PRODUCTION OF TAILORED SYNGAS FOR DIMETHYL ETHER SYNTHESIS BY SORPTION ENHANCED GASIFICATION

Selina Hafner[1*], Nina Armbrust[1], Reinhold Spörl[1], Günter Scheffknecht[1]

[1]*Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart, Pfaffenwaldring 23, D-70569 Stuttgart, Germany*

*Email: *selina.hafner@ifk.uni-stuttgart.de*

Abstract – Dimethyl ether (DME) as one of the most promising biofuels has the potential to substitute fossil based fuels and hence contribute to the reduction of CO_2 emissions originating from the transportation sector. For an optimization of the DME production a syngas which is optimal for downstream DME synthesis shall be produced by a sorption enhanced gasification (SEG) process.
In this paper, experimental results showing the influence of the gasification temperature on the syngas composition in a SEG process with wood pellets as fuel and limestone as bed material are presented. A significant change in syngas composition was observed for gasification temperatures between 600 and 750 °C.
In addition to this, results of investigations about the influence of the gasification temperature on the CH_4 and C_xH_y content in the syngas for a two-stage SEG process are presented.

INTRODUCTION

The transport sector is the second largest sector for the production of global CO_2 emissions (OECD/IEA, 2016). One possibility for the reduction of these emissions is the use of biofuels such as dimethyl ether (DME).

To optimize the production of DME, a flexible and low cost process is needed. For the development of such a process the Horizon 2020 project FLEDGED (FLExible Dimethyl ether production from biomass Gasification with sorption-enhancED processes) was initiated. The project focuses on the investigation of the sorption enhanced gasification from diversified biomass and biogenic residue feedstocks as well as on the steam sorption enhanced DME synthesis as the two key processes. The aim of the SEG process in the FLEDGED project is the production of a H_2 enriched syngas with a module M (1) which is optimal for the downstream DME synthesis.

$$M = \frac{H_2 - CO_2}{CO + CO_2} \tag{1}$$

The SEG for the production of a tailored syngas for DME synthesis is conducted in a dual fluidized bed (DFB) system. In a first reactor the biomass is gasified with steam as gasifying agent and limestone as CaO-based sorbent as bed material. The CaO reacts with CO_2 which is generated during the gasification and forms $CaCO_3$ according to the following formula (Eq. (2)) (Wilcox, 2012).

$$CaO_{(s)} + CO_{2\,(g)} \rightleftharpoons CaCO_{3\,(s)} \qquad \Delta_R H(298K) = -179\ kJ/mol \tag{2}$$

This in-situ CO_2 capture leads to a shift of the syngas composition towards higher hydrogen contents.
The heat demand for the gasification is provided by the circulation of hot bed material between the gasifier and the combustor as well as by the exothermic carbonation reaction.
In a second fluidized bed reactor the formed $CaCO_3$ is regenerated by calcination at high temperatures (800 - 900°C). The heat for the calcination is provided by combustion of residual char and if needed additional fuel.

Due to the equilibrium of the carbonation reaction the gasification temperatures have to be very low compared to conventional gasification processes. These low gasification temperatures lead to relatively high CH_4 contents in the syngas. As CH_4 is inert in the DME synthesis process a higher CH_4 content decreases the efficiency of the process (Iliuta et al., 2011). Therefore, a two-stage SEG gasification process is studied within the FLEDGED project in addition to the one stage process.
In the two-stage process a steam gasification process at temperatures of about 850 °C or higher is coupled with a calcium looping cycle. Due to the high temperatures in the gasifier the CH_4 content can be reduced and in the calcium looping cycle the hydrogen content is shifted to higher concentrations by CO_2 capture.

In this paper the results of small scale tests regarding the adjustment of the M module by variation of the gasifier temperature in the SEG process are presented. This section is a re-evaluation of past experimental data ((Hawthorne et al., 2012), (Poboß et al., 2013)) that was analyzed in order to highlight the capability of the

SEG process to adjust the M module. In addition to this data, results of tests for the reduction of the CH_4 content by an increase of the gasification temperature in the two-stage SEG process are presented.

EXPERIMENTAL SETUP

20 kW_{th} facility for the investigation of the SEG process

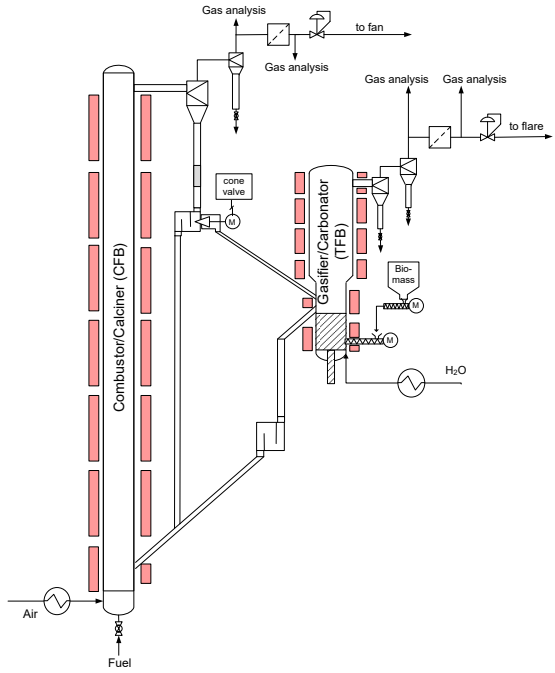

Fig. 1: Scheme of the 20 kW_{th} test facility at IFK, University of Stuttgart adapted from Gredinger et al., 2014

Parametric studies of the SEG process were carried out at a 20 kW_{th} dual fluidized bed facility (Fig. 1), which consists of a turbulent (TFB) and a circulating fluidized bed (CFB) reactor. Both reactors are electrically heated and connected to each other by loop seals. For the SEG experiments, the TFB was used as a gasifier and the CFB as a combustor. The fuel is dosed to the gasifier by a volumetric dosing system. For the fluidization of the gasifier, steam is provided by a gravimetrically controlled steam generator and fed into the reactor through a gas distributor. The maximum bed height of the gasifier can be regulated via an overflow which leads to a constant bed inventory and a constant weight hourly space velocity (WHSV). Via a cone valve the mass flow between combustor and gasifier can be regulated. The gas flows of air into the combustor and nitrogen into the loop seals are controlled by mass flow controls (MFC).

The volume fractions of CO, CO_2, CH_4, H_2 and O_2 in the gasifier as well as in the combustor product gas are analyzed and recorded continuously. After the gas analysis the syngas which is produced in the gasifier is burned by a flare. The technical data of the facility are described in Table 1.

Table 1: Technical data of the 20 kW_{th} DFB facility at the University of Stuttgart

	Combustor/ Calciner	**Gasifier/ Carbonator**
Reactor height	12.4 m	3.5 m
Reactor diameter	70 mm	150 mm
Fluidization velocity	4 – 6 m/s	0,2 – 1 m/s
Temperature	< 900 °C	< 950 °C
Regime	CFB	TFB

For the investigation of the SEG process, wood pellets which fulfill the European standard EN 14961-2 were used as fuel. The ultimate analysis of the wood pellets is shown in Table 2. German limestone, characterized in Table 3, with a particle size of 300 – 600 µm was used as bed material.
The gasifier temperature has been varied between 600 and 850°C. For each temperature the experiments were conducted at steady operational condition for a duration of 1 – 2 h.

Table 2: Analysis of the wood pellets used in the experimental campaigns at the 20 kW_{th} DFB facility

component	unit	value
C	wt %	43.93
H	wt %	6.25
O	wt %	39.5
N	wt %	<0.3
S	wt %	<0.3
Ash	wt %	0.32
H_2O	wt %	9.70
LHV	MJ/kg	15.6

Table 3: Analysis of the limestone used in the experimental campaigns after calcination

component	unit	value
calcium oxide (CaO)	wt %	89.5
silicon oxide (SiO_2)	wt %	7.9
magnesium oxide (MgO)	wt %	0.8
aluminium oxide (Al_2O_3)	wt %	0.7
iron oxide (Fe_2O_3)	wt %	0.4
average particle diameter	µm	300 - 600

8 kW_{th} facility for methane reduction tests

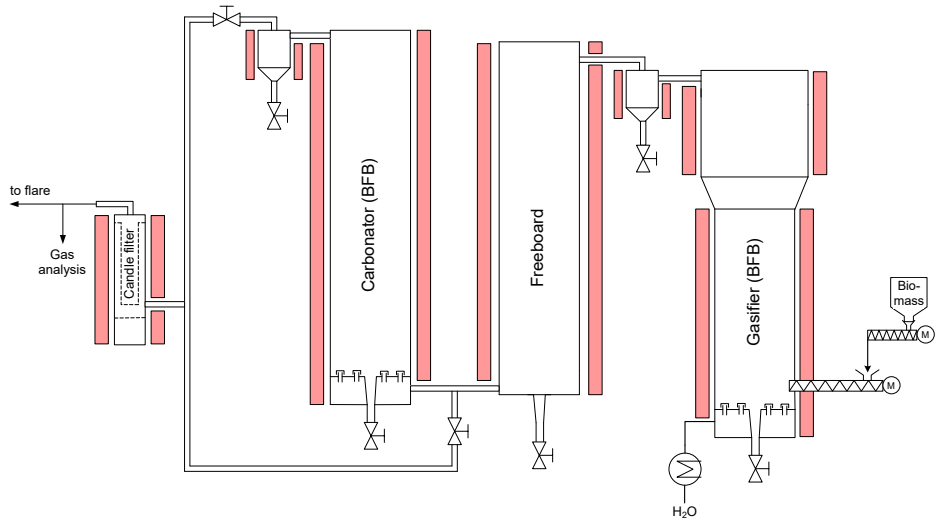

Fig. 2: Scheme of the 8 kW_{th} test facility at IFK, University of Stuttgart

The 8 kW_{th} facility used for methane reduction tests is shown in Fig. 2. The two-stage lab scale facility consists of two bubbling fluidized bed (BFB) reactors, a gasifier with a diameter of 0.07 m and a carbonator with a diameter of 0.11 m. Both reactors have a height of 1 m. For height reduction the freeboard of the gasifier is placed in a separate vessel after the gasifier cyclone and has the same diameter as the carbonator.

The biomass is fed to the gasifier by a volumetrically controlled screw feeder that was calibrated to be able to adjust desired mass flows. This screw feeder provides a defined biomass flow rate to a rapidly rotating screw feeder that feeds into the bed and is necessary to avoid pyrolysis while feeding the biomass into the reactor. The facility is electrically heated and the steam required for the gasification process is heated up to process temperature before entering the gasifier through the gas distributor.
For separation of gas and particles there is a cyclone after each reactor and a candle filter after the carbonator cyclone. Temperature and pressure are measured at several positions and the data are continuously logged together with the other operational parameters and gas concentrations.

All investigations were conducted in semi-batch mode at gasification temperatures of about 650 and 850 °C. As bed material the same limestone as for the SEG investigations in the 20 kW_{th} facility was used (Table 3). Prior to the experiments, the limestone was fully calcined at a temperature of about 850 °C. As fuel, wood pellets with a similar composition as those of the experiments at the 20 kW_{th} facility were used. The analysis of the pellets is shown in Table 4.

Table 4: Analysis of the wood pellets used in the experimental campaigns at the 8 kW_{th} DFB facility

component	unit	value
C	wt %	46.6
H	wt %	6.2
O	wt %	41.1
Ash	wt %	0.7
H_2O	wt %	5.4
LHV	MJ/kg	16.9

RESULTS AND DISCUSSION

Influence of the gasification temperature on M

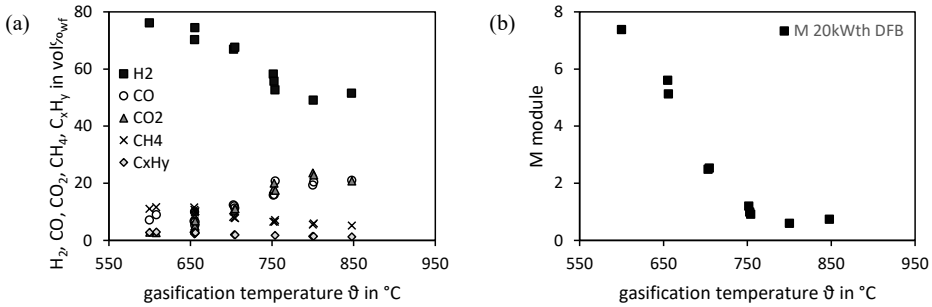

Fig. 3: Syngas composition (a) and M module (b) at different gasification temperatures for investigations at the 20 kW_{th} facility calculated from results previously published in (Poboß, 2016; Poboß et al., 2013)

The results of the conducted SEG experiments in the 20 kW_{th} facility are shown in Fig. 3. During the experiments the gasifier temperature was varied between 600 and 850 °C.
In the diagram on the left the H_2, CO, CO_2, CH_4 and C_xH_y contents in the syngas at the outlet of the gasifier are plotted against the gasification temperature. On basis of the H_2, CO and CO_2 concentrations the M module was calculated.
In the diagram on the right, the calculated M module is plotted against the gasification temperature.
The M module has a value of about 7.5 at 600 °C and decreases with increasing temperature down to a value of about 1 at 750 °C. Above 750°C M remains almost constant with a value of about 0.7. This trend is caused by the equilibrium of the carbonation reaction which results in higher CO_2 capture rates at temperatures below 750 °C and a poor capture above this temperature due to the instability of $CaCO_3$. Therefore, the hydrogen content and resulting M module reach the highest values for low temperatures and are almost temperature independent at high temperatures. When assessing these results, it should also be considered that the syngas yield is decreasing with dropping temperatures, due to a reduced char conversion.
According to the data in Fig. 3, a gasification temperature of about 715 °C is needed to reach a M of 2, which is optimal for DME synthesis.

Influence of the gasification temperature on the CH_4 and C_xH_y content

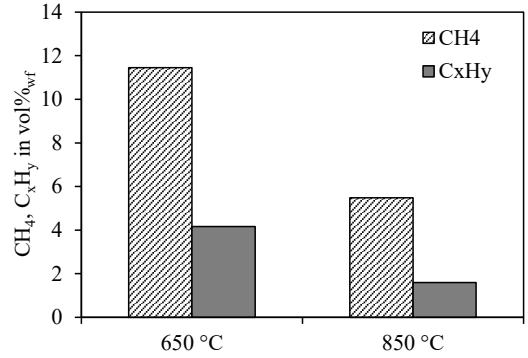

Fig. 4: Methane and C_xH_y concentrations for steam gasification in the 8 kW_{th} facility at different gasification temperatures

In Fig. 4, the measured CH_4 and C_xH_y contents at the outlet of the gasifier are plotted for two different gasification temperatures. These results were obtained from the experiments of the two-stage SEG process at the 8 kW_{th} gasification test system.
At 650 °C a CH_4 content of 11.5 $vol\%_{wf}$ was observed which is much higher compared to 5.5 $vol\%_{wf}$ at 850 °C. The same trend can be seen for the C_xH_y content in the syngas with a value of 4.2 $vol\%_{wf}$ at 650 °C and 1.6 $vol\%_{wf}$ at 850 °C.
It can be concluded that both the CH_4 and the C_xH_y concentrations in the syngas are strongly influenced by the gasification temperature and that it is possible to reduce the CH_4 and C_xH_y concentration by an increase of the gasification temperature in the two-staged SEG process. Hence, the two-stage SEG offers a possibility to operate the SEG process with all its benefits (i.e. flexible adaption of the syngas module M, possibility to capture CO_2 from the sorbent regenerator), while keeping the methane concentrations at a low level. However, these benefits come with an increased complexity of the process. As the experiments have only be conducted at two different gasification temperatures even further reductions of the CH_4 content below those achieved with gasification at 850 °C may be possible.

CONCLUSIONS

The influence of the gasification temperature on the module M in a SEG process and the influence of the gasification temperature in a two-stage SEG process configuration on the CH_4 content were presented. All experiments were conducted with wood pellets as biomass and limestone as active bed material.
Between 600 and 750 °C, the module M is strongly influenced by the gasification temperature, due to the temperature dependent CO_2 capture of the bed material. Above 750 °C, M is no longer temperature dependent as a result of the poor CO_2 capture rate.
The CH_4 as well as the C_xH_y contents are strongly influenced by the gasification temperature. In the experiments the CH_4 content could be decreased from 11.5 vol $\%_{wf}$ at 652 °C to 5.5 vol $\%_{wf}$ at 850 °C.

Within the FLEDGED project further investigations of the SEG process at the presented small scale as well as at a 200 kW_{th} pilot scale facility will be conducted. One main focus of the project is an evaluation of the flexibility of the process in order to adjust the syngas module M flexibly to a subsequent synthesis process. This is particularly important considering a system integrating hydrogen from an electrolysis unit that is only in operation in times of a surplus of renewable power. Besides this, the project aims to extent the experience in respect to gasification feedstocks for the SEG process to other biogenic feedstocks, such as biogenic residues. Tests with such fuels in small and pilot scale at the University of Stuttgart are foreseen.

NOTATION

BFB	bubbling fluidized bed
CFB	circulating fluidized bed
DFB	dual fluidized bed
DME	Dimethyl ether
FLEDGED	FLExible Dimethyl ether production from biomass Gasification with sorption-enhancED processes

LHV	lower heating value, MJ/kg
M	module M=(H_2-CO_2)/(CO+CO_2)
MFC	mass flow control
SEG	sorption enhanced gasification
TFB	turbulent fluidized bed
wf	water free
WHSV	weight hourly space velocity, m/s
$\Delta_R H$	specific reaction enthalpy, kJ/mol
ϑ	gasification temperature, °C

REFERENCES

Gredinger, A., Schweitzer, D., Dieter, H., Scheffknecht, G., 2014. Online Tar Monitoring via FID - Laboratory and Pilot Plant Experiments of an Advanced Online Tar Analyzer Prototype. 10.5071/22ndEUBCE2014-2AV.1.16.

Hawthorne, C., Poboss, N., Dieter, H., Gredinger, A., Zieba, M., Scheffknecht, G., 2012. Operation and results of a 200-kW_{th} dual fluidized bed pilot plant gasifier with adsorption-enhanced reforming. Biomass Conv. Bioref. 2 (3), 217–227. 10.1007/s13399-012-0053-3.

Iliuta, I., Iliuta, M.C., Larachi, F., 2011. Sorption-enhanced dimethyl ether synthesis—Multiscale reactor modeling. Chemical Engineering Science 66 (10), 2241–2251. 10.1016/j.ces.2011.02.047.

OECD/IEA, 2016. CO_2 emissions from fuel combustion: Highlights. OECD Publishing, 1 online resource .

Poboß, N., 2016. Experimentelle Untersuchung der sorptionsunterstützten Reformierung. Universität Stuttgart.

Poboß, N., Zieba, M., Scheffknecht, G., 2013. FuE-Plattform BtG Energetische Nutzung biogener Reststoffe mit AER Technologie zur Poly-Generation von Strom, Wasserstoff, Erdgassubstitut und Wärme: Teilbericht zum Forschungsvorhaben 03KB011C, Universität Stuttgart.

Wilcox, J., 2012. Carbon Capture. Springer US, Boston, MA.

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