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Hydrocarbons in the exhaust gas of biogas-driven combined heat and power units

To determine exhaust gas emissions and electrical efficiency, several biogas driven co-generation units (CGU) were measured on site. If only the concentrations of nitrogen oxides (NO_x) in the exhaust gas were to be minimized, this resulted in increased emissions of unburnt hydrocarbons and a lower electrical efficiency of the engines. Also, the exhaust gas concentrations of NO_x and formaldehyde were found to be interdependent. Lowest formaldehyde emissions were measured in conjunction with NO_x-values far above limit values. The use of a catalytic converter effectively reduced CO and formaldehyde levels in the exhaust gas, but showed little effect on remaining hydrocarbons.

Keywords
Exhaust emissions, hydrocarbons, formaldehyde, biogas, CHPU, electrical efficiency

Abstract
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In order to achieve sustainable and environmentally friendly power production from biogas, increased attention has to be paid to pollutant emissions from co-generation units (CGU). Engine efficiency and emission levels can only be increased simultaneously, if interdependencies are analyzed in detail. So far, the focus has been mostly on factors influencing the emission levels of harmful exhaust gases, i.e. nitrous oxides (NO_x), carbon monoxide (CO) and sulfur dioxide (SO_2). Due to the classification of formaldehyde (HCHO) as a carcinogenic substance, hydrocarbons from the combustion of biogas have come into focus. Hydrocarbons in the exhaust gas stem from incomplete combustion and can reach considerable concentrations if the engine is poorly set and maintained [1]. In the „German Technical Instructions on Air Quality Control“ (TA Luft) the limit value for formaldehyde is 60 mg • m^{-3} for facilities with a firing thermal capacity of more than 1 MW [2]. Having classified formaldehyde as carcinogenic and therefore as a component requiring supervision, the so-called „air pollution control bonus“ was introduced with the amendment of the German Law on Renewable Energy (EEG) in 2009. This bonus grants an additional compensation of 1 Euro cent per kWh electrical energy fed into the grid if the CGU meets a limit value of 40 mg • m^{-3} formaldehyde in the exhaust gas. At the same time, methane as the main hydrocarbon component in the exhaust gas of (bio)gas-driven engines should not be neglected. Methane is a powerful greenhouse gas (GWP=25) and can contribute to the carbon footprint of power production from biogas quite substantially.

In this paper, results from an investigation of average long-term electrical efficiencies of different classes of CGUs are presented. These values serve as a basis for economic calculations of biogas facilities. At the same time, exhaust gas emissions, in particular for formaldehyde and hydrocarbons were measured to determine interaction between emission levels and electrical efficiency of power production.

Materials and methods

The measurements were made at 10 CGU with different power outputs from 30 kW to 530 kW. During a 4-hour measurement, all input streams to the CGU (gas flow, temperature, pressure, and composition as well as combustion air flow and fuel oil supply) and output streams from the CGU (exhaust gas composition and electricity generation) were monitored (**table 1**). Total hydrocarbons were measured with a flame ionization detector (FID). Formaldehyde emissions were quantified according to VDI 3862-2 (DNPH procedure).

Investigations in this project are ongoing. So far, some trends can be recognized which provide insight into factors influencing the level of hydrocarbons in the exhaust gas including formaldehyde. Additionally, the effectiveness of a catalytic converter (Oxi-Kat) was examined.

Emissions of hydrocarbons (C_nH_m)

Hydrocarbons in the exhaust gas of a biogas-driven CGU consist primarily of methane and are therefore often called „methane slip“. Methane slip is favored by valve overlapping and incomplete combustion of fuel due to high oxygen concentration. Increased oxygen concentration for combustion (lean combustion principle) is required to reduce NO_x formation at high temperatures. While atmospheric oxygen cools the combustion, an increased air-to-fuel ratio lowers the laminar flame velocity. This leads to imperfect combustion and higher hydrocarbon emissions.

Depending on engine type and setting, hydrocarbon emissions can differ considerably between individual CGUs. As a general rule, pilot injection gas engines have a higher methane slip due to their higher compression ratio. Hydrocarbon emission levels can be estimated from calculating energy loss during combustion. Measured hydrocarbon emissions are regarded as „methane slip“ and can be related to fuel energy input. At the same time, measured hydrocarbon emissions can be converted to CO_2-equivalents which can then be related to electricity generation in kWh and compared with other methods of power generation.

Figure 1 shows calculated values of methane slip and equivalent CO_2 emissions from the measurements of ten different gas and pilot injection engines. The gas CGUs with power outputs of 100 to 324 kW_{el} showed a very low methane slip ranging from 0.3 to 0.7 % of fuel energy input. This corresponds to a carbon footprint of 17 to 41 g CO_2-eq per kWh. The gas CGUs with 30 kW_{el} and 526 kW_{el} showed a methane slip of 2.5 to 3 % corresponding to emissions of 100 to 150 g CO_2-eq per kWh. These high values can be explained by constructional factors. The 30 kW_{el} engine is designed as a so-called „high-speed“ engine (3,000 rpm) which increases valve overlapping. In the case of the 526 kW_{el} engine, the engine geometry was changed to increase compression ratio and thereby electrical efficiency. This causes higher hydrocarbon emissions. The same principle applies to the pilot injection engines that show similar emissions. The 37 kW_{el} pilot injection engine is a negative example of faulty engine setting which causes a loss of about 19 % of fuel energy (**figure 1**). Corresponding carbon emissions are up to 900 g CO_2-eq per kWh which is clearly above German grid emission levels.

Table 1

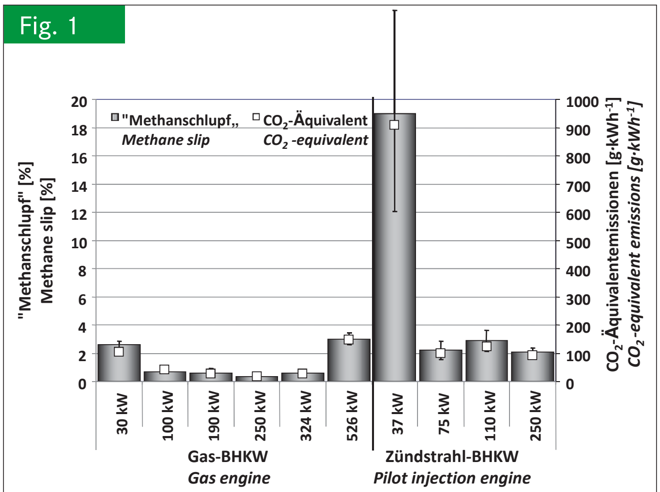
Measuring equipment

Messaufgabe *Measuring task*	**Messgeräte** *Measuring equipment*	**Einheiten** *Units*
Gaszusammensetzung (CH_4, CO_2, O_2, H_2, H_2S) *Gas composition*	AWITE	%, ppm
Gasdruck und –temperatur *Gas pressure and temperature*	Drucksensor, PT100 *Pressure sensor*	mbar, °C
Luftvolumen *Air volume*	Testovent 410, Messimpeller *Testovent 410, measuring impeller*	$m^3 \cdot h^{-1}$
Zündölverbrauch *Consumption of ignition oil*	Wägezelle *Load cell*	kg
Gesamt-Kohlenwasserstoffe *Total unburned hydrocarbons*	Flammenionisations-detektor (FID) *Flame ionization detector*	$mg \cdot m^{-3}$
Abgaszusammensetzung (NO_x, CO, CO_2, O_2, Temperatur) *Exhaust gas composition*	Testo 350	$mg \cdot m^{-3}$ %, °C
Formaldehyd *Formaldehyde*	DNPH-Verfahren nach VDI 3862–2 *DNPH procedure according to VDI*	$mg \cdot m^{-3}$
Strommenge *Electrificy production*	KBR Multimess	kWh
Elektrischer Wirkungsgrad *Electrical efficiency*	Berechnung nach DIN 3046-1 *Calculation according to DIN*	%

Emissions of formaldehyde

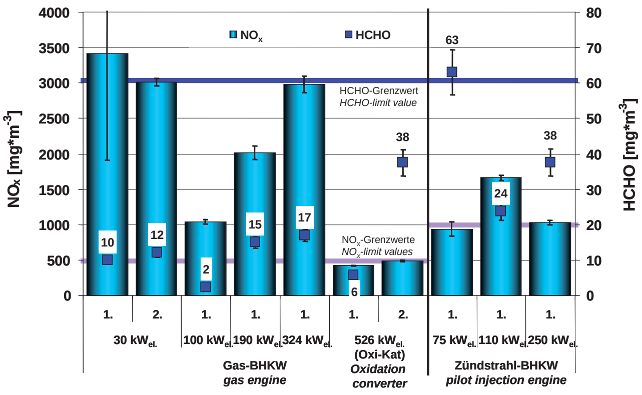
Formaldehyde as part of hydrocarbon output in the exhaust gas was meanwhile classified as carcinogenic by the Federal Office for Risk Assessment (BfR). This was the reason for introducing an „air pollution control“ bonus in the amended German Renewable Energy Law (EEG) of 2009. An additional 1 ct per kWh of electrical energy fed into the grid is paid if the electricity is generated in an engine that meets a limit value of 40 $mg \cdot m^{-3}$ formaldehyde in the exhaust gas (as opposed to 60 $mg \cdot m^{-3}$ according to the „Technical Instructions on Air Quality Control“, TA Luft) (LAI-decision in 2008). To date, there are few reliable data on the factors influencing formaldehyde emissions under real-world conditions. Measurements of the Technical University Munich at two research engines under test conditions indicated a connection between the levels of NO_x and

Fig. 1



Methane emissions (methane slip) and CO_2 equivalent emissions of different CHPU in practice

Fig. 2



NO_x and formaldehyde measurements in the exhaust gas of different CGUs

formaldehyde emissions [3]. Similar results were obtained from investigations at biogas facilities by the Saxon Agency for Environment, Agriculture and Geology [4] and the Bavarian Agency for Environment [5].

In the engine, radical combustion of fuel to carbon dioxide and water follows different steps, with formaldehyde as an intermediate. If due to high combustion air input the flame velocity becomes too low, combustion becomes incomplete and formaldehyde cannot be further oxidized. This also applies to certain zones in the combustion chamber. It is assumed that formaldehyde originates from the top land (space between piston and the first piston ring) where no combustion occurs [3].

Formaldehyde concentrations of individual CGUs measured in these investigations are rather low compared to the limit value of 60 $mg \cdot m^{-3}$ (TA Luft) (**figure 2**). However, it can be seen that low formaldehyde levels appear almost always in conjunction with NO_x concentrations exceeding limit values. This indicates a considerable influence of engine settings on formaldehyde emission levels.

Furthermore the positive effect of a catalytic converter (Oxi-Kat) can be recognized in **figure 2**. The use of an Oxi-Kat with the 526 kW_{el} gas CGU reduced the formaldehyde concentration in the exhaust gas to 6 $mg \cdot m^{-3}$. However, a value of 38 $mg \cdot m^{-3}$ formaldehyde from the second measurement already indicated damage of the Oxi-Kat due to excessive concentrations of H_2S in the biogas.

To examine the influence of engine settings on emission levels and combustion efficiency, several CGUs were measured in three operating states: „NO_x-optimized“, „efficiency-optimized“, and „partial load“ [6]. Here, the influence of engine setting could be seen clearly (**figure 3**).

For the efficiency-optimized mode, the electrical efficiency could be raised by almost 1.5 %, if increased NO_x emissions were accepted. The concentration of unburned hydrocarbons was slightly below the NO_x-optimized setting, while the formaldehyde level exceeded the limit value according to TA Luft already for the NO_x-optimized setting. For partial load, both the results for emission levels and electrical efficiency were particularly poor with a very high output of hydrocarbons and a reduction of electrical efficiency by almost 4 % (**figure 3**).

Catalytic converter (Oxi-Kat)

The use of a catalytic converter is regarded as the cheapest and easiest solution to remove hydrocarbons and especially formaldehyde from the exhaust gas. However, measurements of exhaust gas concentrations upstream and downstream of a catalytic converter at the 526 kW_{el} gas CGU (see **figure 2**) provided some interesting results. Despite a reduction of CO and formaldehyde concentrations in the Oxi-Kat by more than 90 %, no reduction of other hydrocarbons could be detected (**figure 4**). This means that while the output of formaldehyde and CO could be almost avoided by using a catalytic converter, there was no effect on the emission of methane as a greenhouse gas. These findings were also confirmed by [7] who stated that catalytic converters have no oxidation potential for CH_4 as part of C_nH_m emissions.

Conclusions

Hydrocarbon concentrations in the exhaust gas of biogas-driven CGUs depend on several factors among which engine setting plays a prominent role. Beside formaldehyde which is now very much in the focus, methane emissions (methane slip) from CGUs with combustion engines should not be neglected, as they can considerably impair the carbon foot print of electricity from biogas.

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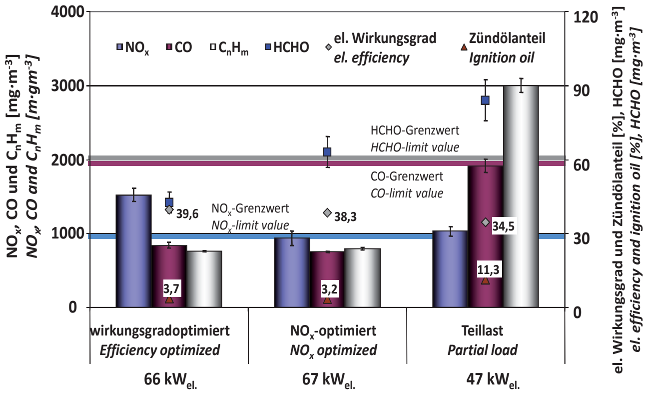
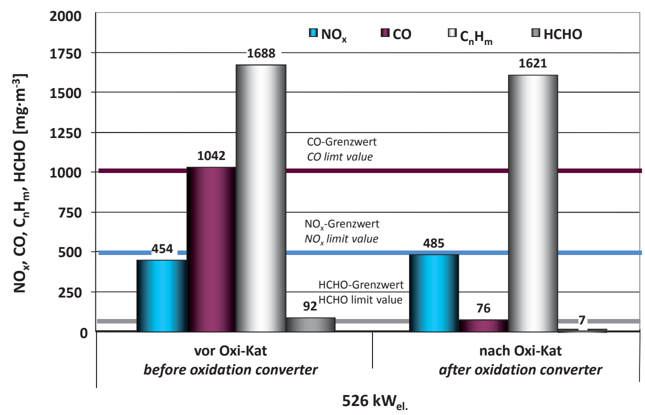
Fig. 3



Exhaust gas emissions and electrical efficiency of a biogas-driven pilot injection engine depending on engine setting

Fig. 4



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