METHANATION OF SYNGAS FROM BIOMASS GASIFICATION: SMALL-SCALE PLANT DESIGN IN ASPEN PLUS™

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Abstract
The goal of this paper is to investigate the upgrading of low-quality syngas from biomass gasification processes into a methane-rich gas stream. The Aspen Plus software package has been used to simulate and compare several plant designs. Reactor sizing and performance are also discussed. Results show that a system with four adiabatic fixed-bed reactors, inter-cooling, and enhanced water removal guarantees an acceptable performance-cost trade-off. An operating pressure of 5 bar has been found to be adequate to reduce the catalyst mass required and to prevent solid carbon deposition. A 99.4% CO conversion, 89.3% CO_2 conversion, and 95.6% CH_4 yield have been achieved, with a final methane molar content of 26.4% and a calorific value of 9.41 MJ/Nm^3.

Introduction
Fossil fuels have been the driving force behind industrial progress due to their cheap costs, high energy-to-volume ratio, and ease of storage and transport. However, they are not sustainable energy sources [1], and their increased exploitation has resulted in a significant rise in CO_2 emissions and negative environmental impacts [2]. To reconcile modern society's expanding energy demands with a sustainable approach to industrial growth, worldwide research on renewable energy utilization drastically increased in the last century. In 2020, renewable energy overtook fossil fuels for the first time, marking a "landmark moment in the history of the EU" [3]. Biomass-derived energy generation has recently gained interest as a promising alternative energy source. Biomass conversion can be achieved through thermochemical, biochemical, and mechanical processes. Gasification is the most intriguing thermochemical pathway for biomass conversion since it produces a versatile syngas, which can be used for the generation of energy (heat/power) as well as for chemical synthesis [4]. Large-scale centralized gasification facilities would not be

ideal for efficient bioenergy generation and waste disposal. Indeed, due to the low bulk densities, most biomass is quite voluminous, resulting in high transportation and storage costs [5]. Thanks to small-scale plants, biomass exploitation might be helpful in improving energy supply in remote places [6]. Catalytic methanation can be used to upgrade syngas produced by biomass gasification. The benefits of synthetic natural gas (SNG) include its high conversion efficiency, interchangeability with natural gas, existing transportation infrastructure (methane pipelines), and proven and efficient end-use technologies.
The aim of this work was to design and simulate a methanation system that employs syngas from a small-scale biomass gasification as raw feedstock using the Aspen Plus software. Different methanation plant schemes were compared, and a sensitivity study was performed to examine the impact of different operating parameters on system performance.

Materials and methods
Aspen Plus™ was used to model the conversion of syngas to bio-methane, with the syngas composition retrieved from an experimental study [7] where biomass gasification with air was performed using a small-scale commercial fixed-bed downdraft gasifier in a micro-CHP plant. Table 1 shows the dry-basis syngas composition adopted in the simulations.

Table 1. Dry-basis syngas composition.

Component	[v/v%] d.b.
CO	15.9
CO_2	9.16
CH_4	1.24
H_2	12.2
N_2	61.5

Thermodynamic analysis. The Aspen Plus RGibbs model was used to perform thermodynamic calculations. In addition to the species reported in Table 1, also water and solid carbon were declared among the simulation compounds. The Peng-Robinson equation of state was chosen as property method because it is suited to describe non-polar or mildly polar gas mixtures under various temperature and pressure conditions. First, a sensitivity study allowed to investigate the trend in the conversion of CO and CO_2, along with the methane and the solid carbon yield, as the reactor temperature and pressure varied (100-1000°C and 1-15-30 atm). Then, leaving the pressure set at 1 bar, the process performance was also evaluated varying the reactor temperature (10-1000°C) and with the amount of added hydrogen as parameter (0 kg/h, stoichiometric conditions, 15% excess).
Kinetic model. The kinetic model by Xu and Froment [8] on a Ni/$MgAl_2O_4$-spinel

catalyst (15.2% Ni) is widely applied in the field of methanation reactor simulation and modeling [9]. The Langmuir-Hinshelwood-Hougen-Watson (LHHW) equations by Xu and Froment consider the CO and CO_2 methanation reactions and the Water-Gas Shift (WGS) reaction. The kinetic of solid carbon formation is not modeled. The kinetic model was validated by comparing simulation results with industrial data reported by Khorsand et al. [10]. Relative errors were always less than 10% suggesting that the model is appropriate.

Reactor sizing & system design. Methanation reactors were simulated using the Aspen RPLUG model, which describes perfect plug-flow reactors in steady-state conditions. Axial mass and heat transfer are assumed to be negligible. The Ergun equation was selected to estimate the pressure drops through the catalytic bed. It was decided to simulate methanation reactors using a single-tube option since the focus is on small-scale applications. The catalyst parameters used in the simulations were taken from Matthischke et al. [11], who refer to a commercial Ni/Al_2O_3 catalyst with sphere-shaped particles. Namely, catalyst particle diameter was 3 mm, bed porosity was 0.39, particle density and bulk density were 1475 kg/m^3 and 900 kg/m^3 respectively.

To set the values of the large number of degrees of freedom of the investigated system, general empirical restrictions gathered by Woods [12] were considered, involving an outlet temperature limit of 550°C to mitigate catalyst sintering and deactivation, a turbulent particle Reynolds number (>100) and an axial Peclet number bigger than 2. Because the purpose of the process is to achieve equilibrium conversion, the length of the reactor was assumed equal to the minimum length needed to achieve thermodynamic equilibrium increased by 20 to 40% as a safety factor. Different plant schemes were considered and simulated, namely:

- a single stage methanation system,
- a single stage recycle reactor,
- a series of FBRs (fixed-bed reactors),
- a system with water condensation.

Sensitivity study & optimization. A sensitivity study was conducted to assess the impact of different parameters (namely, plant pressure, reactor's inlet temperature, condenser location) on plant performance and catalyst mass required.

Results and discussion

Thermodynamic analysis. The thermodynamic analysis allowed to select the proper operating conditions for the process. The main findings can be summarized as follows:

- Low temperature and high pressure favour thermodynamic conversion of the reactants to products, but pressure higher than 8 bar does not give substantial advantage,
- the $H_2/(CO+CO_2)$ ratio should be very close to the stoichiometric. A low hydrogen concentration leads to a low methane production and a significant

amount of solid carbon can deposit on the catalyst surface.

Figure 1 clearly emphasizes how stoichiometric condition are beneficial to obtain high methane yields while mitigating catalyst fouling.

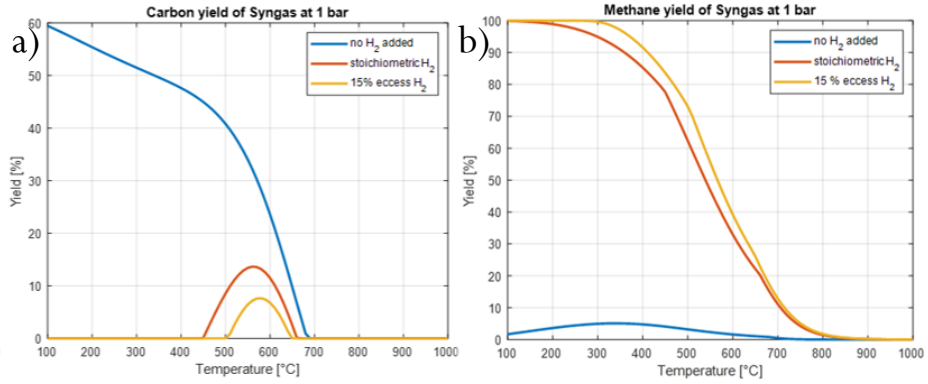

Figure 1. Solid carbon yield (a) and methane yield (b) as functions of reaction temperature and amount of added hydrogen.

Reactor sizing & system design. The multistage adiabatic plant consisting of 5 fixed-bed reactors in series with three condensers- shown in Figure 2- was the end point of the analysis.

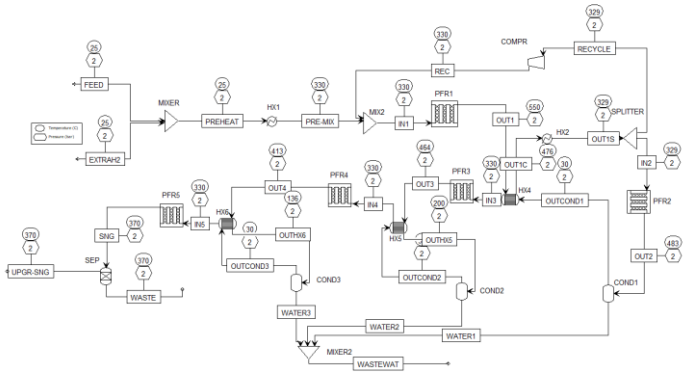

Figure 2. Flowsheet of a multi-stage adiabatic methanation system with inter-condensation.

According to the thermodynamic analysis, water removal can improve the performance of the system by shifting thermodynamic equilibrium toward the products, leading to higher methane generation. The system showed in Figure 2 allowed to achieve a global CO and CO_2 conversion of 99.7% and 90.8% respectively, with an overall methane yield of 96.6%.

Sensitivity study & optimization. The main results of the sensitivity study can be

summarized as follows:

- the 5th reactor in Figure 2 gives little contribution to the overall conversion of carbon oxides while requiring great amount of catalyst; therefore it can be deleted,
- higher pressures mildly favor methane yield but increase catalyst requirements,
- a reactor inlet temperature of 350°C instead of 330°C helps reducing catalyst requirements while having little effect on CO_x conversion,
- a single condenser located after the third reactor is more economically viable compared to the three condensers of Figure 2. Indeed this configuration minimizes catalyst mass while guaranteeing adequately high CO_2 conversions.

Finally, an optimal system characterized by four stages, reactor inlet temperatures of 350°C, an operating pressure of 5 bar, an outlet temperature from the recycle fixed-bed reactor of 550°C, and a single condenser located after the third adiabatic stage was identified. A molar recycle ratio of 2.8 allows having an outlet temperature from the recycle reactor of 550°C. With a total catalyst mass of 20 kg, the optimized system achieves a 99.4% CO conversion, an 89.3% CO_2 conversion and an overall methane yield of 95.9%. Figure 3 illustrates the flowsheet of the optimized plant scheme and Figure 4 shows the CH_4 volume fraction (%) vs. Temperature chart, which summarizes the conversion steps from syngas to SNG.

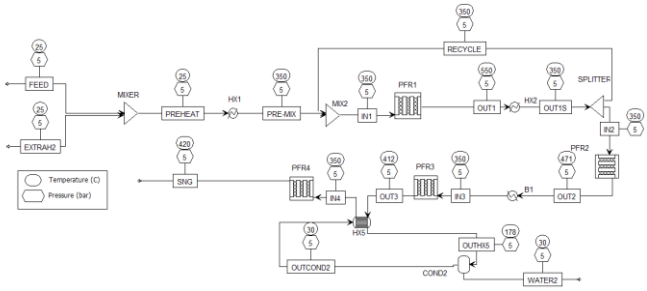

Figure 3. Aspen Plus flowsheet for the optimized system.

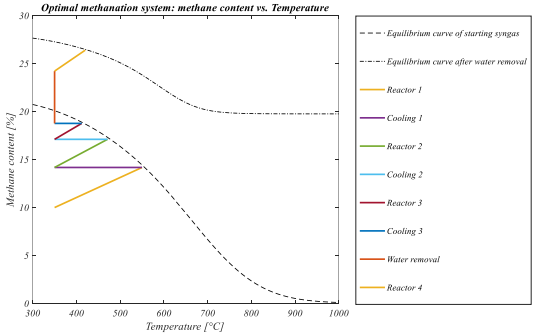

Figure 4. CH_4 content vs Temperature chart for the optimized adiabatic operation.

Conclusion. The research for new clean energy sources is a compulsory necessity worldwide, and biomass can play a key role in the present de-carbonization effort. Methanation is an intriguing method of generating clean energy and storing fluctuating renewable energy as chemical energy. The development of novel catalysts that are more adaptable and resilient against sulfur poisoning and carbon deposition, as well as research into more efficient reactor concepts that can achieve higher performance, are just a few of the issues that come up during the design and construction of biomass-to-SNG plants and to which the future research should devote its attention.

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