

PROCESS MODELING OF THE PRODUCTION OF SYNTHETIC NATURAL GAS FROM BIOMASS-DERIVED SYNGAS

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Abstract

The production of Synthetic Natural Gas (SNG) by syngas obtained from biomass gasification is a challenging process. In particular, since methanation (as Fischer-Tropsch synthesis) is conducted catalytically, strict limits are present in terms of undesired species in the produced gas before the fuel synthesis stage. Moreover, if the syngas is obtained through air-gasification also the hydrogen content should be improved through an appropriate conditioning stage, to obtain a reasonable yield in the desired product. In this work, a brief description of the cleaning and conditioning stages required to improve the quality of the syngas is proposed, and three configurations for the methanation stage of the improved syngas obtained through air gasification of biomass are analyzed and discussed.

Introduction

The synthesis of fuels from renewable sources is considered to be an interesting option for the aim of reducing the carbon footprint of sectors like industries and transport [1]. Numerous approaches can be adopted to reach this objective including biological processes such as the fermentation of sugars, the use of renewable electricity to obtain hydrogen and the so so-called e-fuels, or the use of residual lignocellulosic biomass. The latter is particularly interesting because residual biomass is abundant as a waste stream from other processes, and it is not expensive. In addition, biomass is known to be carbon neutral, since the carbon dioxide emitted by the exploitation of this feedstock is equal to that stored by the biomass during its lifetime. In this work, the focus was put on the synthesis of SNG starting from biomass-derived syngas. In particular, the next section presents the steps required to obtain a valuable product, since the raw syngas obtained through gasification is not suitable for direct synthesis. Cleaning and conditioning stages are required to improve the syngas quality and to make it suitable for methanation. Then three possible configurations for the methanation stage are presented.

Cleaning and conditioning stages

Since biomass has a heterogeneous composition, numerous undesired species can be found in the product syngas, like HCl, H₂S, alkali metals, particulate matter, and tars.

These species and, in particular, tars are related to the operating conditions and the different type of gasification agent (air, oxygen, or steam), and also to the reactor configuration. To obtain a suitable gas for further utilization some requirements have to be satisfied and these limits are related to the use of the gas.

Contaminant	Application			
	IC engine	Gas turbine	Methanol synthesis	FT synthesis
Particulate (soot, dust, char, ash)	<50 mg m ⁻³ (PM10)	<30 mg m ⁻³ (PM5)	<0.02 mg m ⁻³	n.d. ^a
Tars (condensable)	<100 mg m ⁻³		<0.1 mg m ⁻³	
Inhibitory compounds (class 2-heter atoms, BTX)				<0.01 μL L ⁻¹ <1 μL L ⁻¹
Sulfur (H ₂ S, COS)		<20 μL L ⁻¹	<1 mg m ⁻³	<0.01 μL L ⁻¹
Nitrogen (NH ₃ , HCN)		<50 μL L ⁻¹	<0.1 mg m ⁻³	<0.02 μL L ⁻¹
Alkali		<0.024 μL L ⁻¹		<0.01 μL L ⁻¹
Halides (primarily HCl)		1 μL L ⁻¹	<0.1 mg m ⁻³	<0.01 μL L ⁻¹

Figure 1. Typical syngas applications and associated cleaning requirements [2].

In Fig. 1 (taken from [2]), it can be seen that more stringent limits are required when fuel synthesis is considered, in order to avoid catalyst poisoning. In particular, limits related to tar content are quite challenging to be satisfied, since the other contaminants can be more easily removed using sorbents that work at high temperature, such as *ZnO* [3], *Al₂O₃*, *CaO* [4], or by low-temperature operations such as wet scrubbers [2]. In the tar content also molecules like benzene, toluene and xylene are considered, which usually are not removed in other processes such as in CHP applications. To remove heavier tars and part of the BTX contained in the raw gas the approach ideated by ECN named as OLGA process [5] which involves the use of two scrubber columns with liquid rapeseed methyl ester, seems to be the most interesting choice, since it combines good thermal efficiencies and good removal of such undesired species. After this stage, to obtain that specification on the tar levels, a further polishing stage is required like the utilization of an active carbon bed, as done in [6], or a pre-reforming stage where at a temperature of around 500 °C the gas leaving the process is mixed with steam to obtain the conversion of BTX in syngas. Here also part of the carbon monoxide is converted into carbon dioxide and extra hydrogen through the water gas shift reaction. In addition, if the syngas has to be used in a fuel synthesis stage like methanation, the ratio between hydrogen and carbon monoxide should be at least equal to three, in order to obtain stoichiometric conditions, otherwise part of the reactants will not react. So to obtain such ratio other stages can be added as the pre-reformer described above or a water gas shift section to improve the hydrogen content, or alternatively hydrogen obtained from the surplus of renewable sources such as wind or solar energy through the electrolysis of water [7] can be added to the syngas to improve the H₂/CO ratio. These are considered as conditioning stages required before the methanation stage.

Fuel synthesis stage

After the correct design of the previous stages, it is possible to convert the upgraded syngas through methanation into SNG. In this work, three schemes have been evaluated based on the syngas obtained through air gasification of wood chips, and improved to reach a ratio between hydrogen and carbon monoxide equal to three using a water gas shift reactor.

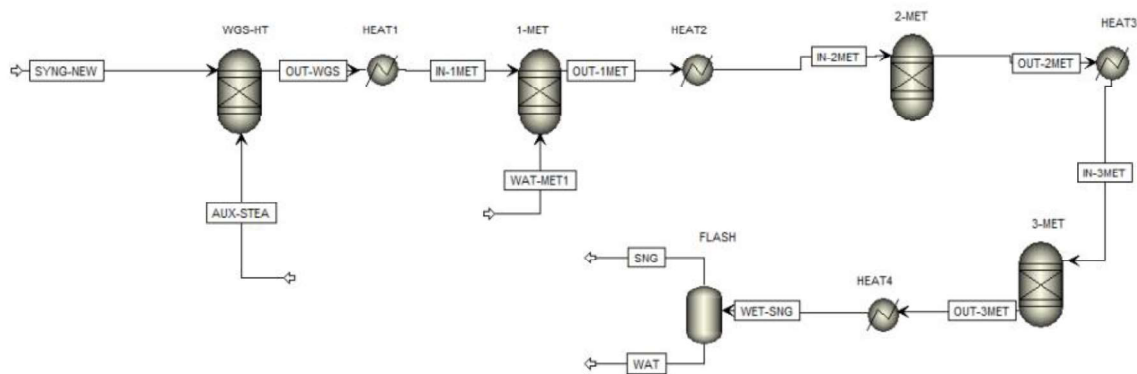


Figure 2. First configuration studied to obtain SNG, named configuration (a)

Figure 2 reports the Aspen flowsheet of the first configuration, which works without the use of external hydrogen. Methanation is carried out in three adiabatic Gibbs reactors, with intermediate cooling, simulating the typical plug flow reactors configuration for this process, as seen in [8]. Temperature and an auxiliary water stream are chosen such to avoid solid carbon formation, to increase the methane yield, and to avoid too high temperature-related issues like sintering of the commonly used Ni catalyst [8]. Then after the last reactor, a flash is used to remove the water obtained from the methanation reactors. In Table 1 the molar composition of the stream that enters the first methanation reactor of the flowsheet, named IN-1METH, and of the stream with the final product named SNG, are reported.

Table 1. Molar composition of “IN-1MET” and “SNG” streams of configuration (a)

Composition (%mol)	IN-1METH	SNG
CO	5.81	0.02
CO ₂	21.11	30.22
H ₂	18.37	2.16
CH ₄	3.33	12.79
N ₂	33.97	48.33
H ₂ O	17.41	6.48

From this table, it is possible to observe that almost all of the carbon monoxide has reacted and consequently also the hydrogen content has been greatly reduced. However, in configuration (a), which is the easiest configuration studied for the fuel synthesis stage, the final product is rich in CO₂, which has to be removed in a further

Table 2. Molar composition of “IN-SAB1” and “SNG” streams of configuration (b)

Composition (%mol)	IN-SAB1	SNG
CO	0.02	0.34
CO ₂	30.22	17.71
H ₂	2.16	7.83
CH ₄	12.79	22.32
N ₂	48.33	45.33
H ₂ O	6.48	6.47

It was verified then that adding another methanation unit (3-SAB) to configuration (b) working at the same conditions as the other carbon dioxide conversion units, and utilizing the stoichiometric hydrogen required to theoretically completely convert the CO₂ present in the stream IN-SAB1, will lead to a final product in which the main components are: N₂ (41%), CH₄ (31%), CO₂ (4.8%), H₂ (15.5%), H₂O (6,4%), CO (negligible). This limiting case is obtained at p=1 atm and it is shown below in Fig. 4, and named configuration (c).

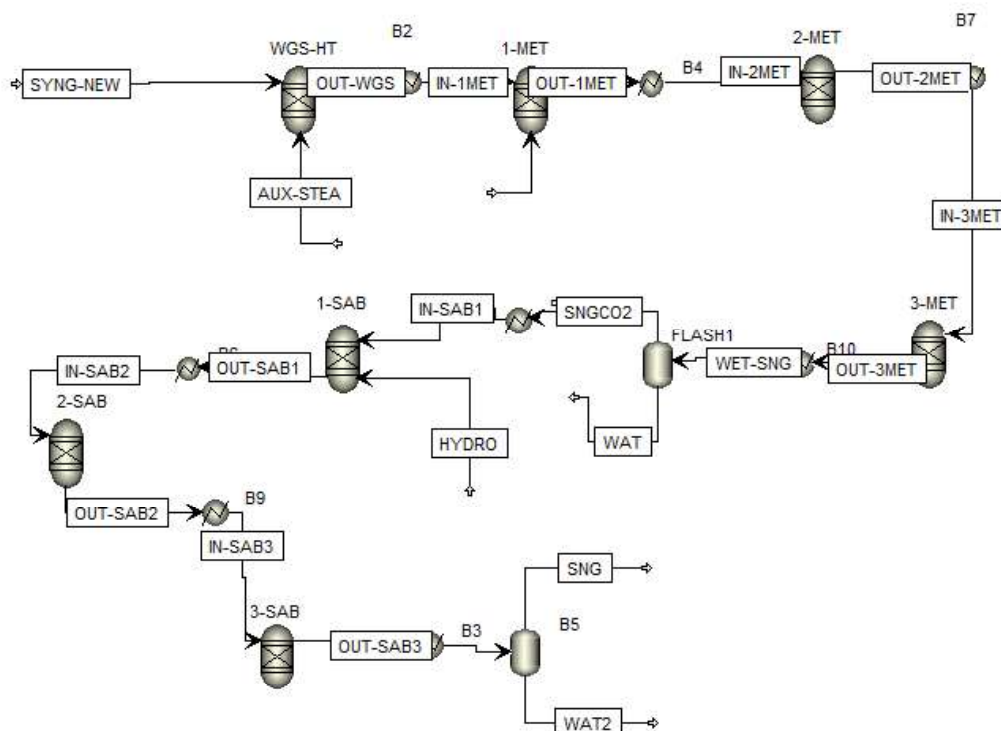


Figure 4. Third configuration studied to obtain SNG, with three additional reactors for CO₂ methanation, named configuration (c).

Next steps

The Olga process and a pre-reforming stage will be integrated into the Aspen model through equilibrium simulations for real syngas with tar-species, to describe this challenging required cleaning stage. Subsequently, a kinetic approach will be

followed to design the units required for the cleaning and the fuel synthesis stages leveraging what was learned from this initial equilibrium approach.

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