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METHANATION OF MILENA PRODUCT GAS FOR THE PRODUCTION OF BIO-SNG

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ABSTRACT: Synthetic Natural Gas (SNG) from biomass, also called “Green Gas”, is a very promising product, because it can be used for all applications that are already known for natural gas. Compared to other biomass conversion routes, the major advantage of SNG production is the potential to use the existing gas infrastructure. ECN is developing the Milena indirect gasifier, which is very suitable for SNG production, because it produces already high amounts of methane in the gasification. The methane content in the product gas accounts for already a large amount of the total energy content. This is beneficial to the overall process efficiency and is also good for the methanation process, where the conversion from syngas to methane is a strongly exothermic reaction and where it is difficult to control the process temperature. The methanation process has been studied in the past, but application has been scarce. In order to determine the optimal methanation conditions for the Milena product gas, thermodynamic equilibrium calculations were done with AspenPlus.
It was found that in the methanation process there is a risk of carbon formation, especially at lower temperatures and also at higher pressures. Adding additional steam to the product gas can reduce the risk of carbon formation. If carbon formation can be suppressed, the methane yield increases with lower temperatures and higher pressures. At lower temperatures (below 300 °C), the effect of the pressure on the methane yield is not as strong as at higher temperatures. The maximum energy efficiency of the methanation of the Milena product gas is 88%. This gives a maximum biomass to SNG yield of 70% with the Milena gasifier. This is a high efficiency, because the Milena gasifier produces already a large amount of methane. The overall yield could be increased if conditions can be found for the gasifier to produce even more methane.
Keywords: advanced conversion systems, catalytic conversion, methane

1 INTRODUCTION

Synthetic Natural Gas (SNG) from biomass, also called “Green Gas” or Bio-SNG, is a sustainable gas with the same quality as natural gas. It is a very promising product, because it can be used for all applications that are already known for natural gas. Bio-SNG can be produced from wet biomass streams by anaerobic digestion or supercritical water gasification and from relatively dry biomass streams by gasification [1-3]. The production of SNG by biomass gasification and subsequent methanation has been demonstrated in 2003 [2-4]. Compared to other biomass conversion routes, the major advantage of SNG production is the potential to use the existing gas infrastructure. Promising near future applications for SNG are co-generation at household level (especially in fuel cells) and as alternative fuel for transportation.

Methanation is a catalytic process that converts synthesis gas (mainly carbon monoxide and hydrogen) into methane with a nickel-based catalyst. Other gas components such as ethylene and BTX (benzene, toluene, xylenes) can also be converted to methane depending on the type of catalyst. During the methanation process the main reactions are:

$$CO + 3\ H_2 \Rightarrow CH_4 + H_2O \quad \Delta H_R = -217\ kJ/mol$$
$$CO_2 + 4\ H_2 \Rightarrow CH_4 + 2\ H_2O \quad \Delta H_R = -178\ kJ/mol$$

From the heat of reaction given above it can be seen that the methanation process is strongly exothermic. Thus, part of the energy of these components is lost in the form of heat. Also, this heat has to be removed from the reactor efficiently. Besides the issue of heat removal, also the risk of carbon formation (coking) has to be dealt with in methanation. Carbon can be formed by several mechanisms, such as:

$2\ CO \Rightarrow CO_2 + C$ (Boudouard reaction)
$CO + H_2 \Rightarrow C + H_2O$

The formation of carbon is undesired, because it results in loss of conversion efficiency, but also in deactivation of the catalyst by carbon deposition. Adding steam to the synthesis gas can suppress this reaction.

The methanation of synthesis gas from coal has been discovered already in 1902 and investigated intensely in the seventies and eighties. The advantage for methanation of synthesis gas from biomass is that at the lower temperature gasification processes, some methane is already formed during gasification. ECN is developing the Milena indirect gasifier, which is very suitable for SNG production, because it produces high amounts of methane in the gasification. The methane content in the product gas accounts for already a large amount of the total energy content. This is beneficial to the overall process efficiency. Also, this is good for the methanation process, because it lowers the amount of heat that is produced and has to be removed from the process and, therefore, it makes the process temperature easier to control. On the other hand, the Milena gasifier also produces much BTX and tars, which have to be used efficiently in the process. The tars can be removed with ECN Olga technology and re-used as fuel for the combustor section of the gasifier and BTX should be converted to methane.

Methanation is a crucial part of the process and its conditions affect the overall process efficiency and also the up-stream processes of gasification and gas-cleaning. In order to determine the optimal methanation conditions for the Milena product gas and the consequences for the up-stream processes, it is necessary to have a thorough understanding of the thermodynamic equilibrium conditions in the methanation process.

2 OBJECTIVES AND METHODOLOGY

The aim was to determine the optimal conditions for the methanation of the Milena product gas by process modeling. The two main factors studied were the risk of carbon formation and the conversion efficiency to the methane product. The main variables studied were:
- temperature
- pressure
- amount of steam added

The modeling was done in AspenPlus software and the results were validated with HSC Chemistry. For the Milena gasifier a typical gas composition was taken (Table I), which is based on a wood feedstock with a water content of 25%. For the methanation calculations all the tar and a part of BTX were assumed to be removed.

Table I: *Milena raw product gas composition*

Component	vol. % wet	vol. % dry
CO	18.7	29.0
H_2	20.3	31.5
CO_2	13.0	20.1
H_2O	35.4	
CH_4	8.9	13.7
C_2H_4	2.9	4.5
BTX	0.7	1.1
Tar	30 g/m_n^3	46 g/m_n^3

4 RESULTS

4.1 Energy distribution in the Milena product gas

To illustrate the importance of a high methane content in the product gas, the energy distribution in the product gas was calculated. The result is given in Figure 1 and shows that, although on a volume basis the methane content is only 8.9%, on energy basis the share of methane in the product gas is already as high as 27% of the raw product gas. This makes the Milena product gas very attractive for the production of SNG.

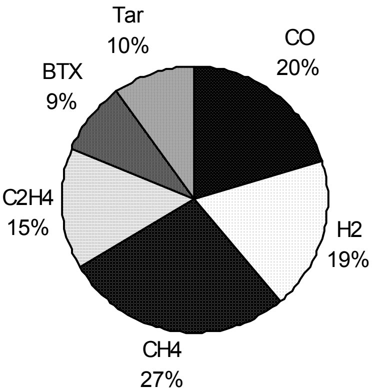

Figure 1: *Distribution of the energy in the Milena product gas*

4.2 Carbon formation

Carbon formation was, as expected, found to be a serious threat. As shown in Figure 2, at thermodynamic equilibrium carbon formation is present below 650 °C, regardless of the pressure. The pressure has an influence on the extent of the carbon formation, but only above 550 °C, where lower pressures give less carbon formation. Carbon formation is completely suppressed above 650 °C at 1 bar and above 800 °C at 40 bar.

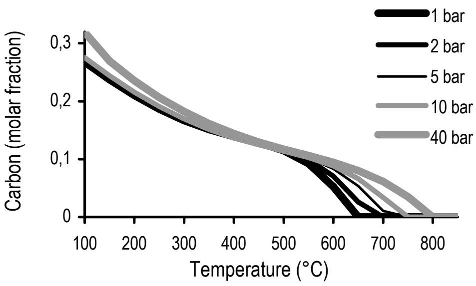

Figure 2: *Carbon formation at thermodynamic equilibrium*

Carbon formation is suppressed by steam present in the gas. A variation of the steam content in the gas entering the methanation was modeled and the effect on carbon formation is given in Figure 3. It is clear that at low temperatures, independent of the pressure, large amounts of steam are necessary in the gas to prevent carbon formation based on thermodynamic equilibrium. At higher temperatures less steam is necessary and the exact amount depends on the pressure. Although the steam content of the raw Milena product gas is already as high as 35.4%, according to the thermodynamic equilibrium this is not even enough to suppress carbon formation at low temperatures (200-500 °C).

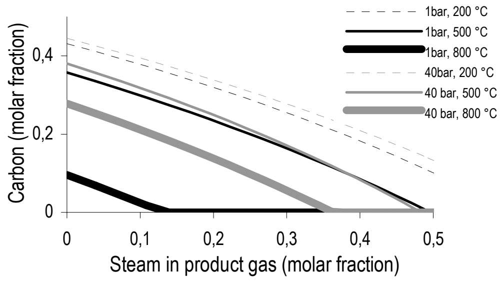

Figure 3: *Carbon formation at thermodynamic equilibrium for different steam contents*

In the real practice of methanation, it has generally been observed that carbon formation is a problem, but that the amount of steam necessary to prevent this, is lower than predicted by the thermodynamic equilibrium, although still considerable.

4.3 Methanation efficiency

For the modeling of the efficiency of the methanation process it has been assumed that the steam content of 35.4% in the Milena raw product gas is sufficient to suppress carbon formation. Thus, for these calculations, carbon formation reactions are excluded from the model.

The conversion from the Milena product gas to methane depends on the temperature and the pressure of the methanation. In Figure 4 the concentrations of methane, carbon monoxide, hydrogen and carbon dioxide at the thermodynamic equilibrium are presented at different temperatures and pressures. It is clear that at low temperatures, the main products are methane and carbon dioxide, whereas at high temperatures the main products are hydrogen and carbon monoxide. Also, at higher pressures more methane is present: at 1 bar the methane content decreases already rapidly at temperatures above 300 °C, whereas at 40 bar the methane starts to decrease significantly only at temperatures above 500 °C.

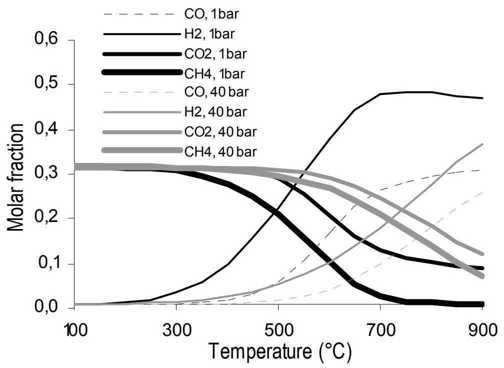

Figure 4: *Methanation products at different conditions*

The same effect is visible in Figure 5, where the energy efficiency of the methanation process is shown. Since methane is the desired end product, here only the energy of the methane compared to the energy of the (cleaned) Milena product gas is given. The maximum energy efficiency of the methanation is 88% and this is reached only at lower temperatures. The remainder of the energy is released as heat. At higher temperatures, the lower energy efficiency is caused because less methane is formed and the energy is still confined in the hydrogen and carbon monxide.

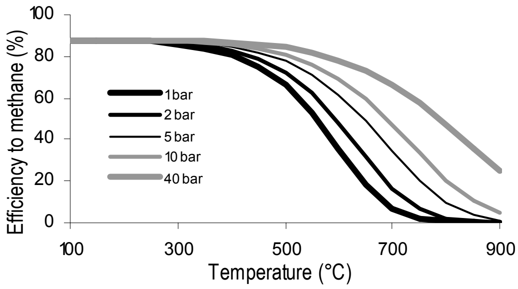

Figure 5: *Energy efficiency from product gas to methane*

4.4 Summary

To reach a high efficiency in converting the Milena product gas to methane, low temperatures and high pressures are preferred in the methanation, based on thermodynamic equilibrium. In practice, reaching low temperatures (below 300 °C) is very difficult, because of heat transfer and catalyst properties. Also, the risk of carbon formation is highest at lower temperatures and higher pressures, because thermodynamic equilibrium predicts carbon formation. Adding steam to the product gas can reduce (the risk of) carbon formation, although the Milena product gas already contains a large amount of steam. The maximum efficiency of the methanation process is 88% for the Milena product gas. Combined with a gasification and tar-cleaning cold gas efficiency of 79%, this gives a maximum SNG yield of 70% with the Milena gasifier. This could be increased if more methane can be produced in the gasifier.

5 CONCLUSIONS

Thermodynamic equilibrium showed that carbon is formed at low temperatures and high pressures. Adding additional steam to the product gas reduces carbon formation. If carbon formation can be suppressed, the methane yield increases with lower temperatures and higher pressures. At lower temperatures (below 300 °C), the effect of the pressure on the methane yield is not as strong as at higher temperatures. The maximum energy efficiency of the methanation of the Milena product gas is 88%. This gives a maximum biomass to SNG yield of 70% with the Milena gasifier. This is a high efficiency, because the Milena gasifier produces already a large amount of methane. The overall yield could be increased if conditions can be found for the gasifier to produce even more methane.

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