Monitoring the Bed Material Activation in the GoBiGas-Gasifier

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Abstract - The GoBiGas-plant was constructed by Göteborg Energi AB to produce 20MW of bio-methane though gasification of biomass. The gasifier is a dual fluidized bed gasifier and one of the major hurdles during the commissioning of the plant was to control and limit the amount of tar produced from the gasifier. The yield of tar was efficiently decreased by adding potassium to activate the olivine used as bed material. However, the activation is not permanent and must be maintained and for this purpose, the aim of this work was to develop a method for monitoring the bed material activation. A clear correlation between the concentration of CH_4 and the total yield of tar was found and is therefore used to regulate the amount of potassium added to the process to keep the olivine active and avoid tar related problems. With a CH_4 concentration of 9% or less, tar related problems are avoided in the GoBiGas-plant however, this correlation is plant specific. To generalize the method a syngas modulus was defined and implemented to monitor the fuel conversion in the process (and thereby the activation of the bed material), and to simplify the optimization of the gasifier by reducing the need for time-consuming tar analysis.

Introduction

To decrease the fossil dependency and to reduce the CO2 emissions the Swedish government has defined the goal of having a fossil free vehicle fleet by the year 2030[1]. One of the measures to reach this goal is through the development of industrial-scale production of biofuels based on lignocellulosic biomass and waste. The GoBiGas-plant, owned by Göteborg Energi AB, is one of the leading projects in these endeavors with the aim of producing 100-120 MW of biomethane. To reduce the risk the GoBiGas project was divided in two phases where the first phase was limited to 20 MW of SNG with the purpose of demonstrating the technique. Phase 1 of the GoBiGas project was commissioned in 2014 and has successfully demonstrated the technology by producing biomethane from wood pellets and now delivers bio-methane to the existing natural gas grid[2]. Initial results shows that the gasifier operates with a cold gas efficiency of 73-80%, which could be further increased by optimization of the process[3]. One of the major challenges during the commissioning was related to the gasification section and the amount of tar in the product gas, which caused problems by fouling on down-stream equipment.

The GoBiGas gasifier is a dual fluidized bed (DFB) gasifier where part of the fuel is gasified with steam in the gasifier and the remaining fuel is combusted in a connecting combustion chamber where heat is produced. The heat is transported back to the gasifier with a fluidized bed material. To limit the tar yield from a DFB gasifier, active bed material can be used to catalyze the tar conversion[4]. Olivine is a commonly used material in gasification unit and it requires activation to efficiently convert tar. At GoBiGas several methods for activation of olivine was considered[5, 6], and it was decided to apply a method used at Chalmers.

The activation method is based on published knowledge from coal gasification[7] and validated for biomass gasification in the Chalmers gasifier[5]. At GoBiGas 0-30 l_n/h of K_2CO_3-solution (40%$_{mass}$ solved in water) is added to the combustion chamber in the process, which has significantly decreased the yield of tar, and the problematics related to the tar. The activation of the olivine by potassium addition is, however, not permanent and needs to be monitored and maintained. The activation level is here viewed as proportional to the level of fuel conversion in the gasifier where the conversion of tar is the most important for the operation of the process.

To measure the amount of tar in the product gas is complex and time-consuming, the method currently applied at GoBiGas is an offline measurement based on solid phase adsorption (SPA), which has previously been described in detailed[8, 9]. The SPA method enables good quantification of specific tar components, however, the processing and analysis of the samples takes a few hours. To be able to monitor and control the tar yield a continuous and less time-consuming method is required. Therefore, the aim of this work was to develop and implement a simplified method for monitoring the fuel conversion and thereby the activation of the bed material.

Table 1. Summary of the major global reactions, where $C_zH_vO_w$ and C(s) represents the raw gas, char respectively. $\alpha_{1\text{-}9}$ indicates the molar amount of the different components related to the Tar, and Tar^* represents a changed composition of the remaining Tar.

Description	*Reaction*	*Ref.*
Char combustion	$C(s) + O_2 \rightarrow CO_2$	*{R1}*
Volatile combustion	$C_zH_vO_w + \left(z + \frac{v}{2} - w\right) O_2 \rightarrow (z)CO_2 + (v/2)H_2O$	*{R2}*
Char gasification	$C(s) + CO_2 \rightarrow 2CO$	*{R3}*
Char gasification	$C(s) + H_2O \rightarrow CO + H_2$	*{R4}*
Reformation of tar components	$Tar + \alpha_1 H_2O + \alpha_2 CO_2 \rightarrow \alpha_3 Tar^* + \alpha_4 C_xH_y + \alpha_5 CH_4 + \alpha_6 CO + \alpha_7 H_2 + \alpha_8 C(s) + \alpha_9 CO_2$	*{R5}*
Reformation of light hydrocarbons	$C_xH_y + xH_2O \rightarrow xCO + \left(\frac{x}{2} + y\right) H_2$	*{R6}*
Methane reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	*{R7}*
Water gas shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$	*{R8}*

Method

Two methods has been applied for monitoring the gasification process at GoBiGas based on the cold gas components, H_2, CO, CO_2 and CH_4; 1) An empirical correlation relating the total amount of tar to the concentration of CH_4; 2) a syngas modulus to monitor the fuel conversion and simplify the optimization of the plant.

The syngas modulus used for monitoring the fuel conversion is based on the measurement of the concentration of H_2, CO and CO_2. Inspired by van-Kevelen diagrams, which is e.g. used to illustrate differences in solid fuels[10], the approach is based on the H/C-ratio and O/C-ratio[11]. With such a diagram, the effect that the major global reactions in a gasifier has on the gas composition can be illustrated. The major reactions considered here, R1-R8, are listed in Table 1 and the change in the composition of the syngas due to the reactions is illustrated in Figure 1.

The example shown in Figure 1 is based on the measured gas composition from pyrolysis of wood pellets in a bench-scale fluidized reactor operated at 830 °C. The arrows in Figure 1 indicate the changes in the O/C- and H/C-coordinates caused by the reactions. The conversion of organic compounds (OC), including tar and light hydrocarbons, is illustrated as a striped area, as the composition of the syngas generated by the conversion can differ depending on whether the OC is converted through cracking reactions or reforming reactions. However, the OC conversion generally causes an increase in the H/C-ratio (especially if H_2O is included in the reaction). Due to the rather low oxygen contents of organic compounds that are thermally stable above 800°C[12, 13], the O/C-ratio can be expected to approach the value of 1 when OC is converted through steam reforming. The water gas shift reaction (WGSR) is distinguished from the other reactions as it gives a change in the coordinates with a constant direction, while other reactions instead gives a change towards a constant coordinate. Using reference coordinates based on the composition of the gas from pyrolysis a graphical evaluation of the fuel conversion can be performed.

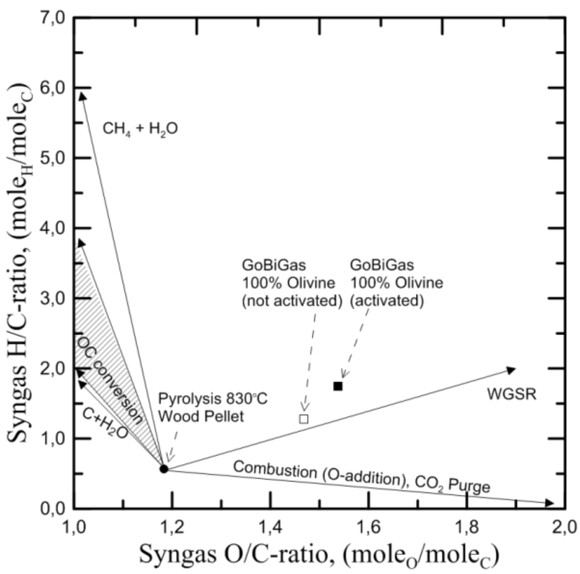

Figure 1. Illustration of how the syngas composition change with different reactions, described in detail by Larsson[13], and the examples are base on gas measurements from the GoBiGas-Gasifier.

Table 2. Summary of the H/C-ratio and the O/C-ratio of the dry ash free wood pellets and the pyrolysis gas (including CO,H_2,CO_2) at a temperature of 840 ºC

	H/C	*O/C*
Dry ash free fuel	*1.452*	*0.638*
Pyrolysis gas(H_2,CO,CO_2)	*0.589*	*1.185*

The composition of the gas from pyrolysis can be measured lab-scale experiments or estimated from literature[14]. The H/C-ratio and O/C-ratio for the wood pellets used and the pyrolysis gas from the wood pellets are listed in Table 2.

The WGSR is a comparatively fast reaction, sensitive to variations in the process and it yields significant changes in the gas composition. However, for biomass gasification the WGSR has a low impact on the cold gas efficiency compared to other reactions, and compared to the conversion of tar it is of low importance for the operation of the unit. By definition, reactions where char or hydrocarbons are converted moves the coordinate above the WGSR-line of the pyrolysis gas, while oxygen or CO_2 addition can moves the coordinate below the same line. Based on this an modulus, Ψ, is here defined as the ratio between the perpendicular distance from the WGSR-line of the pyrolysis gas to the coordinate of the measured gas, and the perpendicular distance from the WGSR-line of the pyrolysis gas to the WGSR-line based on the composition of the dry fuel, illustrated in Figure 2. The equations for quantifying the modulus is summarized in table 3, where the terms based on the composition of the pyrolysis gas is denoted *pyro*, the dry ash free fuel, *daf fuel*, and the measured gas composition based on CO,H_2,CO_2, *measured*.

The modulus is defined so that if all of the fuel is converted into H_2, CO and CO_2 without any addition of O_2 or CO_2 the modulus attain a value of 1 and if the WGSR is the only reaction occurring the modulus attain a value of 0. Note, that if O_2 or CO_2 is added the modulus can attain a negative value so if for instance a direct gasifier is to be evaluate the amount of O_2 added should be compensated for by adding it to the O/C ratio of both the fuel and the pyrolysis gas.

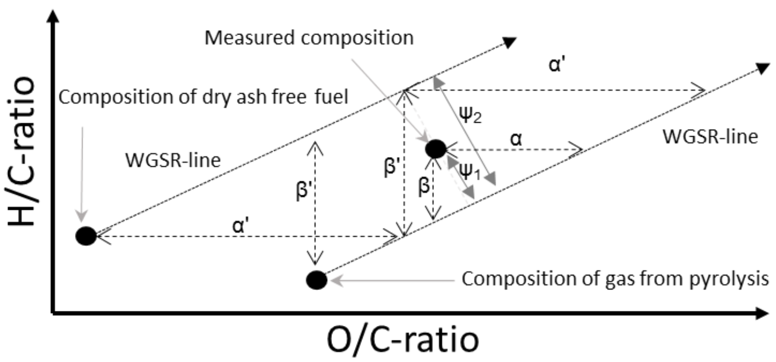

Figure 2. Illustration of variables used to calculate the syngas modulus, Ψ.

Table 3. Summary of the equation used to calculate the syngas modulus

Syngas modulus: $\Psi = \Psi_1 / \Psi_2$
$\Psi_1 = \dfrac{\alpha\beta}{\sqrt{\alpha^2+\beta^2}}$
$\Psi_2 = \dfrac{\alpha'\beta'}{\sqrt{\alpha'^2+\beta'^2}}$
$\alpha = \left({}^{O}/{}_{C}\right)_{pyro} - \left({}^{O}/{}_{C}\right)_{measured} + \left(\dfrac{\left({}^{H}/{}_{C}\right)_{measured} - \left({}^{H}/{}_{C}\right)_{pyro}}{2}\right)$
$\beta = \left({}^{H}/{}_{C}\right)_{measured} - \left({}^{H}/{}_{C}\right)_{pyro} - 2\left(\left({}^{O}/{}_{C}\right)_{measured} - \left({}^{O}/{}_{C}\right)_{pyro}\right)$
$\alpha' = \left({}^{O}/{}_{C}\right)_{pyro} - \left({}^{O}/{}_{C}\right)_{daf\ fuel} + \left(\dfrac{\left({}^{H}/{}_{C}\right)_{daf\ fuel} - \left({}^{H}/{}_{C}\right)_{pyro}}{2}\right)$
$\beta' = \left({}^{H}/{}_{C}\right)_{daf\ fuel} - \left({}^{H}/{}_{C}\right)_{pyro} + 2\left(\left({}^{O}/{}_{C}\right)_{daf\ fuel} - \left({}^{O}/{}_{C}\right)_{pyro}\right)$

Result and Discussion

The analysis of the tar sampled with the SPA method was correlated to the concentration of CH_4 in the dry gas to enable an indirect way to monitoring the yield of tar from the GoBiGas-gasifier. Figure 3 shows that there is a very clear correlation and for the specific unit. The correlation could partially be due to that both the concentration in the dry gas of tar and CH_4 is diluted with products from char conversion, WGSR and reformation of tar. Further, the correlation indicates that the activation level of the olivine affects also the yield of CH_4, which should be further studied with a proper mass balance over the system.

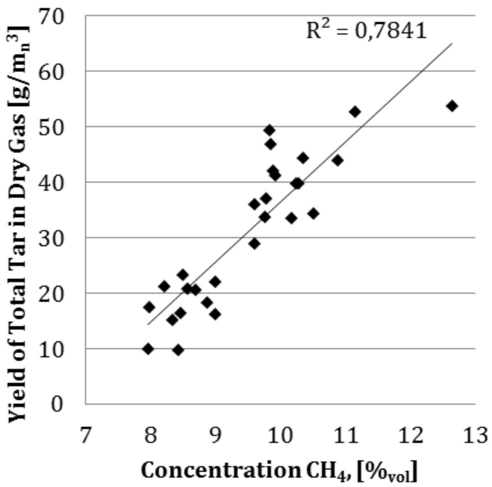

Figure 3. Yield of tar as a function of the concentration of CH_4 in the dry gas

The most troublesome tar is the heaviest compounds as they have a higher dew point and can more easily condense and cause problems in the product gas cooler. The heaviest tar components with a significant yield is Chrysene, which also can be correlated to the concentration of CH_4, see Figure 4. With a concentration of Chrysene of 200 mg/m_n^3 dry gas the dew point of the Chrysene in the wet gas is around 160 ºC. Thus, according to figure 4 the Chrysene concentration can be kept below the dew point when the concentration of CH_4 is below $9\%_{vol}$ in the dry gas. The CH_4 concentration out of the GoBiGas-gasifier is controlled by adding potassium (to decrease) and fresh bed material (to increase) in the range of 8.5-9% and this has proven successful without any clogging of the product gas cooler during operation of more than 1000h so far. However, these correlations are unit specific and should be extrapolated with care. Therefore a more generalized method for evaluating the fuel conversion was developed.

The Syngas Modulus is a generalized method for monitoring all aspect of the fuel conversion in the gasifier, excluding the WGSR. Figure 5 show the correlation between Syngas Modulus and the total yield of tar and compared with Figure 3 it can be seen that the correlation is not as good as the correlation with CH4. This can be due to the fact that the Syngas modulus is sensitive to other process parameters such as O_2 addition, or the amount of CO_2 purge that enters the process, which even gives negative values of the Syngas Modulus for some cases.

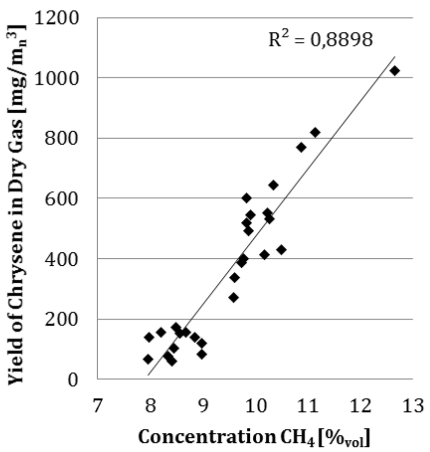

Figure 4. Yield of Chrysene as a function of CH_4 concentration in the dry gas

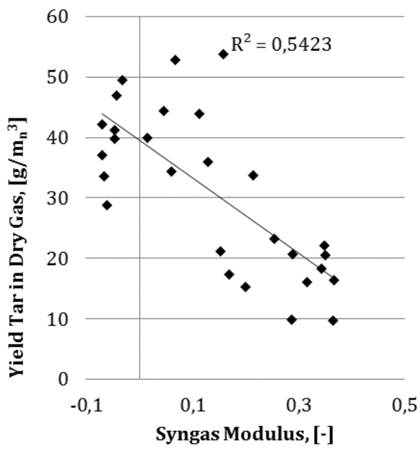

Figure 5. Yield of tar as a function of the syngas modulus

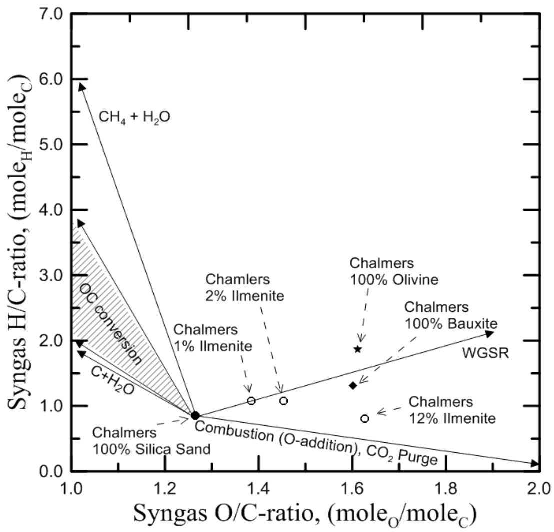

Figure 6. Comparison of the syngas composition using different bed materials in the Chalmers gasifier[11]. OC stands for organic compounds, which include tar and lighter hydrocarbons.

The amount of O_2 and CO_2 added to the gasification process should be minimized to optimize the efficiency of the gasifier and to minimize the need for CO_2 separation if the gas is used for synthesis of biofuels. Thus, the Syngas Modulus will be a powerful tool for optimizing the gasification process at GoBiGas. As example the method can be used to qualitatively evaluate the use of different bed materials as was done for the Chalmers gasifier, see Figure 6[11]. In Figure 6, the effect of oxygen addition can be viewed with the three levels of addition of the oxygen carrying material ilmenite. The comparison indicates that activated olivine is the most suited bed material in the comparison where silica sand is use as a reference. For a complete evaluation of the different bed materials the mass and energy balance of the process should be evaluated[15]. However, Figure 6 illustrates how the method can be used for a qualitative assessment if there is not sufficient information available to close the mass and energy balance. Further, the method enables online monitoring of the fuel conversion based only on measurements of the composition of the cold gas (H_2, CO, CO_2 and CH_4) from a gasifier.

By monitoring the CH_4 concentration and the Syngas Modulus during startup of the GoBiGas-gasifier it has become clear that the activation of the olivine to some extent is lost from one start to another. Therefore, higher levels of potassium addition are required to re-activate the olivine during startup. Figure 7 shows the Syngas Modulus, the concentration of CH_4 and the amount of potassium added to the process during 3 consecutive startup occasions, all with used olivine that has previously been active. During the first period of operation in figure 7, the olivine was poorly activate as shown by the high CH_4 concentration and low value of the Syngas Modulus and the product gas cooler was clogged at this occasion. The trends show how adding additional potassium activates the olivine with time. Even though the bed was activated towards the end of the first operational period and the bed material was kept in the process to next run, low activation of the olivine was experienced during the beginning of the second run.

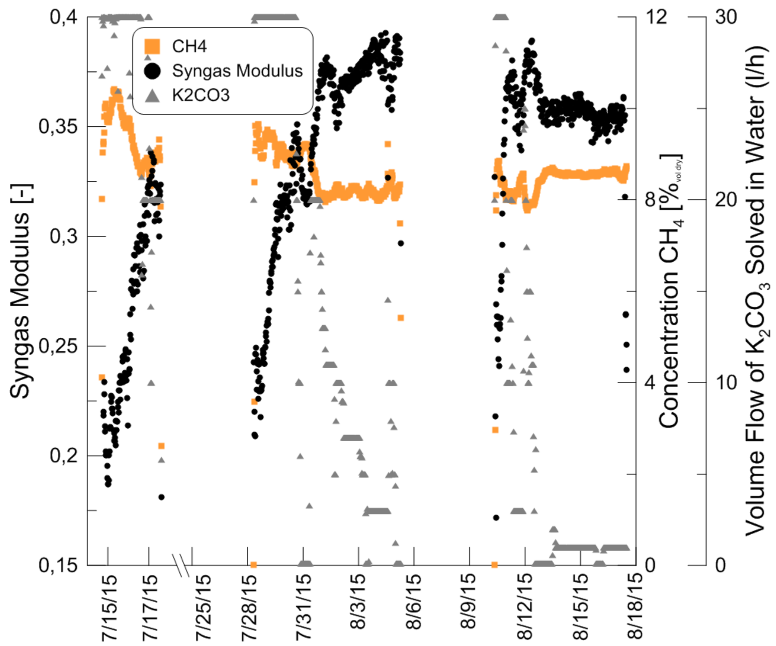

Figure 7. Trends for the syngas modulus (left y-axis), the CH_4 concentration (right y-axis) and the amount of potassium added to the process (far right y-axis) is shown for 3 consecutive startups, all with used and previously active bed material.

After a brief stop a third startup was performed where the loss of activation was not as sever and stable operation was attained. During stable operation, less than 5 l/h solution (less than 0.2g $_{\text{potassium}}$/kg$_{\text{dry ash free fuel}}$) is required. It is not clear why the activation is lost, contributing factors could be; attrition of the particles during cooling (shutdown) or heating (startup), or due to loss of potassium to the gas phase during heating[16]. With the methods presented in this work for monitoring the activation the process can be started without major tar related problems using a high addition of potassium. The role of the potassium for activation of olivine has been described by Marinkovic et al[5], however further research on how sufficient activation of the olivine can be ensured prior to the start of the fuel feed is required to completely avoid any tar related problem.

Conclusions

A Correlation between CH_4 and the total amount of tar as well as specific troublesome tar components such as Chrysene was found. For the GoBiGas-gasifier a CH_4 concentration lower than 9% is sufficient to avoid condensation of tar in the product gas cooler. The concentration of CH_4 in the product is controlled by adding K_2CO_3 to the process, which increase the activation of the olivine and thereby enhances the fuel conversion. Further, the suggested Syngas Modulus can be used to monitor how the conversion of the fuel into syngas is affected by operational parameter. The modulus is sensitive towards O_2 and CO_2 addition and can be a very useful tool for optimizing the process e.g. by minimizing unwanted oxygen addition to the gasifier. By monitoring the gas CH_4 concentration and syngas modulus during startup it is clear that the activation of the olivine is not permanent and higher amount of K_2CO_3 needs to be added during start up than during stable operation.

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Notation

α, α’	Variable [-]	ψ	Syngas modulus [-]
β, β’	Variable [-]		

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