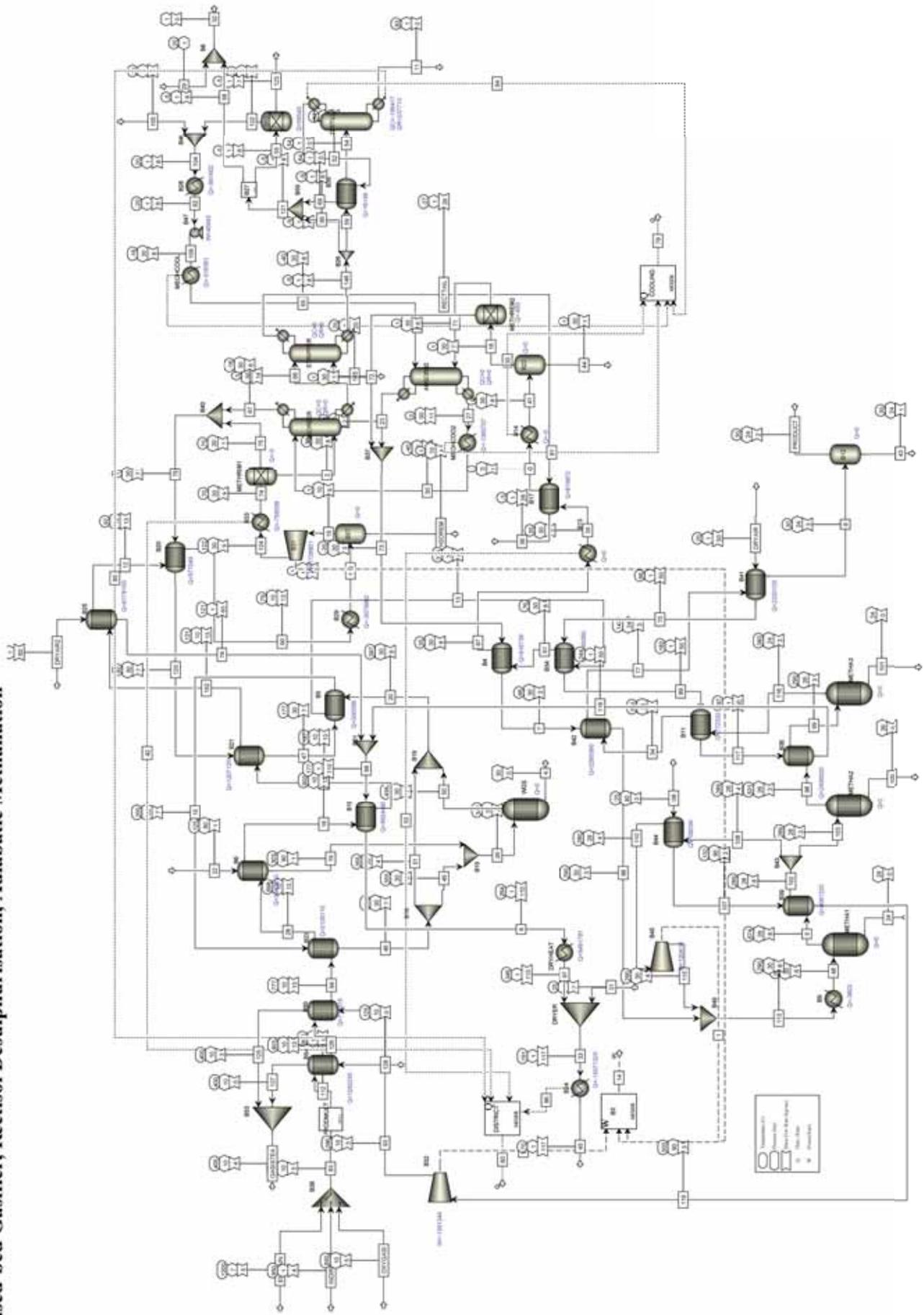
# Fluidised-bed Gasifier, ZnO Desulphurisation, Adiabatic Methanation



# Fluidised-bed Gasifier, Rectisol Desulphurisation, Isothermal Methanation



# Fluidised-bed Gasifier, Rectisol Desulphurisation, Adiabatic Methanation



## Appendix B, Gasifier Ouput Data

Table B1: Gasifier output data supplied by E.ON Gas Sverige AB.

	Indirect atmospheric gasifier	Entrained flow pressurised gasifier	Oxygen-blown pressurised (Fluidised-bed) gasifier
<b>Fuel after dryer</b>			
Lower heating value (MJ/kg)	15,543	15,543	16,601
Mass flow (kg/s)	3,2635	3,44962	2,9631
Coal flow after dryer (kmol/s)	0,11624	0,12287	0,11175
temperature (°C)	102,04	165,23	180,1
μC	0,4278	0,4278	0,45297
μH	5,10E-02	5,10E-02	5,40E-02
μN	1,70E-03	1,70E-03	1,80E-03
μO	0,35139	0,35139	0,37206
μS	3,40E-04	3,40E-04	3,60E-04
μH <sub>2</sub> O	0,15	0,15	0,10
μAsh	1,78E-02	1,78E-02	1,88E-02
Nitrogen from fuel injection (kg/s)	0	?	0
<b>Steam to gasifier</b>			
Mass flow (kg/s)	1,1748	0	1,3038
Temperature (°C)	400	0	400
<b>Oxygen to gasifier</b>			
Mass flow (kg/s)	0	1,6384	0,51106
Temperature (°C)	0	25	25
<b>Char and ash from gasifier</b>			
Mass flow (kg/s)	0,42028	0	0,10612
Temperature (°C)	850		850
μC	0,90344		0,63237
μAsh	9,66E-02		0,36763
Char flow (kmol/s)	0,03161	0	0,00559
<b>Product gas from gasifier</b>			
Lower heating value (dry gas) (MJ/nm <sup>3</sup> )	12,597	10555	11402
Mass flow (kg/s)	4,018	5,070	4,6744
Mol flow (without ash) (kmol/s)	0,22139	0,239	2,221E-01
Coal flow from gasifier (kmol/s)	0,08463	0,12287	0,11175
Temperature (°C)	850	1300	850
Pressure (bar(a))	1,04	7	10
CO vol-%	17,255	45,567	13,69
CO <sub>2</sub> vol-%	12,302	5,7653	22,282
CH <sub>4</sub> vol-%	8,668	4,65E-02	11,827

H <sub>2</sub> vol-%	29,423	19,669	24,916
N <sub>2</sub> vol-%	8,95E-02	0,20846	0,127
H <sub>2</sub> S vol-%	1,56E-02	1,54E-02	1,50E-02
H <sub>2</sub> O vol-%	32,248	28,728	27,144
ash (kg/s)	0,01739	6,13E-02	1,67E-02
<b>Combustion bed</b>			
Air flow (kg/s)	6,4446	0	0
Air temperature (°C)	347,2	0	0
Flue gas flow (kg/s)	6,8365	0	0
Flue gas temperature (°C)	950	0	0

## Appendix C, Stream Tables

Table B2: Stream table from Aspen Plus for entrained-flow gasifier with zinc oxide bed desulphurisation and PSA gas upgrade.

Stream	Gasifier outlet	ZnO inlet	ZnO outlet	To water remover	From water remover (liquid stream)	WGS inlet	WGS outlet	WGS bypass	Methanation inlet	Methanation outlet	Second water removal inlet	Second water removal outlet (gas stream)	Second water removal outlet (liquid stream)	PSA inlet	PSA product gas	PSA offgas	Dryer gas inlet	Dryer gas outlet
<b>Mass Flow kg/sec</b>																		
CO2	2,191	2,191	2,191	2,191	0,033	1,882	12,999	0,276	13,275	13,275	13,275	8,35378939	4,921	8,354	0,251	8,103	8,161	8,161
O2	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0	0,000	0,000	0,000	0,000	22,084	22,084
H2O	4,473	4,473	4,473	4,473	3,961	10,577	6,026	0,066	6,092	8,613	8,613	0,01203861	8,601	0,012	0,000	0,012	0,062	8,685
H2	0,343	0,343	0,343	0,343	0,000	0,299	0,808	0,044	0,852	0,005	0,005	0,00536044	0,000	0,005	0,005	0,001	0,000	0,000
CO	11,032	11,032	11,032	11,032	0,021	9,602	2,527	1,409	3,937	0,016	0,016	0,01528429	0,001	0,015	0,014	0,002	0,000	0,000
H2S	0,005	0,005	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0	0,000	0,000	0,000	0,000	0,000	0,000
COS	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0	0,000	0,000	0,000	0,000	0,000	0,000
NH3	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0	0,000	0,000	0,000	0,000	0,000	0,000
N2	0,050	0,050	0,050	0,050	0,000	0,044	0,044	0,006	0,050	0,050	0,050	0,04810215	0,002	0,048	0,000	0,048	83,448	83,448
CH4	0,006	0,006	0,006	0,006	0,000	0,006	0,006	0,001	0,006	2,252	2,252	2,01018133	0,242	2,010	1,980	0,020	0,000	0,000
SO2	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0	0,000	0,000	0,000	0,000	0,000	0,000
<b>Total Flow kmol/sec</b>	0,864	0,864	0,864	0,864	0,221	1,123	1,123	0,082	1,205	0,925	0,925	0,32070816	0,604	0,321	0,133	0,188	3,858	4,337
<b>Total Flow kg/sec</b>	18,101	18,101	18,097	18,097	4,015	22,410	22,410	1,802	24,212	24,212	24,212	10,4447562	13,768	10,445	2,259	8,185	113,755	122,377
<b>Total Flow cum/sec</b>	16,150	5,888	5,883	2,624	0,004	1,789	2,525	0,131	1,881	1,602	0,312	0,29821654	0,014	0,327	0,135	5,366	206,746	161,526
<b>Temperature C</b>	1300,000	300,434	300,029	70,000	70,000	301,749	538,377	300,000	290,000	310,000	40,000	40,000,00486	40,000	70,000	70,000	70,000	371,410	174,849
<b>Pressure bar</b>	7,000	7,000	7,000	7,000	7,000	30,000	30,000	30,000	30,000	28,000	28,000	28	28,000	28,000	28,000	1,000	1,000	1,000
<b>Vapor Frac</b>	1,000	1,000	1,000	0,744	0,000	1,000	1,000	1,000	1,000	1,000	0,347	1	0,000	1,000	1,000	1,000	1,000	1,000
<b>Liquid Frac</b>	0,000	0,000	0,000	0,256	1,000	0,000	0,000	0,000	0,000	0,000	0,653	0	1,000	0,000	0,000	0,000	0,000	0,000
<b>Solid Frac</b>	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0	0,000	0,000	0,000	0,000	0,000	0,000
<b>Density kmol/cum</b>	0,054	0,147	0,147	0,329	52,257	0,628	0,445	0,630	0,641	0,577	2,985	1,07542045	43,860	0,981	0,981	0,035	0,019	0,027
<b>Density kg/cum</b>	1,121	3,074	3,076	6,896	947,633	12,526	8,874	13,792	12,873	15,114	77,604	35,0240875	998,974	31,962	16,718	1,525	0,550	0,758

**Table B3: Stream table from Aspen Plus for entrained-flow gasifier with Rectisol wash.**

Stream	Gasifier outlet	Water inlet before Rectisol	Water removal (liquid stream) before Rectisol	Rectisol inlet (desulph)	Rectisol outlet (desulph)	WGS inlet	WGS outlet	WGS bypass	Rectisol inlet (CO2 capture)	Rectisol outlet (CO2 capture)	Methanation reactor 1 inlet	Recycle gas	Methanation reactor 2 inlet	Methanation reactor 3 inlet	Water removal inlet (product gas)	Water removal (liquid stream)	Product stream	Dryer Gas inlet	Dryer Gas outlet
Mass Flow kg/sec																			
CO2	2,164	0,162	0,162	2,003	2,028	1,614	11,701	0,414	12,115	0,549	2,362	1,813	0,549	0,549	0,549	0,137	0,413	0,000	0,000
O2	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	15,750	15,750
H2O	4,419	4,409	4,409	0,010	0,000	10,480	6,351	0,000	6,351	0,000	6,447	6,447	1,953	2,235	2,353	2,349	0,004	0,000	8,564
H2	0,339	0,000	0,000	0,338	0,339	0,270	0,732	0,069	0,801	0,789	1,271	0,472	0,143	0,048	0,009	0,000	0,009	0,000	0,000
CO	10,898	0,043	0,043	10,855	10,408	8,284	1,865	2,124	3,988	3,712	5,942	2,230	0,676	0,237	0,054	0,001	0,053	0,000	0,000
H2S	0,004	0,001	0,001	0,004	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
COS	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
NH3	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
N2	0,050	0,000	0,000	0,050	0,049	0,039	0,039	0,010	0,049	0,073	0,313	0,240	0,073	0,073	0,073	0,002	0,071	59,250	59,250
CH4	0,006	0,000	0,000	0,006	0,006	0,005	0,005	0,001	0,006	0,006	5,766	5,760	1,745	1,997	2,101	1,121	1,980	0,000	0,000
SO2	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
MEOH	0,000	0,000	0,000	0,000	0,001	0,001	0,001	0,000	0,001	0,002	0,010	0,007	0,002	0,002	0,002	0,002	0,000	0,000	0,000
Total Flow kmol/sec	0,854	0,250	0,250	0,604	0,588	1,050	1,050	0,120	1,170	0,544	1,625	1,081	0,327	0,296	0,283	0,141	0,142	2,607	3,083
Total Flow kg/sec	17,881	4,616	4,616	13,265	12,832	20,694	20,694	2,618	23,312	5,141	22,111	16,970	5,141	5,141	5,141	2,612	2,529	75,000	83,564
Total Flow cum/sec	15,954	1,971	0,005	0,574	0,383	1,673	2,341	0,191	0,638	0,368	2,536	1,771	0,547	0,533	0,152	0,003	0,149	160,836	115,031
Temperature C	1300,000	1,000	1,000	70,000	-38,255	301,928	531,302	300,000	25,597	-29,205	290,000	278,691	288,405	290,102	30,000	30,000	30,000	468,793	175,664
Pressure bar	7,000	7,000	7,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000	28,000	28,000	26,000	24,000	24,000	24,000	1,000	1,000
Vapor Frac	1,000	0,000	0,000	1,000	1,000	1,000	1,000	1,000	0,650	1,000	1,000	1,000	1,000	1,000	0,501	0,000	1,000	1,000	1,000
Liquid Frac	0,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,350	0,000	0,000	0,000	0,000	0,000	0,499	1,000	0,000	0,000	0,000
Solid Frac	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Density kmol/cum	0,054	0,433	55,270	1,052	1,536	0,627	0,449	0,630	1,833	1,479	0,641	0,610	0,599	0,555	1,865	50,140	0,952	0,016	0,027
Density kg/cum	1,121	9,074	1020,268	23,103	33,510	12,366	8,840	13,733	36,523	13,973	8,718	9,882	9,400	9,641	33,882	827,340	16,984	0,466	0,726



**Scheelegatan 3, 212 28 Malmö • Tel 040-680 07 60 • Fax 040-680 07 69**  
**[www.sgc.se](http://www.sgc.se) • [info@sgc.se](mailto:info@sgc.se)**

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