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A Medium-Scale 50 MW_{fuel} Biomass Gasification Based Bio-SNG Plant: A Developed Gas Cleaning Process

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Abstract: Natural gas is becoming increasingly important as a primary energy source. A suitable replacement for fossil natural gas is bio-SNG, produced by biomass gasification, followed by methanation. A major challenge is efficient gas cleaning processes for removal of sulfur compounds and other impurities. The present study focuses on development of a gas cleaning step for a product gas produced in a 50 MW_{fuel} gasification system. The developed gas cleaning washing process is basically a modification of the Rectisol process. Several different process configurations were evaluated using Aspen plus, including PC-SAFT for the thermodynamic modeling. The developed configuration takes advantage of only one methanol wash column, compared to two columns in a conventional Rectisol process. Results from modeling show the ability of the proposed configuration to remove impurities to a sufficiently low concentrations - almost zero concentration for H₂S, CS₂, HCl, NH₃ and HCN, and approximately 0.01 mg/Nm³ for COS. These levels are acceptable for further upgrading of the gas in a methanation process. Simultaneously, up to 92% of the original CO₂ is preserved in the final cleaned syngas stream. No process integration or economic consideration was performed within the scope of the present study, but will be investigated in future projects to improve the overall process.

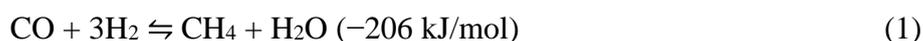
Keywords: absorption process; biomass; gas cleaning; gasification; sulfur; bio-SNG; WoodRoll®

1. Introduction

There is an increased global concern associated with the dependency on fossil feedstocks as the main source for energy as well as for various products, not only due to its harmful effect on the environment, but also the issue of possible supply insecurity. World energy consumption from 1971 to 2009 displays an average energy usage growth per year of approximately 100 million ton oil equivalent, or about 1.5% each year. A major part of this usage, about 80%, is supplied by fossil fuels, implying a profound dependency on fossil resources. In case of EU, the energy dependency data shows that about 64% of gas and 83% of oil demand in 2009 was imported, while these two fuels provide for about 60% of the of total EU energy need. Governments have established regulations to control the emissions and to reduce the amount of imported energy resources. The target for the EU climate policy is to reduce emissions down to 80% of the level of 1990, by 2020 [1].

Natural gas is becoming increasingly important as a primary energy source and is used for production of heat and power for domestic and industrial purposes, as well as a chemical feedstock. It has also gained importance as a transportation fuel. However, natural gas is a fossil fuel contributing to CO₂ emissions. A suitable replacement for natural gas is bio-based Substitute Natural Gas (bio-SNG) produced from renewable resources. A feasible approach to produce bio-SNG is gasification of biomass, followed by methanation [2]. At present, there are many on-going projects, aimed at demonstrating the production of methane using this route [3,4].

Previous system studies of biomass gasification-based methanation processes have shown that the overall biomass to bio-SNG efficiency (on LHV basis) using this route is around 64%–67%, depending on the technologies used in the conversion process [5]. In a general synthesis gas to methane process, the CO and the H₂ in the synthesis gas are converted to methane, according to the chemical reaction in Equation (1), using a nickel catalyst [6]. A clean producer gas from biomass gasification contains (after gas cleaning and conditioning) beside CO, also substantial amounts of CO₂. One possibility to further increase the conversion efficiency is to convert all carbon-containing components, *i.e.*, not only CO but also CO₂, by e.g., applying the Sabatier process. In this case, the bio-SNG production could be increased substantially, using the same amount of input raw feedstock, as pointed out by Mohseni *et al.* [7]. The Sabatier reaction is shown in Equation (2) [6].



The producer gas from biomass gasification varies considerably in composition and contains normally between 15%–60% and 20%–25% of hydrogen and carbon monoxide, respectively, when oxygen or steam blown gasification technologies are used [8]. This implies that the amount of hydrogen is not enough even for the general methanation process in Equation (1), which requires a H₂:CO ratio of at least 3:1. To achieve this ratio in a general process, part of the CO is shifted to H₂ using the water gas shift (WGS) process according to Equation (3).



An additional source of hydrogen is needed to convert all CO and CO₂ and a feasible source is hydrogen produced from electrolysis powered by wind and solar energy. Hydrogen from electrolysis

has the benefit of being flexible in its operation and it could also be used as an approach to store intermittently produced electricity for future use [9]. The electricity, needed for the electrolysis, is approximately 4.3 kWh per produced Nm^3 of hydrogen [10]. The amount of hydrogen for the methanation of the CO and CO₂ content in the gas produced by a 5 MW_{fuel} gasifier will require a power input of approximately 7 MW, corresponding to, e.g. 6–10 wind power plants, assuming a plant size of around 2.5–4 MW and a normal average load of 30% during a year. This implies rather small to medium scale gasifier systems to be operated in conjunction with a few wind power plants or a farm.

In gasification of solid fuels, such as biomass and waste, to produce a synthesis gas, the fuel is partially oxidized in an atmosphere of air, oxygen and/or steam at elevated temperatures, typically between 600 and 1200 °C, to generate a valuable product gas, consisting mainly of H₂, CO, CO₂, CH₄, and light hydrocarbons (C₂ + C₃), tar and other impurities, as such H₂S, CS₂, COS, AsH₃, PH₃, HCl, N₂, NH₃, HCN, particulates and alkali salts [11]. These components have to be removed before utilizing the gas, depending on the application of interest. The type of cleaning process to be used to achieve the required cleanness of the gas depends on downstream application, the composition of the raw gas and the size of the process [12,13]. The downstream cleaning process includes many steps where some steps, such as particulate removal, using cyclones and different filters, are common for several types of gasifiers and other, such as sorption processes, using different sorbents, or physical and chemical washing processes, generally depends on the size of the overall plant. Impurities of particular interest for removal are tars and sulfur compounds. In the case of small to medium scale gasifiers, a major challenge is how to design an effective gas upgrading and cleaning process with the ability to produce a clean gas in as few steps as possible.

The aim of the present study was to investigate the possibility to adapt and develop existing large scale gas cleaning technology for a SNG production plant, based on a medium scale (50 MW_{thermal}) biomass gasifier. The study specifically focuses on the WoodRoll[®] gasification process [14], producing a relatively clean gas without tar, where the main issues are removal of sulfur and other impurities in the raw produced gas. The pre-requisite of the gas cleaning process was that it should remove all impurities, in particular sulfur compounds, but simultaneously keep as much CO₂ as possible in the gas prior to methanation.

The WoodRoll[®] gasification process is divided into three main steps; *drying*, *pyrolysis* and *gasification* [14]. A separation of the processes enables production of a syngas with reduced content of impurities and condensable heavy fractions and also minimizes the nitrogen dilution. As the process is divided in stages a higher degree of fuel flexibility is possible as mixing and purification can be handled in the most efficient stage of operation. The first step, the dryer is indirectly heated in a rotary drum with heat exchange tubes. With proper control of heating and mixing in the reactor the particular process is well proven for a variety of materials. A hot gas reactor is supplying the heat by burning pyrolysis gas from subsequent steps. The dried fuel is then transferred to a pyrolysis reactor. In this second step, the fuel pyrolyzed in a similar rotary drum at much higher temperature (400 °C) producing char and pyrolysis gas, consisting of permanent gases with condensable tars and heavier fractions held in gas phase. Heat is mainly generated from the flue gas from the gasification stage downstream. The char is cooled and grinded to the required size. In the third step, an entrained gasifier, where radiant heat burners supply the heat, combusting the pyrolysis gas, the grinded char and superheated steam are mixed. The steam gasification occurs at a temperature of 1,100 °C. The

superheated steam is produced in a cooling step of the produced raw gas after the gasifier. The raw product gas produced in the WoodRoll[®] process has typically a gas composition consisting of 16%–20% CO, 20%–24% CO₂, 55%–65% H₂ and almost no or small amounts of methane. The subsequent sections start with a short review of gas cleaning for removing sulfur and other impurities, followed by methodology and a description of the modeling results. Finally, a short discussion about applying the gas cleaning process is presented.

2. Gas Cleaning Sulfur and Other Impurities

The specific requirements for a synthesis gas, concerning an acceptable amount of sulfur contaminants are somewhat diverse, with requirements as low as <0.01 ppmv to <1 ppmv reported in the literature [15]. Table 1 outlines the requirement for the major components of a synthesis gas from biomass gasification, considered for further upgrading in an end-user application [15,16]. To allow for later comparisons the acceptable amount of contaminants in the synthesis gas is given in both mg/Nm³ and ppm. These impurities affect the methanation process negatively, reducing the expected lifetime of the catalyst in the process, due to e.g., sulfur poisoning, alkali salt deposition and carbon formation [17].

Gas cleaning processes for removal of sulfur compounds, such as H₂S and CO₂, and generally denoted as acid gases (AG), as well as other compounds of halides and nitrogen compounds are most readily performed by means of a physical and chemical washing process at plant scales larger than approximately 20 MW_{fuel} [18]. In a physical and chemical process, the gas is washed with a suitable solvent, physical or chemical, in a packed (structured or unstructured) column or tray column at a temperature where the impurity absorption is efficient.

Table 1. Acceptable amount of contaminants in a synthesis gas entering an end user application [16].

Contaminant	Removal level	
Particles	Essentially complete	-
Tars	Below dewpoint	-
Na + K	<10 ppbv	-
(HCl + HBr + HF)	<10 ppbv	<0.015 mg/Nm ³ (a)
NH ₃ + HCN	<1 ppmv	<0.7 mg/Nm ³ (b)
(H ₂ S + COS + CS ₂)	<10 ppbv to <1 ppmv [14]	<0.014 mg/Nm ³ to <1.4 mg/Nm ³ (c)

(a) Calculated as only HCl; (b) Calculated as only HCN; (c) Calculated as only H₂S.

Physical solvents tend to be favored over chemical solvents when the concentration of acid gases or other impurities is very high. Unlike chemical solvents, physical solvents are non-corrosive, requiring only carbon steel construction. The regeneration of chemical solvents is achieved by the application of heat, whereas physical solvents can often be stripped of impurities by reducing the pressure without the application of heat. The absorption loading capacity for a physical or chemical solvent is proportional to the volumetric gas flow rate or the removed acid gases, respectively [18]. The solvent used with the absorbed AG and other impurities is transferred to a regeneration unit for purification and release of the acid gases.

General criteria for selection of the appropriate AG removal process configuration are among others given by the demand of the required gas purity, the raw gas composition, *i.e.*, some solvents do not adsorb COS, and selectivity towards desirable, undesirable gas components and solvent loss [18]. A suitable solvent is essential for an efficient process to optimize the removal of undesired components while not removing desired components of the gas. Two typical solvents for chemical removal of AG are amines and potassium carbonate. Amines used for this purpose are monoethylamine (MEA), diethylamine (DEA), methyldiethylamine (MDEA) and diisopropyl amine (DIPA). MDEA is widely used due to its high selectivity for H₂S, but a drawback is the large fraction of CO₂ slipping through unabsorbed [18,19].

Examples of physical processes are the Purisol[®] process; a typical process for selective removal of H₂S with CO₂ remaining in the treated gas, using N-methyl-2-pyrrolidone (NMP) as the solvent [20]. COS is not as soluble as H₂S, but is hydrolyzed [21]. Another solvent example, suitable for selective removal of H₂S, is the Selexol[®] process, using dimethyl ethers of polyethylene glycol (DEPG) as the solvent [22,23]. The Purisol[®] process is especially suitable for the cleaning of high-pressure, high CO₂ synthesis gas for gas turbine integrated gasification combined cycle (IGCC) systems [24].

Another possible physical solvent is methanol, as used in the Rectisol[®] process, an absorption process with high removal efficiency towards COS, H₂S and CO₂, as well as other impurities like HCN and NH₃ [25]. A typical example of a Rectisol[®] process, including WGS, is illustrated in Figure 1. The main advantage of using methanol as a solvent is the lower costs of the solvent, compared to the amine-based solvents. Another is its high removal efficiency towards COS compared to other solvents [18].

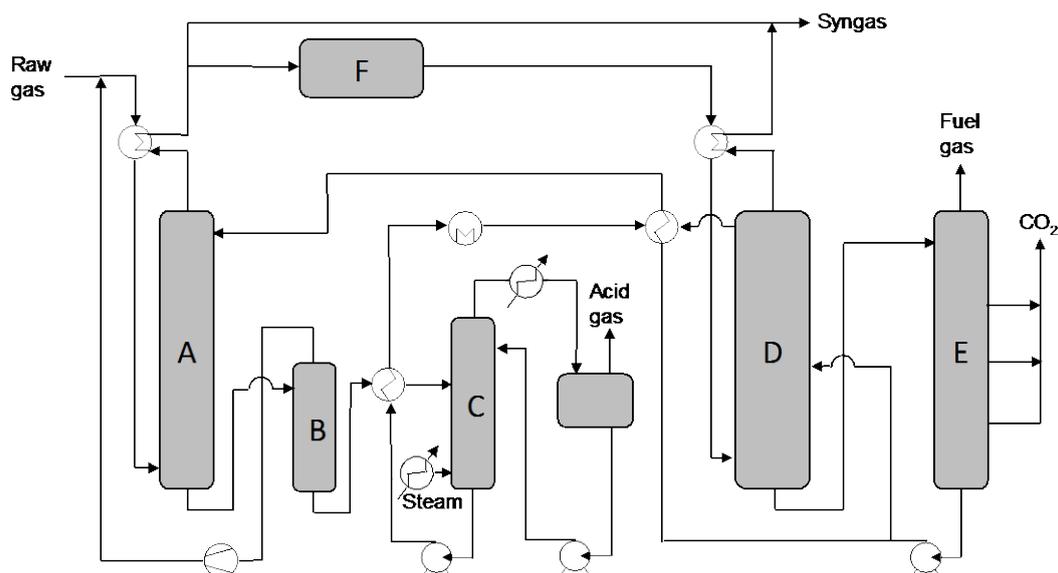


Figure 1. A schematic flow diagram of typical example of a selective Rectisol[®] process for AG removal. **A:** H₂S absorber; **B:** H₂S flash column; **C:** hot regenerator; **D:** CO₂ absorber; **E:** CO₂ flash tower; **F:** WGS. Adapted from Higman and van der Burgt [13].

The solubility of CO₂ and H₂S is dependent on partial pressure and temperature [26]. A packed absorber is most commonly used and the raw gas enters counter-currently to the solvent [27]. In the Rectisol[®] process, gas components such as CO₂, H₂S, COS, HCN and NH₃ as well as nickel and iron carbonyls are absorbed physically and removed from a gas. These components are then desorbed from

the solvent in a regeneration process. The raw gas has to be cooled before entering the plant. Trace components like hydrogen cyanide and ammonia are removed in a prewash step where cold methanol is used. The sulfur compounds are removed by using carbon dioxide-loaded solvent, which generally results in a residual content of sulfur below 0.1 ppm. In the regeneration process, CO and H₂ are recovered by, firstly, flashing at medium pressure, and secondly by heating to boiling temperature and stripping with methanol vapor. In gas mixtures with relatively high hydrogen sulfide, the hot regeneration produces a Claus gas with enough hydrogen sulfide content for further treatment. In cases with low H₂S content or with high content of carbon dioxide, an additional step like stripping and reabsorption is needed. The final content of CO₂ in the syngas can be around 3% [28,29].

3. Methodology

3.1. System Considerations

The study focuses on the development of an efficient gas cleaning and upgrading process for removing the impurities, especially sulfur compounds, but keeping the CO₂ for a gasification system, based on the WoodRoll[®] process. The size of the gasifier considered was set to approximately 50 MW_{fuel}, a size large enough for an economic production of methane, but still not too large for production of hydrogen from wind power. The gas cleaning process should remove impurities to produce a synthesis gas, conforming to the gas requirement needed for the methanation process. In the gasification system, based on the WoodRoll[®] process, the tar is not a problem as mentioned above. Therefore, a process for removing and conversion of tar is not further considered in the present study. Please refer to [30] for a discussion about tar removal.

3.2. Modeling

An extensive survey and analysis of different absorption based technologies was carried out to select the most appropriate starting point for the modeling and simulation, developing the suitable gas cleaning process, according to the specified requirements in Table 1.

The main approach for the modeling and simulation was evaluation of different process scenarios using Aspen Plus as the simulator tool. For the thermodynamic modeling, PC-SAFT was selected. The basis for this is the study performed by Sun and Smith [29], comparing simulation results from Aspen Plus for different thermodynamic models with experimental data from a Rectisol process, concluding that a PC-SAFT model shows the best agreement between the modeling and experimental data. The various process scenarios included different process configurations as well as different operating conditions of each unit. In total, more than hundred scenarios were examined. The most promising process is reported in Section 5 below.

4. Process Data for Modeling

Input in terms of composition of the raw gas from the WoodRoll[®] gasifier is mainly collected from experimental data when possible and, in cases where chemical analyses are missing, values are estimated from a typical woody fuel. Typical measured values for the main gas components together with additional estimated values for other important gas components are presented in Table 3.

5. Modeling of the Gas Cleaning Process

The selection of an appropriate absorption solvent for the process was based on an extensive survey, as stated above. The chemical absorption solvents were ruled out, since physical solvents generally are more favorable when the concentration of acid gases or in particular if other impurities is high. Also, physical solvents are, unlike chemical, non-corrosive, and therefore require less expensive process construction materials, such as carbon steel construction [24]. Table 2 shows the relative solubility of selected gas compounds, compared to CO₂, in the three solvents DEPG, NMP and methanol, which are used in the Selexol[®], the Purisol[®] and the Rectisol[®] processes, respectively. Based on this comparison, the relative difference between the different compounds for each solution is similar for all solutions, except for NH₃ and COS, where a higher relative solubility is obtained in case of methanol. This higher efficiency for removal of NH₃, also valid for other impurities, such as HCN and COS [25], is one reason for preferring methanol as the solvent for the gas cleaning process. Another parameter supporting methanol and the Rectisol[®] process are its ability to remove sulfur to below 0.01 ppmv H₂S, compared to e.g., Selexol[®] where 1 ppmv is a typical level [31].

Table 2. Relative solubility of gas compounds, compared to hydrogen sulfide, in the three solvents DEPG, NMP and methanol (adopted from [24]) DEPG and NMP is calculated using values at 25 °C but in case of methanol –25 °C is presented due to the high volatility of methanol.

Gas	DEPG at 25 °C	NMP at 25 °C	MeOH at –25 °C
H ₂	0.013	0.0064	0.0054
CO	0.028	0.021	0.02
CO ₂	1	1	1
CH ₄	0.066	0.072	0.051
NH ₃	4.8	-	23.2
COS	2.3	2,7	3.9
H ₂ S	8.8	10.2	7.06

Other important aspects, influencing favoring methanol, are the flexibility and ease in reconfiguring the process [24], and that the solvent is both inexpensive and abundant. A drawback of using methanol, as a solvent, is, however, the low operating temperature at –60 to –75 °C, much below the methanation step ranges [31]. In this case Selexol[®], using DEPG as solvent, operating at ambient temperature would be a better choice. However, the superior removal of sulfur compounds and other impurities by the solvent methanol, compared to other physical solvents, outweigh this drawback at the present stage of analysis.

5.1. The Modified Rectisol[®] Process

The configuration of the concluding gas cleaning and upgrading process for the 50 MW scale is displayed in Figure 2. This process is based on Rectisol[®] process and is designed to keep the carbon dioxide in the main stream while removing other impurities to the lowest possible concentrations. The process mainly includes the following major parts, as indicated in Figure 2:

- A-1: A water scrubber
- A-2: A methanol wash
- F: A flash tank for used methanol
- D-1: A flashed methanol distiller
- D-2: A dehydration of cleaned methanol

A simplified description of the process is as follows; the first step (E-1) is the cooling and pressurization of the raw syngas to make the gases more soluble in liquids. The working temperature and pressure is normally varied between -30 to 0 °C and above 25 bar, respectively. Although such working conditions are energy demanding and expensive, the conditions are less energy demanding than a conventional Rectisol® processes, operating at temperatures between -50 and -20 °C and pressures of 30 to 45 bars to meet the cleaning requirements. This step consists of five to six condensers with intercooling in which water condensate is removed from the raw syngas. For the sake of simplicity, this is not shown in Figure 2.

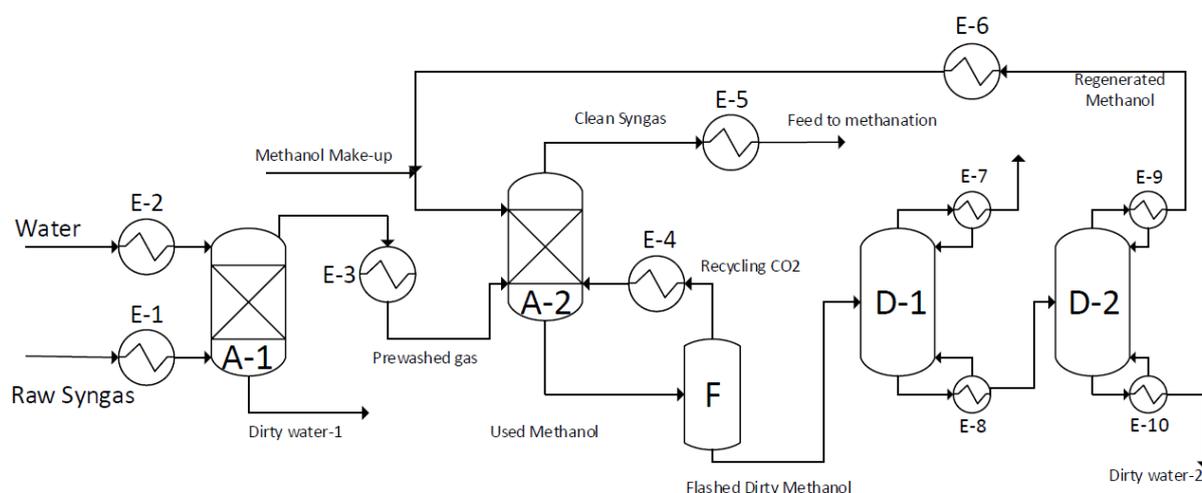


Figure 2. An Aspen process flow diagram of the modified Rectisol® process for the 50 MW scale gasifier.

In the second step, the water scrubber (A-1), the water removes HCl, NH₃ and a part of HCN. This step makes the regeneration of the used methanol easier and more efficient as discussed in more detail below. The methanol wash (A-2) basically removes the major impurities, such as H₂S, COS, CS₂, and HCN, producing a clean gas with only traces of impurities left in the gas. At the same time approximately half of the carbon dioxide is removed from the raw syngas and dissolved in the used methanol. The clean outlet gas from the methanol wash contains a certain amount of methanol, *ca.* 3 g/Nm³, as shown in Table 2. In a general gas cleaning process, aimed at a pure syngas production, a downstream water scrubber is applied to remove the methanol in the outlet gas. In the present study, a certain amount of methanol in the cleaned outlet gas is acceptable. Therefore, a water scrubber is not included in the present process. However, part of the methanol in the cleaned outlet gas will condense in the gas cooler (E-5). To reduce operating costs, the methanol used in the methanol (A-2) should be regenerated. The used methanol passes through a flash tank (F) to reduce the pressure. This allows most of dissolved gases, together with a small volume of methanol, to escape from the liquid to the gas

phase. Therefore, the outlet streams of the flash tank (F), consists of a liquid stream of partially cleaned methanol and a gas stream of a mixture of methanol, carbon dioxide and impurities. The gas is recycled to the methanol wash (A-2), via compression and cooling step (E-8) to preserve the carbon dioxide in the final clean syngas. The flashed methanol liquid stream is distilled in the flashed methanol distiller (D-1), where the heavy key bottom products of the column goes to a further step of dehydration distillation (D-2) to provide with a clean methanol in the light key distillate products of the column. Regenerated methanol is cooled and pressurized (E-6) and recycled to the methanol wash (A-2).

5.2. The Gas Quality and Process Performance

The process described above is able to remove the impurities to a content as required or close to required for a synthesis gas for further upgrading to methane, comparing numbers in Table 1 with results in Table 3. The Aspen Plus modeling results in Table 3, show that the content of impurities, such as H₂S, COS, CS₂, HCl, NH₃ and HCN, is substantially decreased comparing the raw syngas with the clean syngas after the methanol wash. The concentration of H₂S, CS₂, HCl, NH₃ and HCN, and the concentration level 0.01 mg/Nm³ for COS are, as obtained by the modeling, acceptable for further upgrading in a methanation process. Nevertheless, this result is based on a not experimentally verified modeling and should be treated as such. In any case, a guard bed, located between the cleaning process and the Sabatier reactor, to further lower the content of COS, may be included if needed. Simultaneously, as the acid gases are removed, up to 92% of the original CO₂ is preserved in the final cleaned syngas stream. The high carbon dioxide content in the final syngas is achieved by recycling of CO₂ from the flash tank (F) to the methanol wash (A-2) via the compression step. Without this recycling, the amount of the CO₂ saving would not have exceeded 60% of the CO₂ entering the process.

Among the impurities, COS displays the smallest solubility in methanol. Since water was also unable to remove COS from the gas stream, a larger number of equilibrium stages in the methanol wash (A-2) and greater methanol flow rate were employed. However, this implies a larger loss of CO₂.

Therefore, to achieve a selective removal of H₂S and more importantly COS, compared to CO₂, a delicate design optimization for the methanol wash (A-2) was performed ensuring enough time for the solvent to absorb the H₂S and COS, while keeping CO₂ in the gas stream. The result of this design optimization renders the optimum solvent flow rate in the column, and number of equilibrium stages of column (A-2). The CO₂ still dissolved is separated from the dirty methanol in the flash tank (F), together with impurities and traces of methanol. This gas stream is compressed and recycled back to the methanol wash as described above.

Specifications for the recycled streams are listed in Table 4. The pressure and temperature of the recycled CO₂ stream should be increased from 1.5 bar to above 36 bar and reduced to 248 K, respectively, as indicated in Table 3. A compressor normally has an outlet temperature limitation and therefore it is not possible to achieve the conditions needed with only one compressor step [32]. A series of compressors with inter-cooler should be employed to fulfill the desired pressure, as well as a final cooler step to reduce the temperature of the compressed gas to the desired temperature of 248 K.

Table 3. Flow specifications of the product gas and its constituent substances at different steps in the process as obtained from the ASPEN calculations. The specified raw gas is the main gas components in the gas obtained from the WoodRoll[®] gasifier gasifying wood together with estimated values for other important components.

	Raw Product Gas	After Water Scrubber	After Methanol Wash
Composition (%)			
Water	19	7.53×10^{-5}	0
Carbon monoxide	18	17.68	17.97
Carbon dioxide	15	22.03	20.74
Hydrogen	48	60.20	61.18
Contaminants (mg/Nm³)			
Hydrogen sulfide	5.97×10^2 *	7.20×10^3	≈0
Carbonyl sulfide	4.64×10^2 *	5.60×10^3	0.01
Carbon disulfide	7.46×10^2 *	9.10×10^3	0
Hydrogen chloride	3.42×10^2 *	0	0
Ammonia	1.49×10^2 *	0	0
Hydrogen cyanide	9.39×10^2 *	7.60×10^2	0
Methanol	0	0	3.08×10^3
Total flow (kmol/s)	0.18	0.15	0.15
Total flow (kg/s)	2.92	2.38	2.27
Total flow (m ³ /s)	6.22	0.12	0.09
Temperature (K)	413	251	267
Pressure (bar)	1	25	35

* Calculated values is obtained from the char composition, which is 79 mass-% C, 13 mass-% O, 3.3 mass-% alkali metals, 3 mass-% H, 0.6 mass-% Si, 0.5 mass-% N, 0.3 mass-% S, 0.2 mass-% P and 0.1 mass-% Cl.

Table 4. Flow specifications of the recycled gas at different steps in the process.

Composition (%)	After Dirty Methanol Flash	Compressed Cooled Gas
H ₂ O	5.02×10^{-7}	5.02×10^{-7}
CO	8.46×10^{-3}	8.46×10^{-3}
CO ₂	94.69	94.69
H ₂	0.01	0.01
Total flow (kmol/s)	0.06	0.06
Total flow (kg/s)	2.38	2.38
Total flow (m ³ /s)	0.83	3.09×10^{-3}
Temperature (K)	273	248
Pressure (bar)	1.5	36

The loss of methanol should be kept at a minimum due to the costs. From the detailed results, shown in Table 5, calculated by Aspen Plus, the make-up of methanol to be added to the process to account for losses can be calculated to 10 kg/h. This loss is of the order of magnitude to be expected for a plant of the size addressed as compared to a conventional Rectisol[®] process [18].

Table 5. Methanol flow specifications.

Composition (%)	Fresh Methanol	Used Methanol	Regenerated Methanol
H ₂ O	0	2.82×10^{-5}	≈0
CO	0	0.18	≈0
CO ₂	0	33.53	≈0
H ₂	0	2.04×10^{-4}	≈0
H ₂ S	0	1.14×10^{-3}	≈0
COS	0	5.72×10^{-4}	≈0
CS ₂	0	1.14×10^{-4}	≈0
HCl	0	≈0	≈0
NH ₃	0	≈0	≈0
HCN	0	2.43×10^{-4}	≈0
CH ₃ OH	100	66.06	≈100
Total flow (kmol/s)	0.15	0.21	0.15
Total flow (kg/s)	4.71	7.20	4.71
Total flow (m ³ /s)	7.57×10^{-3}	9.78×10^{-3}	8.74×10^{-3}
Temperature (K)	251	246	368
Pressure (bar)	35	35	3

The water scrubber is the key unit to reduce the loss of methanol by removing a part of the impurities. Results from different tested scenarios show that HCN could not be removed from the used methanol with conventional regeneration processes for physical solvents. In order to avoid extra costs of regeneration process or methanol make-up, a water wash column (A-1) was designed to remove a part of impurities, especially HCN. The required water flow rate is about 220 kg/h, and the used dirty water can be handled in a biological water treatment process as reported by Lurgi, the company, which is the license holder of the Rectisol[®] process [28]. The required amount of water should be compared with the amount used in the 50 MW_{fuel} gasification process, 6000–8000 kg/h, and also dirty condensed water, 300–500 kg/h, produced in the cooling of the syngas. These amounts are estimated from gasification tests at 500 kW_{fuel}, using a reactive fuel in a WoodRoll[®] pilot plant. The required water flow used in the modified Rectisol[®] process is well below what is used in the gasification process and also lower than the amount of dirty condensed water produced. Since a water treatment plant is anyway needed for the gasification process, the additional costs of investment for the additional amount of dirty water will not be significant. At less reactive fuels, the amount of condensed water will be even higher from the gasification process.

5.3. Comparison with a Conventional Rectisol[®] Process

The study does not intend to provide with a detailed economic comparison with a convention Rectisol[®] process or any other process, based on physical solvents, but only to highlight the main differences. A detailed description of both single-stage and two-stage (selective) Rectisol[®] process is given in literature [18,29]. The single-stage removes contaminants together with CO₂ in a single methanol wash as shown in Table 6, and the two-stage take advantage of two absorption columns, with methanol as solvent, to remove the contaminants. Table 6 presents the flow specification of the two entering streams, the raw syngas and the methanol solvent, to the absorption column and the clean

syngas leaving the column in a conventional single-stage Rectisol[®] process. The molar flow rate ratio of the solvent to raw syngas can be estimate to be 1.21 in the case of a conventional single-stage Rectisol[®], while it is about 0.83 in the case of the suggested configuration. This implies a relative improvement of around 30% for the proposed process. Moreover, the less severe working conditions in terms of working pressure and temperature should be used in case of the suggested configuration. As shown in Figure 1, the selective Rectisol[®] process also separates CO₂ from the feed stream and delivers a separate stream mainly consisting of CO₂. Since the detailed calculations and specifications of conventional Rectisol[®] process are kept confidential [18,29], it is not clear if the conventional selective Rectisol[®] process can remove the impurities to less than 0.1 ppm in the produced CO₂ stream. Moreover, results of Aspen Plus modelling on the different scenarios for selective Rectisol[®] process, together with previous works done on this matter [18,29] show that the production of a separate ultra-clean stream of CO₂ is hard to achieve in a selective Rectisol[®] process. On the other hand, the suggested process configuration, shown in Figure 2, with only one-step methanol wash, meets the cleaning demand for a downstream methanation. The main reason behind using two methanol wash units in selective Rectisol[®] process is to achieve a selective cleaning of H₂S together with other contaminants, over CO₂ [13,18]. However, having two methanol wash units in a process also two regeneration units is needed as well.

Table 6. Flow specifications of a single-stage Rectisol process [29].

Composition (%)	Raw Product Gas	Methanol	Purified Syngas
Carbon monoxide	19.01	0	3.42
Carbon dioxide	34.20	0	27.58
Hydrogen	46.07	0	68.17
Methane	0.18	0	0.25
Hydrogen sulfide	0.13	0	0
Methanol	0	1	1.2×10^{-2}
Total flow (kmol/s)	1.17	1.42	0.79
Temperature (K)	253	223	234
Pressure (bar)	34	44	33

The proposed gas cleaning process in Figure 2 has only one methanol wash unit, suggesting this configuration could save costs both in investment and in the operation of the process. A conventional Rectisol[®] process is normally equipped with a N₂ stripping column in the regeneration process of used methanol directly after the flash tank [29], which is not shown in Figure 2, as it is absent in the proposed process configuration. The reason for this is mainly the impact water scrubber (A-1) have on the quality of the gas fed to methanol wash (A-2), *i.e.*, the impurities is already removed from the gas by water scrubber (A-1) and therefore the regeneration of used methanol from methanol wash (A-2) requires less processing.

6. Conclusions

In the present work, a modified gas-cleaning configuration, based on conventional Rectisol[®] technology, has successfully been developed, using Aspen Plus modeling. The gas cleaning process is

intended as a part of a SNG production plant for cleaning of a raw product gas from biomass gasification, using a 50 MW_{fuel} WoodRoll[®] gasification process. The analysis was focusing on a process keeping the bulk of the carbon dioxide in the stream and simultaneously removes the undesired contaminants, allowing for methanation of both carbon monoxide and carbon dioxide. The main conclusions and findings can be summarized as follows:

- A preliminary tentative comparison with a conventional Rectisol[®] process, suggest that the proposed configuration can take advantage of only one methanol wash column, compared to two columns in a conventional Rectisol[®] process. This implies lower investment costs as well as lower operational costs in case of the developed process.
- The designed Rectisol[®] process cleans the gas and simultaneously retains 92% of the entering CO₂ in the process product gas stream.
- The make-up of methanol to be added to the process to account for losses in the process can be calculated to less than 10 kg/h, which is acceptable for a plant of the size investigated.
- The water in the process is the key element to reduce the loss of methanol by removing a part of impurities from the feed gas and the total water flow in the process is calculated by Aspen Plus and is estimated to 220 kg/h.
- The methanol to raw syngas molar flow rate ratio of the proposed configuration is about 0.83, compared to 1.21 for a conventional single stage Rectisol[®] process. This implies a relative improvement of around 30% for the proposed process.

7. Future Work

Process integration of the modified process has not been considered in the present study. A techno-economic analysis, accounting for installation, and operational and maintenance costs, is proposed as a future work in order to evaluate the cost benefits for the gas cleaning process itself, as well as in the context of a complete system. For instance, the proposed gas cleaning process can be implemented in different gasification process scenarios. The general desire is to minimize the number of process steps with sustained performance, regarding robustness and yield, to achieve a more cost efficient process. Two examples of systems, aimed at production of methane or biogas, using additional hydrogen from wind or solar power, are illustrated in form of a tentative block diagram in Figure 3. The general steps in the system includes gasification, gas cleaning and upgrading, consisting of several steps depending on the quality of the product gas and needs of the end user application, the solar or wind power plant, the electrolyzer, and finally the methanation step.

Depending on the cleaning and upgrading processes used, the production of the methane can be carried out in one or two process steps. A process where the impurities are removed, but CO, CO₂ together with hydrogen remains in the gas, suggests methanation in one process step. Using a conventional ultra-gas cleaning process, separating impurities together with CO₂, requires methane production in two separate process steps or in one step, providing simultaneous methanation of both CO₂ and CO is available [33,34]. Both processes would benefit from more efficient and simplified process in order to reduce costs. However, to achieve an overall optimized process efficiency the proposed gas cleaning process need to be integrated in the overall process and optimized as part of the

overall process. This process integration is out of the scope of the present study, but will be investigated in future projects.

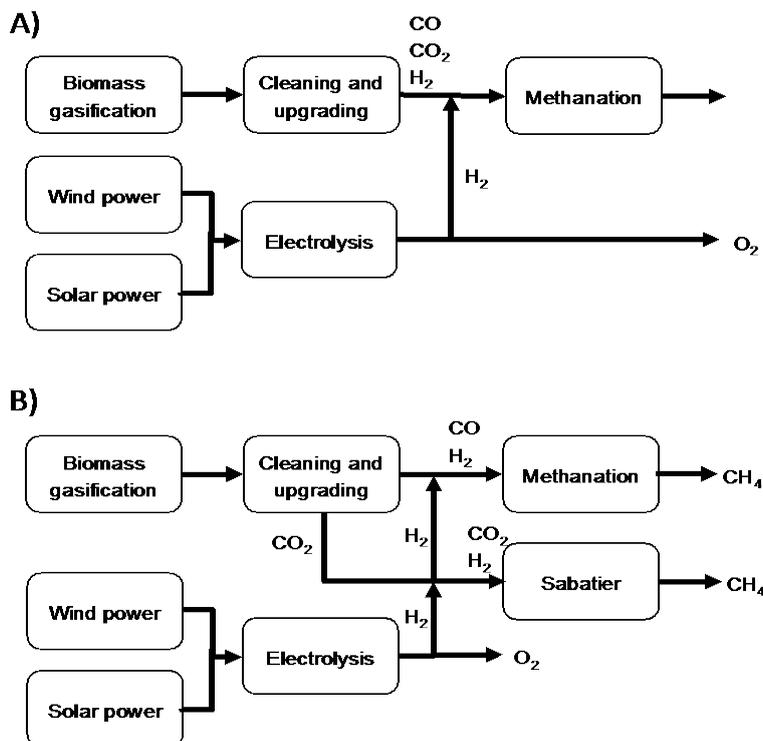


Figure 3. Two simple block diagrams of processes for methane production from biomass including additional hydrogen from solar or wind power. (A) includes a single methanation step and (B) a methanation step and a Sabatier process converting the CO₂.

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Conflicts of Interest

The authors declare no conflict of interest.

References

1. European Union. *European Strategic Energy Technology Plan (SET Plan)-Towards a Low-Carbon Future*, ISBN 978-92-79-15667-0; Publications Office of the European Union: Luxembourg, Luxembourg, 2010.
2. Karl, J. Distributed generation of substitute natural gas from biomass. In Proceedings of the 16th European biomass conference and exhibition, Valencia, Spain, 2–6 May 2008; pp. 2515–2519.
3. Arvidsson, M.; Heyne, S.; Morandin, M.; Harvey, S. Integration opportunities for Substitute Natural Gas (SNG) production in an industrial process plant. *Chem. Eng. Trans.* **2012**, *29*, 331–336.
4. Seemann, M.C.; Schildhauer, T.J.; Biollaz, S.M.A. Fluidized bed methanation of wood-derived producer gas for the production of synthetic natural gas. *Ind. Eng. Chem. Res.* **2010**, *49*, 7034–7038.

5. Mozaffarian, M.; Zwart, R.W.R. *Feasibility of Biomass/Waste-Related SNG Production Technologies*; Technical Report, ECN publication No: ECN-C-03-066; ECN: Petten, The Netherlands, 2003.
6. Basu, P. *Biomass Gasification and Pyrolysis—Practical Design and Theory*; Academic Press Elsevier: Burlington, MA, USA, 2010.
7. Mohseni, F.; Magnusson, M.; Görling, M.; Alvfors, P. Biogas from renewable electricity-increasing a climate neutral fuel supply. *Appl. Energy* **2012**, *90*, 11–16.
8. Lau, F.S.; Carty, R.H. Development of the IGT RENU GAS[®] process. In Proceedings of the 29th Intersociety Energy Conversion Engineering Conference Development, Monterey, CA, USA, 7–12 August 1994; OSTI Report: CONF-940812-19.
9. Jörgensen, C.; Ropenus, S. Production price of hydrogen from grid connected electrolysis in a power market with high wind penetration. *Int. J. Hydrog. Energy* **2008**, *33*, 5335–5344.
10. StatoilHydro, (information handout). *Hydrogen Technologies—World Leader in Electrolysis for Hydrogen Solutions*; StatoilHydro: Stavanger, Norway, 2008.
11. Neathary, J.K. Biomass gasification. In *Thermochemical Conversion of Biomass to Liquids Fuels and Chemicals*; Crocker, M., Ed.; RSC Publishing: London, UK, 2010; pp. 67–94.
12. Engvall, K.; Kusar, H.; Sjöström, K.; Pettersson, L.J. Upgrading of raw gas from biomass and waste gasification: Challenges and opportunities. *Top. Catal.* **2011**, *54*, 949–959.
13. Higman, C.; van der Burgt, M. *Gasification*, 2nd ed.; Gulf Professional Publishing Elsevier: Oxford, UK, 2008.
14. Amovic, A.; Donaj, P.; Moner, B.; Alzuheri, R.; Ljunggren, R. Fuel testing procedure for pyrolysis and gasification of biomass using TGA and WoodRoll test plant. In *SGC Rapport 2014:293*; SGC: Malmö, Switzerland, 2014. Available online: <http://www.sgc.se/ckfinder/userfiles/files/SGC293.pdf> (accessed 20 April 2015).
15. Gills, D.B. (UOP), technology to maximize value of synthetic gas. In Proceedings of the Seminar on Clean Fuels from Coal/Pet Coke, CHT, New Delhi, India, 13 December 2006.
16. Boerrigter, H.; den Uil, H.; Calis, H.P. Green diesel from biomass via Fischer-Tropsch synthesis: New insights in gas cleaning and process design. In *Pyrolysis and Gasification of Biomass and Waste*; Bridgewater, A.V., Ed.; CPL Press: Newbury, UK, 2003; pp. 371–383.
17. Torres, W.S.; Pansare, S.G.; Goodwin, J., Jr. Hot gas removal of tars, ammonia, and hydrogen sulfide from biomass gasification gas. *Catal. Rev. Sci. Eng.* **2007**, *49*, 407–456.
18. Arthur, L.K.; Richard, B.N. *Gas Purification*, 5th ed.; Gulf Publishing Company: Houston, TX, USA, 1997.
19. Pani, F.; Gaunand, A.; Richon, D.; Cadours, R.; Bouallou, C. Absorption of H₂S by an aqueous methyldiethanolamine solution at 296 and 343 K. *J. Chem. Eng. Data* **1997**, *42*, 865–870.
20. Fischer, K.; Chen, J.; Petri, M.; Gmehling, J. Solubility of H₂S and CO₂ in N-Octyl-2-pyrrolidone and of H₂S in methanol and benzene. *AIChE J.* **2002**, *48*, 887–893.
21. Kriebel, M. Gas Production. In *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed.; VCH Verlagsgesellschaft GmbH: Weinheim, Germany, 1989; pp. 257–258.
22. Ranke, G.; Mohr, V.H. The Rectisol Wash: New Developments in Acid Gas Removal from Synthesis Gas. In *Acid and Sour Gas Treating Processes*; Newman, S.A., Ed.; Gulf Publishing Company: Houston, TX, USA, 1985; pp. 80–111.

23. Kubek, D.J.; Polla, E.; Wilcher, F.P. Purification and Recovery for Gasification. In Proceedings of the Gasification Technologies Conference, San Francisco, CA, USA, 8–11 October 1996.
24. Burr, B.; Lyddon, L. *A Comparison of Physical Solvents for Acid Gas Removal*; Bryan Research & Engineering, Inc.: Bryan, TX, USA, 2008. Available online: <http://www.bre.com/portals/0/technicalarticles/A%20Comparison%20of%20Physical%20Solvents%20for%20Acid%20Gas%20Removal%20REVISED.pdf> (accessed on 4 January 2015).
25. Weiss, H. Rectisol wash for purification of partial oxidation gases. *Gas Sep. Purif.* **1988**, *2*, 171–176.
26. Mork, M.; Gudmundsson, J.S. *Natural Gas Cleaning*, Department of Petroleum Engineering and Applied Geophysics, NTNU: Trondheim, Norway, 14 November 2011. Available online: <http://www.ipt.ntnu.no/~jsg/undervisning/prosessering/gammelt/kompendium2005/11-RensingNaturgass.pdf> (accessed on 4 January 2015).
27. Hochgesand, G. Rectisol and Purisol. *Ind. Eng. Chem.* **1970**, *62*, 37–43.
28. Lurgi, G. *The Rectisol® Process, Lurgi's Leading Technology for Purification and Conditioning of Synthesis Gas*. Available online: http://uicgroupecho.wikispaces.com/file/view/B_0308e_Rectisol.pdf (accessed on 4 January 2015).
29. Sun, L.; Smith, R. Rectisol wash process simulation and analysis. *J. Clean. Prod.* **2013**, *39*, 321–328.
30. Dayton, D. *A Review of the Literature on Catalytic Biomass Tar Destruction*; Technical Report, Report NREL/TP-510-32815; National Renewable Energy Laboratory (NREL): Golden, CO, USA, 2002.
31. Koytsoumpa, E.I.; Atsonios, K.; Panopoulos, K.D.; Karellas, S.; Kakaras, E.; Karl, J. Modelling and assessment of acid gas removal processes in coal-derived SNG production. *Appl. Therm. Eng.* **2015**, *74*, 128–135.
32. Hanlon, P.C. *Compressor Handbook*, 1st ed.; McGraw-Hill: New York, NY, USA, 2001.
33. Aksoylu, A.E.; Önsan, Z.I. Hydrogenation of carbon oxides using coprecipitated and impregnated Ni/Al₂O₃ catalysts. *Appl. Catal. A: Gen.* **1997**, *164*, 1–11.
34. Jiménez, V.; Sánchez, P.; Panagiotopoulou, P.; Valverde, J.L.; Romero, A. Methanation of CO, CO₂ and selective methanation of CO, in mixtures of CO and CO₂, over ruthenium carbon nanofibers catalysts. *Appl. Catal. A Gen.* **2010**, *390*, 35–44.