



EUROPEAN COMMISSION
Innovation and Networks Executive Agency

HORIZON 2020 PROGRAMME
RESEARCH and INNOVATION ACTION
Call Identifier: H2020-LCE-2016-RES-CCS-RIA
Competitive Low-Carbon Energy

GA No. 727600



**Flexible Dimethyl ether production from biomass gasification
with sorption enhanced processes**

Starting date: 1st November 2016
Duration: 48 months

WP 2 – Deliverable D2.7:
Results from methane reduction tests at lab-scale facilities

Dissemination level	PU Public CO Confidential, only for members of the consortium (including Commission Services)	PU
Written By	Marcel Beirrow Selina Hafner Max Schmid	
Due date	2019-10-31	Issue date 2019-10-25

Track changes

Version	DATE	Changes	CHECKED	APPROVED
V1	2019-10-25	First release		

WP lead institution: CSIC

Authors' contacts

Author name	Organisation	e-mail address
Marcel Beirow	USTUTT	Marcel.Beirow@ifk.uni-stuttgart.de
Selina Hafner	USTUTT	Selina.hafner@ifk.uni-stuttgart.de
Max Schmid	USTUTT	Max.schmid@ifk.uni-stuttgart.de

Contents

Executive summary	4
1 Reduction of the methane content in the syngas by using the two-stage gasification process.....	5
1.1 The two-stage gasification process	5
1.2 Description of the test facilities at USTUTT.....	5
1.2.1 5 kW _{th} lab scale facility.....	5
1.2.2 20 kW _{th} lab scale facility.....	6
1.3 Two-stage gasification with wood pellets.....	8
1.3.1 Experimental results.....	8
1.4 Two-stage gasification with ECO-pellets	11
1.4.1 Methods.....	11
1.4.2 Experimental parameters.....	12
1.4.3 Experimental results.....	13
1.4.4 Conclusion.....	14
2 Methane reduction experiments with an O ₂ -fired burner system	16
2.1 O ₂ fired burner system	16
2.2 Experimental results.....	16
2.3 Conversion of methane	16
2.4 Effect of the CH ₄ conversion to the selectivity to H ₂ , CO, CO ₂ and H ₂ O.....	17
2.5 Heat input to a cracking/reforming stage from CH ₄ conversion.....	18
2.6 Conclusion	18
Acknowledgment.....	19

Executive summary

Within the FLEDGED process, the sorption enhanced gasification aims at the production of a tailored syngas that is optimal for DME synthesis. To fulfill the requirements it needs to have a Module M ($M = (H_2 - CO_2)/(CO + CO_2)$) with a value of 2 and as methane cannot be converted in the DME synthesis, the syngas should also have a low methane content.

The relatively low gasification temperatures in the SEG process lead to a syngas with a rather high methane content, reducing the overall efficiency of the FLEDGED-process. Therefore, two different approaches for the reduction of the methane content have been investigated.

One possibility for reducing the methane content within the syngas is to operate the SEG gasification in two stages. In the first stage, biomass is gasified at high temperatures (above 850 °C), resulting in high biomass conversion and low methane and tar concentrations. In the second stage, CO_2 is absorbed at temperatures between 650 and 750 °C for an enhanced hydrogen and a reduced CO_2 content in the syngas.

Another option would be the implementation of a high temperature cracking/reforming stage for methane reduction right after the gasifier. The energy that is required for such a reforming stage can be provided by a direct firing system using methane that is recycled from the DME process as fuel. Depending on the oxygen to fuel ratio, the amount of heat or formation of product from partial oxidation of methane can be defined.

In this document results from experiments regarding two-stage gasification and the use of an O_2 -fired burner are presented. For the two-stage gasification experiments, wood pellets and waste pellets have been used as the fuel. The results showed, that a significant reduction of the methane content can be achieved for both fuels when using the two-stage gasification instead of the one-stage SEG process.

In the experiments with the O_2 -fired burner, the influence of different oxygen to fuel ratios on the conversion of methane, the selectivity of H_2 , CO, CO_2 and H_2O and the possible heat input into a cracking/reforming stage has been investigated.

1 Reduction of the methane content in the syngas by using the two-stage gasification process

1.1 The two-stage gasification process

The principle of the two-stage gasification process is presented schematically in Fig. 1. The complete process involves three fluidized bed reactors, which include a gasifier and a carbonator connected in series regarding the gas flow and a regenerator as third reactor. Solid looping takes place in two loops, namely the regenerator-gasifier loop and the gasifier-carbonator-regenerator loop. In the gasifier, the biomass is gasified with steam in a temperature range of 800-850 °C. Within this temperature range, high biomass conversion and low methane, C_xH_y and tar concentrations can be expected. The necessary heat for the endothermic gasification reactions is provided by the circulating flow of CaO transferred from the regenerator to the gasifier. The regenerator is operated in a temperature range above 900 °C, where the calcination reaction (reverse Eq. 1) takes place. The gasifier product gas is fed into the carbonator, that is operated in a temperature range from 600 to 700 °C. In this reactor, in-situ adsorption of carbon dioxide takes place by the CaO sorbent according to the carbonation reaction (Eq. 1). Due to CO_2 absorption, the equilibrium of the water-gas shift reaction (Eq. 2) is shifted to the hydrogen product. By choosing the operational parameters in the carbonator, product gas composition can be adjusted.

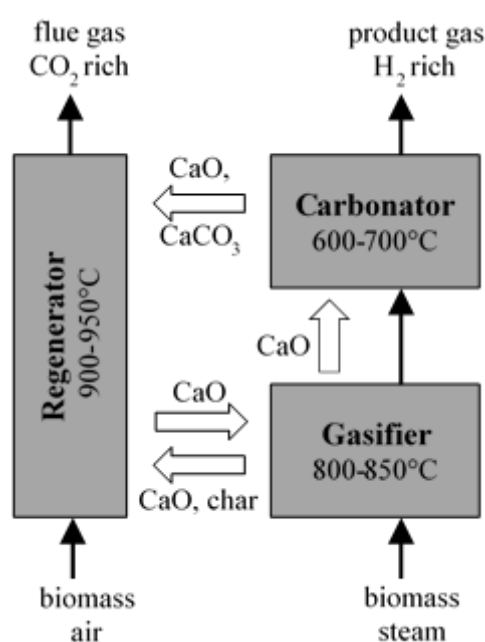


Fig. 1 Scheme of the gasification process

1.2 Description of the test facilities at USTUTT

1.2.1 5 kW_{th} lab scale facility

Fig. 2 shows schematically the 5 kW two-stage lab scale facility at USTUTT. The facility consists of a bubbling fluidized bed gasifier with 1.0 m height and 7.0 cm diameter and a BFB carbonator with 1.0 m height and 11.4 cm diameter. To reduce the height of the gasifier, the freeboard (5) is separated from

the gasifier and mounted after the cyclone. To ensure a long residence time for gaseous reactions, the freeboard diameter is increased up to 11.4 cm as compared to the diameter of gasifier. The biomass feeding system consists of two dosing screws: (i) a gravimetric screw feeder to control the biomass flow rate and (ii) a rapidly rotating screw feeder to avoid pyrolysis, which introduces the biomass into the gasifier above the distributor in the lower third of the gasifier bed. The two reactors, freeboard, cyclone and candle filter as well as the connecting pieces between the reactors are electrically heated. Preheated steam is generated in the steam generator and heated up to the process temperature before entering the BFB gasifier.

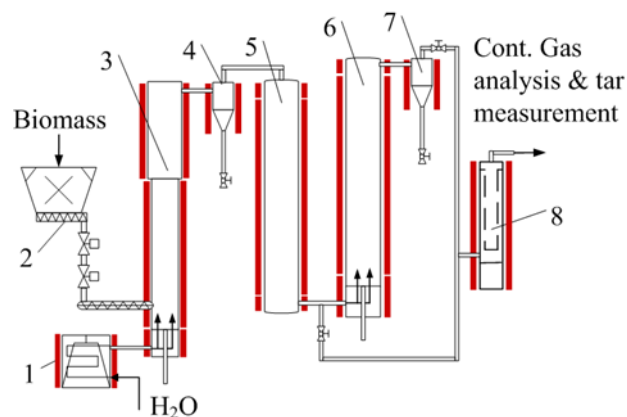


Fig. 2 Scheme of the 5 kW_{th} lab scale facility at USTUTT: (1) steam generator, (2) dosing unit, (3) BFB gasifier, (4) cyclone, (5) freeboard, (6) BFB carbonator, (7) cyclone, (8) candle filter.

1.2.2 20 kW_{th} lab scale facility

Fig. 3 shows schematically the bubbling fluidized bed (BFB) reactor of the 20 kW_{th} test facility at USTUTT that has been used for investigations on the methane reduction in syngas for non-woody biomass. The facility is electrically heated, which enables a good temperature regulation inside the reactor. Fuel is dosed gravimetrically and steam is provided by a steam generator that is gravimetrically controlled. The reactor is equipped with two cyclones and a candle filter for a reduction of the particle concentration in the syngas. The gas flows going into the reactor are controlled by mass flow controllers.

The gas composition is analyzed after the candle filter. Standard gas components such as H₂, CO, CO₂, O₂ and CH₄ are measured continuously after fine filtration, washing in isopropanol for tar removal and condensation. Lower hydrocarbons C_xH_y (C₂H₄, C₂H₆, C₃H₆, C₃H₈, C₄H₁₀) are measured via micro-GC after the same treatment as for the measurement of the standard gas components.

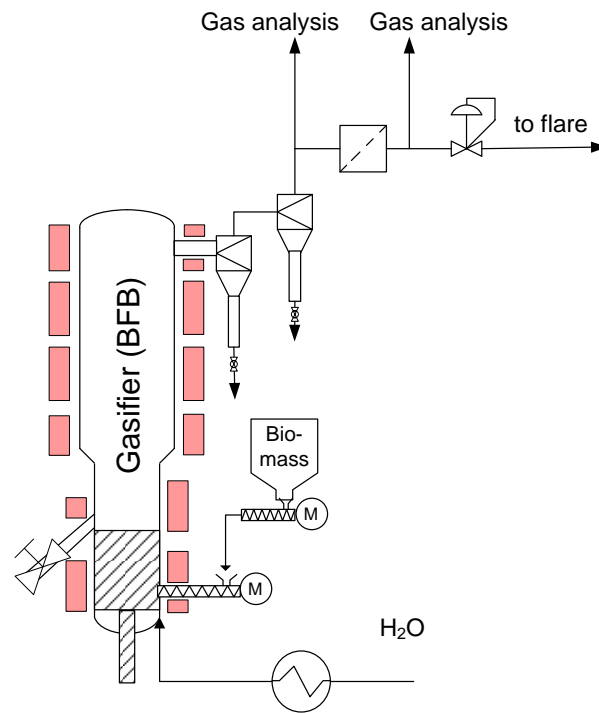


Fig. 3. Scheme of the Gasifier of the 20 kW_{th} test facility at USTUTT

1.3 Two-stage gasification with wood pellets

In this section, two-stage gasification experiments using wood pellets as biomass are presented. The experiments have been conducted in the facilities that are described above. In all experiments, limestone that has been fully calcined prior to the experiment has been used as bed material. The composition of wood pellets and the limestone are presented in Table 1 and Table 2 respectively.

1.3.1 Experimental results

1.3.1.1 Contribution of the carbonator to the amount of methane in the syngas

In a first step, the influence of the second reactor (carbonator) in the two-stage gasification process is evaluated. For this, the syngas yield of the different gas components after the first reactor (gasifier) and second reactor (carbonator) was compared. The syngas yield was calculated based on the volume flow that was measured by the controlled dilution of the syngas with nitrogen. Fig. 4 shows a decrease of the CO and CO₂ yield between the outlet of the gasifier and the outlet of the carbonator. Simultaneously, the hydrogen yield increases, but, the methane yield remains the same. This indicates that the methane yield is practically not influenced at temperatures of around 645 °C in the carbonator. Under the condition of sufficient bed inventory, further investigations of the molar gas amounts reveal that the carbonator can be characterized by only the carbonation reaction ($\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3$) and the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$).

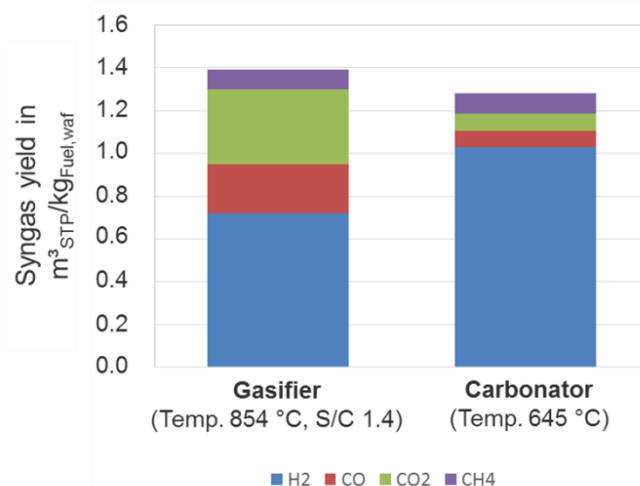


Fig. 4 Gas yields from first (Gasifier) and second (Carbonator) reactor in a two-stage gasification process

1.3.1.2 Comparison between one-stage and two-stage gasification processes

As gas yields are based on the measurement of the syngas volume flow, which was measured based on controlled nitrogen dilution, it is suspect to a measurement uncertainty. To reduce this uncertainty, in the following assessments only volume concentrations from online gas measurement devices are used. Furthermore the measured gas concentrations in-between the gasifier and the subsequent carbonator cannot be compared directly as the syngas contains different CO₂ concentrations, due to the carbonation reaction. In order to compare methane concentrations between a one-stage and a two-stage gasification process it is important to calculate those to the same CO₂ concentrations.

The dry methane concentration in the process is given by:

$$X_{\text{CH}_4, \text{wf}} = \frac{N_{\text{CH}_4}}{N_{\text{CO}_2} + N_{\text{H}_2} + N_{\text{CO}} + N_{\text{CH}_4} + N_2} \quad (1)$$

And with data from the online gas analyzer (N₂-free) the dry gas concentration is:

$$X_{CH_4, wf} = \frac{X_{CH_4}}{X_{CO_2} + X_{H_2} + X_{CO} + X_{CH_4}} \quad (2)$$

To avoid influences by different CO₂ concentrations due to the carbonation reaction, a relative gas concentration defined as follows is used:

$$X^*_{CH_4} = \frac{N_{CH_4}}{N_{H_2} + N_{CO} + N_{CH_4}} \quad (3)$$

With this value, a comparison between the methane concentration after the gasifier and carbonator is possible and CO₂ which is absorbed has no influence anymore in $X^*_{CH_4}$. Only the water gas shift reaction (Eq. 2) which influences $N_{H_2} + N_{CO}$ is considered. This reaction replaces each mole of H₂ (N_{H_2}) reacted with CO (N_{CO}), in other words, the sum of the both stays constant. Due to the definition, neither the change of H₂O nor CO₂ in the WGS has influence on the concentration $X^*_{CH_4}$. This is only valid, if N_{CH_4} is actually not changing and the methane concentration after the gasifier $X^*_{CH_4,1}$ is equal to the concentration after the carbonator $X^*_{CH_4,2}$. The ratio of those concentrations should be one:

$$\frac{X^*_{CH_4,1}}{X^*_{CH_4,2}} = \frac{N_{CH_4,1}}{N_{CH_4,2}} = 1 \quad (4)$$

Based on the presented conversion calculation, in Fig. 5 results for a two-stage (left) and a one-stage (right) SEG process are shown. While for the two-stage gasification and the coupled configuration, gas concentrations at the outlet of the carbonator and gasifier are considered, the CH₄ ratio for the one-stage gasification includes gasifier outlet gas concentrations from independent experiments with 650 °C and 850 °C gasifier temperature. The results show a CH₄ ratio of 100 percent for the two-stage gasification. This confirms the result of chapter 1.3.1.1 wherein the CH₄ yield is not influenced by the carbonator (2nd stage). In contrast, the CH₄ ratio of the two separated one-stage gasification experiments shows a value over 120 % which means that the one-stage gasification at 650 °C generates higher CH₄ concentrations in the syngas compared to gasification at 850 °C. The two-stage process (left) is based on a S/C ratio of 1.4. The one-stage process (right) is based on a S/C ratio of 2.6, which is very conservative.

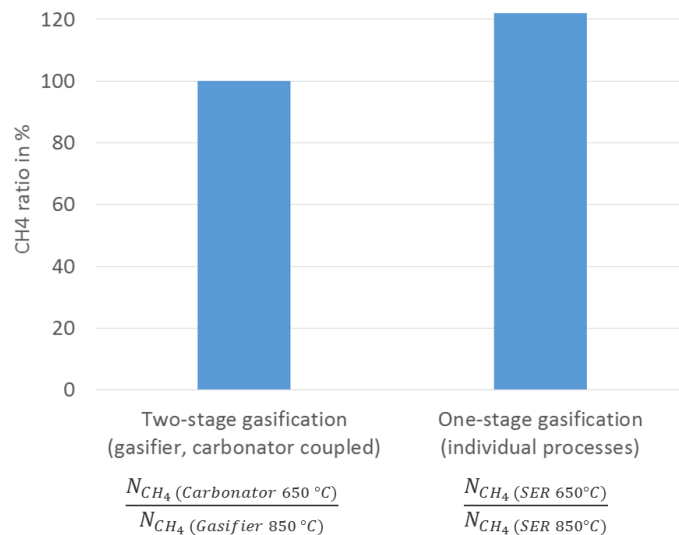


Fig. 5. Comparison of ratio in CH₄ concentrations for two-stage and one-stage gasification

The results of the conducted experiments highlight, that in two-stage SEG concepts that focus on methane reduction, the gasifier (1st reactor stage) plays a determining role, while the second stage (carbonator) has no influence on methane. Thus, any future activities on methane reduction in two-stage SEG will focus on the gasifier alone.

1.3.1.3 Adjusting the syngas composition in a two-stage gasification process

In Fig. 6 the M module; $(y_{H_2} - y_{CO_2}) / (y_{CO} + y_{CO_2})$ is considered, which characterizes the composition of the syngas with the components H_2 , CO and CO_2 . It can be seen that this module is increased after the CO_2 capture in the carbonator. For a two-stage gasification process, the operation of the carbonator is independent of the gasifier and the operation temperature can be chosen to adjust the M module. A DME synthesis requires a M module with a value of two, which means that the operation temperature in the carbonator has to be set higher than 650 °C to prevent too high hydrogen contents.

Due to a damage of the 5 kW_{th} experimental rig (Fig. 2), additional experiments on two-stage gasification were carried out coupling two different fluidized bed systems to simulate this reactor configuration. Unfortunately, in this configuration, the 2nd reactor (carbonator) required more gas for proper fluidization than it could be provided by the 1st reactor (gasifier). To provide additional gas, N_2 was injected to the gas distributor of the carbonator. In Fig. 6 (right side), the effect of syngas dilution can be observed. With this measure, the M module of the syngas is in the range of two. The reason for this can be found in a reduction of the partial pressure of CO_2 , which leads to a less efficient capture of CO_2 and hence impacts the water gas shift reaction. In addition, the gas residence time in the bed was reduced when nitrogen was added. As a consequence of this, equilibrium CO_2 concentrations for the respective carbonator temperature were not reached.

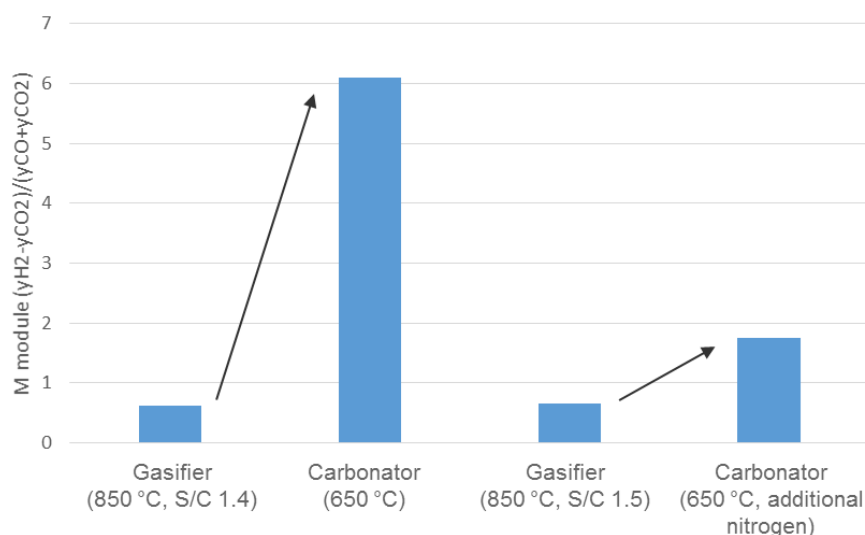


Fig. 6. M-module at different reactor stages (gasifier, carbonator) and effect of higher syngas dilution by additional nitrogen into the carbonator

As the electrical heating in the 5 kW_{th} experimental rig that was used in most experiments on two-stage gasification is limited to a maximum temperature of 850 °C in the gasifier, the scope of the conducted experiments was limited to this temperature, even though, higher temperatures up to 900/950 °C would be interesting to further reduce methane yields in SEG. In addition, no significant contribution of methane reforming reactions on CaO in the gasifier could be observed due to low temperatures in this reactor. At higher temperatures such reforming reactions may allow to reach relatively low CH_4 levels in the SEG syngas and reforming reactions may also allow for a conversion of methane that is recycled back to the gasifier from a synthesis reactor.

1.3.1.4 Effect of S/C ratio to syngas composition from gasifier

In the following, first results from the investigation of the amount of steam dosed into the gasifier to the syngas composition are shown. In Fig. 7, the S/C ratio (moles H_2O per moles carbon) was varied between the value of 0.8 and 2.2 and it can be seen that the M module is relatively stable by compensation of changes in concentrations of H_2 , CO and CO_2 . For the whole range of S/C variations

of the CH₄ concentration remain more or less at a constant level and hence, it can be considered independent from the amount of steam in the gasifier. This can be associated to a generation of methane mainly during fuel pyrolysis, which is not influenced considerably by S/C. For all operation points, a gasification temperature of 850 °C was used.

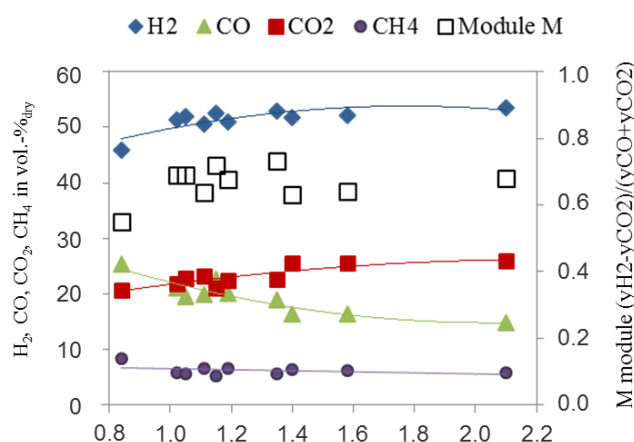


Fig. 7 Effect of S/C ratio to the syngas composition and M module (at gasifier outlet)

1.3.1.5 Conclusion

In the framework of WP 2, experiments to reduce the methane yield in SEG derived syngas from wood pellets were carried out in a two-stage gasification process and compared to the “conventional” one-stage SEG gasification. In comparison to one-stage SEG, a two-stage SEG process with a gasifier (850 °C) and the carbonator (650 °C) enables lower CH₄ concentrations and lower CH₄ yields. A result of the experiments is that the methane yield is practically not influenced by the carbonator (2nd stage). Hence, the carbonator can be characterized by the carbonation and water gas shift reactions. Also the S/C ratio has no significant impact on methane production. Based on the operation temperature in the carbonator, the composition of the syngas can be adjusted for a downstream DME synthesis. For methane reduction purposes, further experiments (e.g. with non-woody biomass) focus on the operation of the gasifier (1st stage) with higher operation temperatures. Testing of the coupled 2nd stage (carbonator) are irrelevant in respect to methane yields that are produced by the SEG process.

1.4 Two-stage gasification with ECO-pellets

In this chapter, the results of investigations on two-stage gasification with waste pellets from Econward (ECO-pellets) as non-woody biomass for methane reduction in syngas are presented. As the results from two-stage gasification with wood pellets that are presented in the previous section reveal that the methane yield is practically not influenced in the carbonator, the experiments presented in this document focus on the gasifier only.

1.4.1 Methods

In the previous section, results from two-stage gasification of woody biomass have been presented. The results from these experiments reveal that the methane yield is practically not influenced in the carbonator at temperatures of around 645 °C and that the carbonator can therefore be characterized by only the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$) and the carbonation reaction ($\text{CaO} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3$).

As the carbonator (second stage) has no influence on methane, it was decided to focus on the gasifier alone for future experiments. Therefore the investigations regarding two-stage gasification of non-woody biomass for methane reduction in syngas were conducted under semi-batch conditions in a bubbling fluidized bed reactor used as gasifier.

1.4.2 Experimental parameters

The experiments presented in this document have all been conducted in the electrically heated BFB reactor that is described in chapter 1.2.2. Pellets made out of biogenic waste material from the Econward plant (ECO-pellets) have been used as fuel. The composition of the ECO-pellets as well as the composition of wood pellets that are used as reference fuel are given in Table 1. There are two different batches of ECO-pellets. One batch (ECO 04/17) that has been sent to USTUTT in April 2017 with an ash content of about 41 wt%,db and a second one (ECO 05/18) from May 2018 with a lower ash content of about 33 wt%,db. For the experiments that have been conducted for investigating the possible methane reduction in a two-stage gasification process, ECO-pellets from May 2018 have been gasified at temperatures between 799 and 854 °C. The results of these experiments are compared to data achieved from semi-batch SEG-gasification tests with ECO-pellets from April 2017 that have been conducted earlier in the project at temperatures lower than 800 °C. As the dry and ash free composition of both batches is almost the same, it is assumed that the syngas composition is practically not influenced by the slightly different compositions of the pellets that have been used. The ECO 04/17 pellets had to be dried prior to the experiments to avoid mold formation during storage. For the ECO 05/18 pellets a different packaging has been chosen for transportation and the moisture content has been lower, therefore it has not been necessary to dry the pellets. During SEG- and the methane reduction tests, the Steam-to-Carbon molar ratio was kept constant at 1.5 mol/mol with a fuel mass flow of 3.7 kg/h. The limestone was fully calcined prior to the experiments. Its chemical composition is shown in Table 2. The mass of the bed inventory was kept constant at about 10 kg. The syngas volume flow was calculated based on gas concentrations measured with and without controlled nitrogen dilution.

Table 1: Composition of ECO-pellets used for the experiments and of Wood pellets as reference fuel

	H _u	Y _{H2O}	Y _{ash}	Y _V	Y _{FC}	Y _C	Y _H	Y _N	Y _S	Y _{Cl}
	J/g,ad	wt%,ad	wt%,db	wt%,daf						
ECO-pellets (04/17)	11138	1.92	40.5	88.2	11.8	52.8	6.8	2.3	0.4	1.0
ECO-pellets (05/18)	11622	8.01	33.2	90	10	53.8	6.4	2.5	0.6	1.0
Wood pellets	17358	6.0	0.2	82.7	17.3	50.8	6.1	0.2	0.1	0.02

Table 2. Chemical composition of the limestone used for the experiments

	X _{CaO}	X _{MgO}	X _{SiO2}	X _{Al2O3}	others	X _{CO2} ¹
	wt%, db					
German limestone	55.1	0.7	0.4	0.1	0.2	43.5

¹Mass fraction of CO₂ that is released as CO₂ during calcination

1.4.3 Experimental results

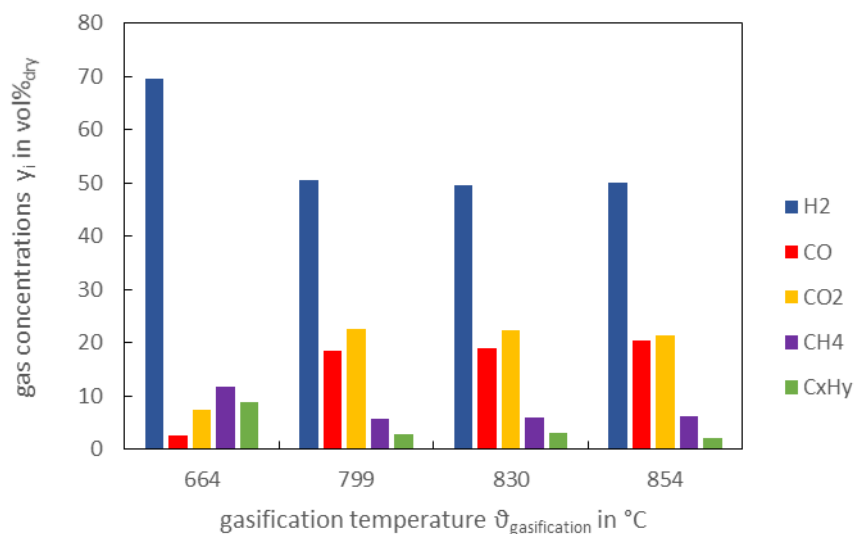


Fig. 8 Syngas compositions at gasification temperatures between 664 and 854 °C for gasification of ECO-pellets under semi-batch conditions

Fig. 8 shows the syngas compositions for the gasification of ECO-pellets at gasification temperatures between 664 and 854 °C. By enhancing the gasification temperature from 664 to temperatures of 799 °C and higher, the H₂-concentration decreased from 70 to about 50 vol%_{dry}, while the concentrations of CO and CO₂ are strongly increasing. The results do also reveal that the CH₄-concentration can be reduced from 12 vol%_{dry} at 664 °C to 6 vol%_{dry} at temperatures above 799 °C. In addition to the reduction of the CH₄-concentration, a reduction of the C_xH_y-concentration from 9 vol%_{dry} at 664 °C to about 3 vol% at temperatures of 799 °C and higher could be reached during the experiments. By increasing the gasification temperature from 799 to 854 °C, no significant change in the CH₄- and C_xH_y-concentrations has been observed.

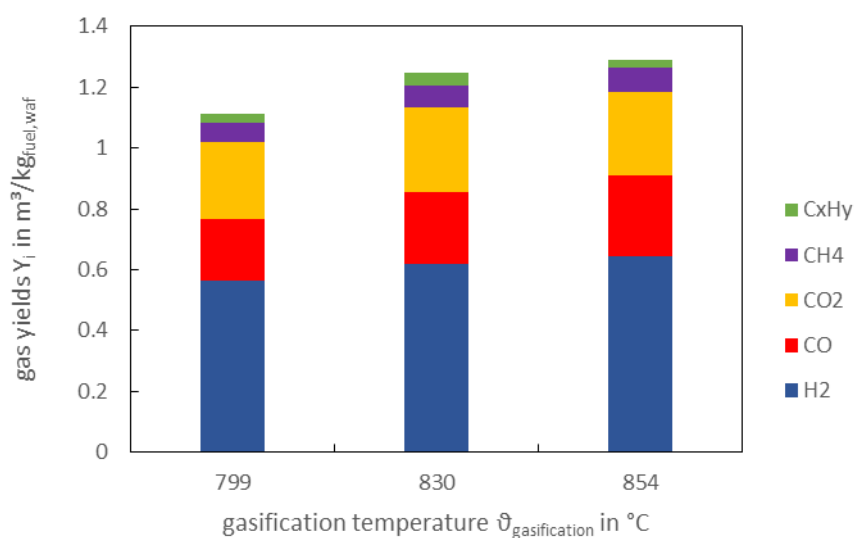


Fig. 9. Syngas yields at gasification temperatures between 799 and 854 °C for gasification of ECO-pellets under semi-batch conditions

The influence of the gasification temperature on the gas yield for gasification temperatures between 799 and 854 °C is presented in Fig. 9. As can be seen an increase of the gasification temperature from 799 to 854 °C leads to an increase of the product gas yield from 1.1 to 1.3 m³/kg_{fuel,waf}. While the H₂-yield and the CO-yield increase considerably from 0.56 to 0.65 m³/kg_{fuel,waf} and from 0.21 to 0.26 m³/kg_{fuel,waf} respectively, there is only a slight increase in the CH₄-yield (from 0.06 to 0.08 m³/kg_{fuel,waf}). The C_xH_y-yield remains almost constant at a value of about 0.03 m³/kg_{fuel,waf}.

For a better evaluation, the methane reduction X_{CH_4} that is possible by gasification at higher temperatures compared to a gasification at a temperature of 664 °C was calculated by Eq. 1.

$$CH_4 - reduction = 1 - \frac{y_{CH_4}(\vartheta_{gasification})}{y_{CH_4}(664\text{ °C})} \quad (1)$$

In Fig. 10, the CH₄-reduction is plotted vs. the gasification temperature for gasification temperatures between 727 and 854 °C. The experiments with gasification temperatures of 727 and 754 °C have been conducted with ECO-pellets from April 2017 (41 wt%,_{db} ash) while for the experiments at higher temperatures ECO-pellets from May 2018 (33 wt%,_{db} ash) were used as fuel. By increasing the gasification temperature from 664 to 727 °C, the methane concentration could be reduced by 26 %. A CH₄-reduction of about 50 % has been reached at a gasification temperature of 799 °C. Further increase of the temperature had no significant influence on the CH₄-reduction.

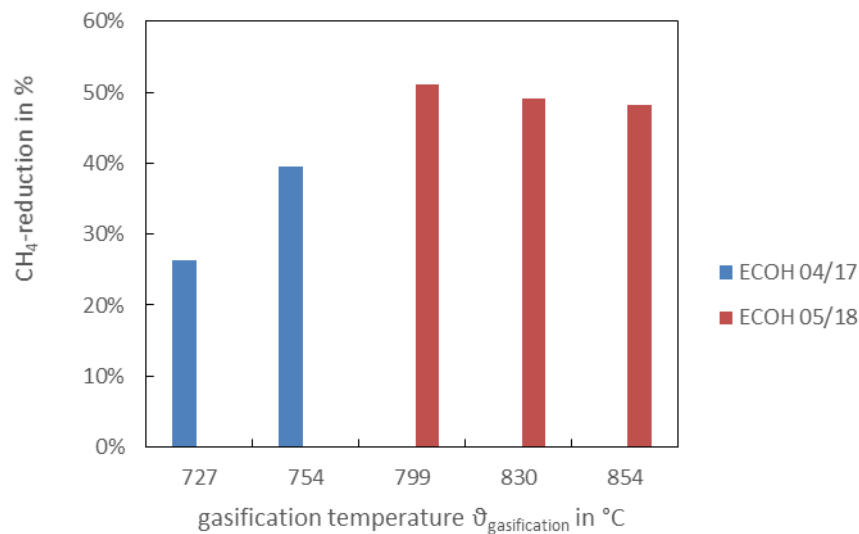


Fig. 10. Methane reduction compared to the methane concentration at a gasification temperature of 664 °C for gasification temperatures between 727 and 854 °C

1.4.4 Conclusion

To investigate the possible reduction of the methane content in the syngas by using a two-stage gasification process for the gasification of non-woody biomass, experiments have been carried out in an electrically heated lab scale facility under semi-batch conditions using ECO-pellets as biomass. The experiments have been conducted at gasification temperatures between 799 and 854 °C, which is the temperature range in which the gasifier in a two-stage gasification process would be operated. The results of these experiments have been compared to experiments that have been conducted under the same conditions, but at lower gasification temperatures (664 – 754 °C) representing the temperature range of the gasifier in a one-stage SEG process. To assess the possible reduction of the

methane concentration by using a two-stage gasification process compared to a one-stage SEG process, methane concentrations at a gasification temperature of 664 °C served as basis of valuation. It has been shown, that the methane content can be reduced significantly by enhancing the gasification temperature up to 799 °C compared to gasification at 664 °C. In this temperature range, it was possible to reduce the methane content by 50 % from 12 vol%_{db} to 6 vol%_{db}. In addition, the C_xH_y-content could be decreased considerably from 9 vol%_{db} at 664 °C to 2 vol%_{db} at 854°C.

2 Methane reduction experiments with an O₂-fired burner system

In the following, results from experiments with an O₂ fired burner, which can be used to convert methane from the DME process, are shown. This direct firing system will provide the energy for a high temperature cracking/reforming stage that the syngas will pass straight after the gasification. Depending on the oxygen to fuel ratio, the amount of heat or formation of product from partial oxidation of methane can be defined. The partial oxidation of methane in a non-premixed burner system is investigated experimentally at high temperatures and atmospheric pressure. The aim of this work is to determine the efficiencies of CH₄ conversion and selectivities of H₂ and CO, which are major components of the syngas. Furthermore, the amount of additional heat input from the burner to a cracking/reforming stage is determined.

2.1 O₂ fired burner system

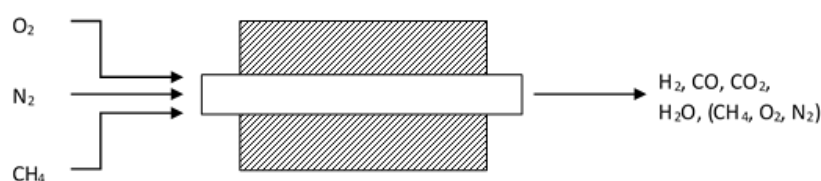


Fig. 11. O₂ fired burner system

Fig. 11 shows schematically the O₂ fired burner system. The burner is placed in a tube furnace (Elite Thermal Systems Ltd TSH12/50/610) equipped with a PID temperature controller (EUROTHERM 3216). All the Experiments are performed keeping the feed volumetric flow rate of CH₄ constant at 0,8 l/min (at STP: standard conditions of 0 °C temperature and 1.01325 bar pressure) at different volumetric flow rates of O₂ and a constant volumetric flow rate of N₂ of 5,9 l_{STP}/min to prevent reaction temperatures higher than 1200 °C. The variation of the flow rate of O₂ is dependent on a desired lambda. In this study, lambda or the stoichiometric ratio is defined as the ratio of the actual oxygen to methane ratio to the stoichiometric oxygen to methane ratio as follows:

$$\lambda = \frac{\dot{N}_{O_2} / \dot{N}_{CH_4}}{\dot{N}_{O_2}^{stoich} / \dot{N}_{CH_4}^{stoich}}$$

$$\text{with } \dot{N}_i = \frac{\dot{V}_i \cdot \rho_i}{M_i}, i = O_2, CH_4$$

where \dot{N}_i = the molar flow rate of gas i [kmol/h]

\dot{V}_i = the volumetric flow rate of gas i [m³/h]

ρ_i = the density of gas i [kg/m³]

M_i = the molar mass of gas i [kg/kmol]

To study the effects of different oxygen concentrations on gas products, different values of lambda between 0.5 and 1.0 were chosen. With the tube furnace, all the gases are preheated to a temperature of 950 °C.

2.2 Experimental results

2.3 Conversion of methane

The experiments were performed in the partial oxidation condition with a minimum oxygen to fuel ratio of $\lambda = 0.5$ and up to the stoichiometric conversion conditions ($\lambda = 1$). From Fig. 12 it can be seen that with $\lambda = 0.5$ only 46 percent of volumetric flow rate of methane is converted and 55 percent are remaining in the gas stream. By increasing the amount of oxygen to stoichiometric conversion conditions ($\lambda = 1$), 91 percent of the methane is converted and only 9 percent of methane remains in

the syngas. This syngas mainly consists of the products H_2 , CO , CO_2 , H_2O (and unconverted CH_4). For synthesis processes, a high conversion of methane to H_2 and CO is important.

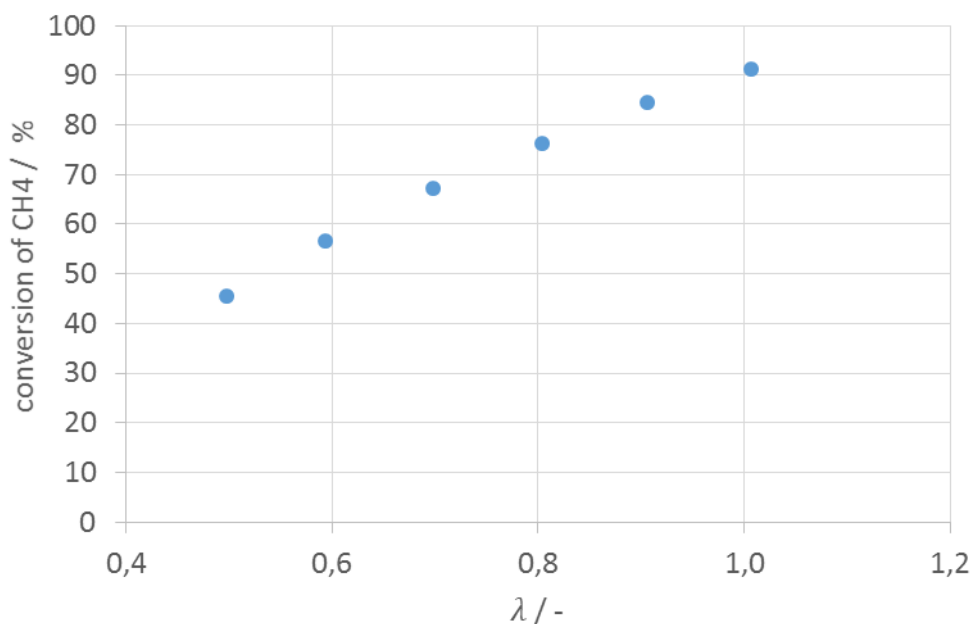


Fig. 12. Conversion of CH_4 for different values of λ (oxygen to fuel ratio)

2.4 Effect of the CH_4 conversion to the selectivity to H_2 , CO , CO_2 and H_2O

In Fig. 13 the selectivity (formed amount of component i , based on converted amount of CH_4) to H_2 , CO , CO_2 and H_2O is shown. It can be seen, that the lower the conversion of CH_4 , the higher is the selectivity to H_2 and CO . For a high CH_4 conversion, the formation of H_2 and CO is reduced, but the selectivity to CO_2 and H_2O increases.

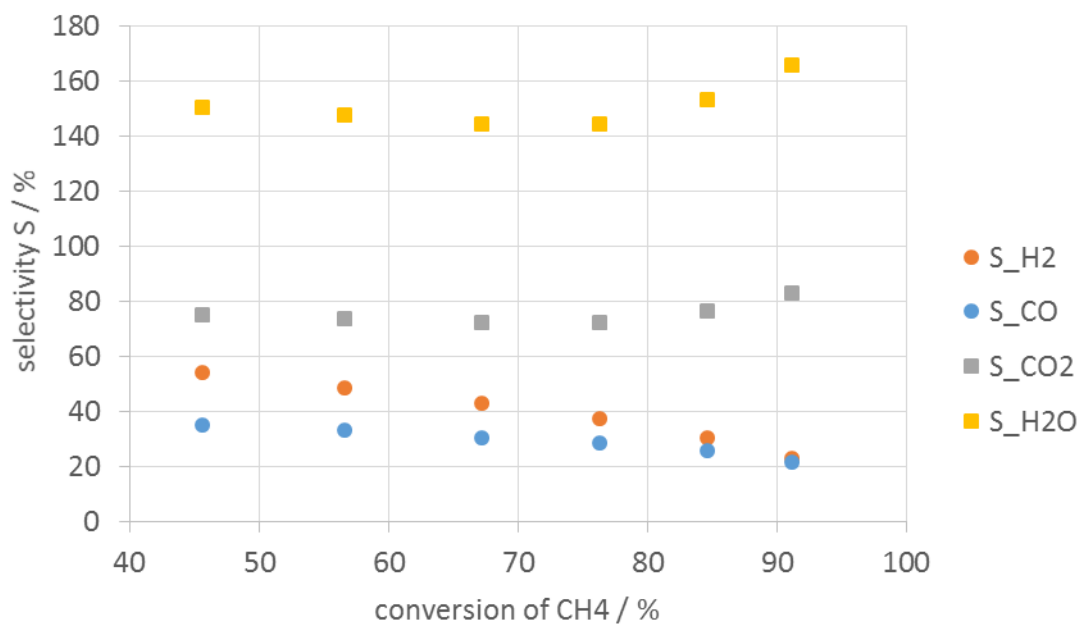


Fig. 13. Selectivity to H_2 , CO , CO_2 and H_2O , based on CH_4 conversion

2.5 Heat input to a cracking/reforming stage from CH₄ conversion

Depending on the operation of the O₂ fired burner system, the heat output from the burner is different. For the products CO₂, CO, H₂, CH₄ (unconverted) and H₂O, the standard enthalpy of reaction of the methane reformation was calculated and normalized with the constant molar flow rate of CH₄ at the inlet of the burner (0,8 l_{STP}/min). Compared to the standard enthalpy of reaction of CH₄ (890,6 kJ/mol_{CH4}) it can be recognized that with $\lambda = 0.5$ a heat input of only 30 % and with $\lambda = 1.0$ a heat input of around 70 % can be transferred to a cracking/reforming stage, see Fig. 14.

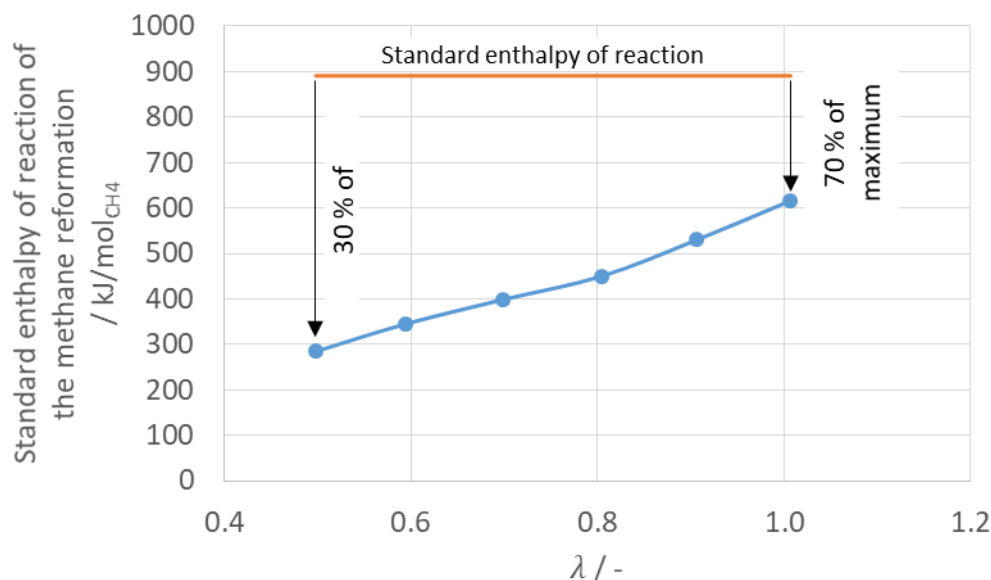



Fig. 14. Standard enthalpy of reaction of the methane reformation for different values of λ and normalized with the constant molar flow rate of CH₄ at the inlet of the burner

2.6 Conclusion

With an O₂ fired burner system, recirculated methane from the DME process can be used to heat up the syngas for a cracking/reforming stage straight after the gasifier and hence, reduce tar concentrations. The heat output that can be supplied from the burner system depends on the conversion rate of methane. The conversion rate can be set by the oxygen to fuel ratio $\lambda = (N_{O_2}/N_{CH_4})_{act} / (N_{O_2}/N_{CH_4})_{stoich}$. While with high conversion rates of CH₄, the contribution of heat output from the O₂ burner system is high, also the reaction products H₂, CO, CO₂ and H₂O are fed to the syngas line and hence, the syngas composition is affected. A selectivity analysis reveals that for low conversion rates the conversion of CH₄ to H₂ and CO is higher. For high conversion rates, the conversion of CH₄ to the products CO₂ and H₂O is increased. Which operating condition of the burner is optimal for the plant, has to be individually tested, however, the system offers a wide range to switch between a high heat input and the targeted influence of the synthesis gas with the components H₂ and CO.

Acknowledgment

The FLEDGED project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 727600 .