METHANE PRODUCTION FROM BIOMASS-DERIVED SYNGAS: ISSUES AND BENEFITS

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Abstract
The use of biomass is considered to be interesting for the production of biofuels such as bio-methane or bio-methanol in order to limit the use of fossil fuels. The first step to obtain these substances by thermal processes is typically the gasification of biomass for syngas production, which can be then used as the feedstock for catalytic hydrogenation processes. Different oxidizing agents and can be used, as air, steam, a blend of air and steam, oxygen etc. Methane has the advantage to be easily stored and transported using the existing infrastructure.
The main problems related to syngas catalytic methanation are: i) the requirement to remove pollutants contained in the syngas, such as tar, to prevent catalyst deactivation; ii) the adjustment of the syngas H/C ratio which is typically too low with respect to the stoichiometric requirement for methanation. Pollutant abatement and improvement of the H/C ratio are identified as cleaning and conditioning processes of the syngas, respectively.
In this paper, the principles and effect of syngas methanation are discussed. In addition, an overview about the contaminants and the operations of gas cleaning and gas conditioning is given.

Introduction
The effects of global warming and climate change continue to be evident due to the use of fossil fuels [1]. Events such as the rise of the earth's temperature, and the occurrence of the melting of glaciers are becoming more and more common. So it is necessary to develop new ways to sustain the energy demand that our society needs, and renewable energies are recognized as the most promising choice thanks to the low emissions involved in their exploitation. The use of biomass looks promising, thanks to the capacity of being carbon neutral.
Numerous thermochemical or biochemical processes exist to convert biomass in chemical products or energy, such as combustion, pyrolysis, gasification, anaerobic digestion etc. In particular, methanation is a catalytic process that is used to convert the syngas obtained from gasification into Synthetic Natural Gas (SNG), which desired reactions are the following:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H = -\frac{206KJ}{mol}\ at\ 298\ K \qquad (1)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H = -\frac{164KJ}{mol} at\ 298\ K \qquad (2)$$

Since the main product of gasification is syngas, a mixture of CO and H_2, reaction (1) has been studied in more detail, but for both reactions it is possible to note that they are extremely exothermic and involve a reduction of volume. So higher conversions can be reached at high pressures and at low temperatures. In addition, the occurrence of other reactions, such as water-gas-shift, Boudouard reaction, dry-reforming, etc. [2] should be considered.
Obviously, the catalyst plays a key role in the success of a methanation process ensuring high chemical activity and selectivity towards the desired product. It should possess elevated thermal and chemical stability, and, if possible, be relatively cheap. Numerous studies have been conducted on different catalysts, and the best one for commercial applications has been found to be a Ni-based catalyst, possibly enhanced by promoters, MgO, La_2O_3, CeO_2 and supported by alumina [3–7]. The heterogeneous gas-solid reaction kinetic models are built on Langmuir - Hinshelwood or Eley-Rideal mechanisms [3,6].

Effects of methanation and applications

Syngas-obtained from biomass gasification can be used for multiple purposes such as thermal and electrical energy generation (cogeneration [8]), fuel synthesis, or production of H_2 used in fuel-cells [9]. Depending on the final use of the syngas different characteristics are required [10]. What we can see from [9] is that syngas characteristics such as toxicity, lower and upper explosion limits, are highly influenced by gasification conditions such as the choice of the oxidation agent. In fact, not all of the gasification techniques look promising to generate high methane concentrations. For example, syngas produced from steam-gasification appears to be more promising than the others thanks to its high content of hydrogen and for the absence of inert gases like nitrogen. Some of the advantages related to the methanation of the raw syngas are the improved effect on flammability interval (Figure 1), which is now smaller and safer compared to the original syngas, the improved value for high calorific value, smaller concentration of carbon monoxide, and presence of a safer and more manageable substance as methane.
In order to perform methanation and avoid Ni catalyst deactivation, with phenomena such as fouling or poisoning of the active phase, it is necessary to remove undesired substances from the raw syngas and to improve its H/C ratio.

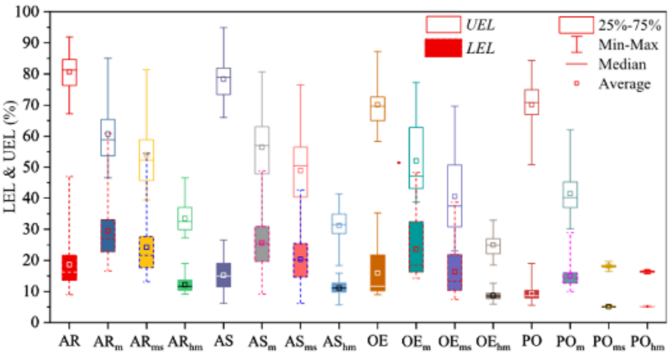

Figure 1.Effect of methanation on flammability limit [9]

Contaminants and operations of cleaning and conditioning

Typical contaminants contained in syngas are reported below:
- Particulate matter: residual solid-carbon, inorganic matter, catalyst, and bed material from the gasification reactor.
- Tars: derived from the pyrolysis of the biomass, and not converted into incondensable gases. They are formed by different compounds like oxygenated products, heavier deoxygenated hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) [11].
- Sulphur: these compounds are mainly present as hydrogen sulphide H_2S and carbonyl sulfide COS.
- NH_3 and HCN: their concentration typically depends on the biomass composition and nature. Ammonia is the most common form.
- Alkali compounds: alkali and alkali earth metals are often contained in biomass feedstock, and their concentration is often higher than in coal.
- Chlorine: chlorides are the predominant halide in syngas, usually in the form of hydrochloric acid (HCl), which is formed by the reaction that occurs from chlorine in biomass as alkali metal salts react with water vapour to form HCl.

In the last years, numerous techniques have been proposed to remove these contaminants. Such techniques can be described using the following classification taken from [10], based on the working temperature:
-*Hot gas clean-up* (HGC): Including all the operations that are usually conducted in the temperature range [350-1000 °C], has historically focused on removal of particulate matter and tar, with the goal of minimizing maintenance of syngas combustion equipment, and to remove these contaminants with a higher energy efficiency. In literature it has been found that this kind of approach is suitable for the removal of almost all the contaminants:
- Particulate removal can be conducted with filters, cyclones, and electrostatic separators [12].

- Tars can be removed through catalytic cracking, thermal cracking and physical separation using sorbents. In particular, the catalyst (Ni-based, zeolites, or minerals such as dolomite and olivine) used for the catalytic cracking shows also a good activity in NH_3 reduction, allowing a simultaneous removal of contaminants [10].
- Sulphur compounds, alkali compounds and chlorine are removed using sorbents that can work at high temperature such as ZnO [13], Al_2O_3 , CaO [14].
- *Cold gas clean-up* (CGC): These operations are often conducted at temperatures below 100 ºC and, unlike the Hot Gas Clean-up, a liquid sorbent is used. The separation of the contaminants can be conducted in wet scrubbers. The efficiency can be improved using devices that enhance the turbulence and hence the contact between the gas and the liquid phases, such as in spray scrubbers, impactor scrubbers, venturi scrubbers. These operations are the most used in the last years, considering that they can carry out a simultaneous removal of different contaminants [10]. In fact, for example using a proper device working with water is possible to remove particulate matters, tars, and NH_3. Also, the choice of the proper liquid in the scrubber is crucial to increase the gas cleaning [15]. However, cleaning operation at low temperature is not the optimal choice if the goal is to obtain a high energy efficiency [10].
-*Warm gas clean-up (WGC)*: These operations are conducted in an intermediate range of temperature with respect to the previously described processes, typically [100-350 ºC]. Researchers have found that working in this temperature range could mitigate the drawbacks of both the hot gas clean-up and cold clean-up technologies since high-cost materials are no more required and low temperature is not necessary [10]. However, not all the contaminants can be removed in this way, but there are some examples of combined removal, such as the Olga process [16], which allow the simultaneous removal of tars and particulate matter. Chlorine can also be successfully removed in this range using lime-based slurry systems [17].

Gas conditioning: in this classification we have all the operations whose objective is to improve the H_2/CO stoichiometric ratio to obtain a more suitable composition for processes such as methanation. Operations such as thermal cracking or catalytic cracking of tars can reduce the level of these contaminants and simultaneously enhance this ratio [15]. Another operation that is usually conducted before or during the methanation step is the water-gas-shift reaction (with the addition of external steam) which can form more hydrogen and decrease the level of CO. For example, in the Comflux process [6] WGS is conducted in the same reactor by adding steam, to progressively enhance the formation of hydrogen that will be used for the methanation reaction. Enhancing the simultaneous methanation and WGS reactions looks like an interesting idea to limit the flow rate of hydrogen-make-up, and also to promote the gasification of coke (due to the addition of steam), that can cover the active phase of the catalyst [18,19].

Conclusions

The next steps in this research program will be a deeper research in literature to find more information about the processes that will be more effective for the production of methane, using a syngas obtained from air gasification, or air and steam gasification. Also, the correct design of cleaning and conditioning operations to improve the syngas quality, will be studied in detail. Furthermore, before the start of an experimental campaign, an initial simulative approach (using Aspen plus) will be conducted, for the optimization, from a technical and economic point of view, of the cleaning and conditioning operating parameters and of the methanation operating parameters. The experimental campaign will be aimed at confirming the results obtained from the simulation activity, and to be able to carry out an effective syngas methanation preventing the deactivation of the catalyst.

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