# Syngas Biomethanation in Trickle Bed Bioreactors by Mixed Microbial Consortia

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## Introduction

Biomethane is deemed to play a key role in the transition to a greener energy sector due to its potential to substitute fossil fuel derived natural gas in the grid. The present study introduces a novel technological platform, combining a thermochemical (gasification) and a biological (syngas biomethanation) process for the production of  $CH_4$  from  $2^{nd}$  generation biomass in continuous mode. The aim is to tackle the main bottlenecks of syngas biomethanation (gas-to-liquid mass transfer rate and low microbial cells concentration) with the use of a trickle bed reactor (TBR), where biofilm is formed in a packed column, thus providing a high surface-to-volume ratio for the mass transfer of the sparingly soluble syngas compounds (H<sub>2</sub> and CO) (Asimakopoulos et al., 2018). The biological conversion was performed by enriched mixed microbial consortia (MMC), which is a cheap catalyst and can operate without the need of sterilization of the reactor. Experimental activities performed in lab scale studied the effects of temperature on syngas biomethanation and assessed the potential to produce natural gas grade biomethane with the supply of exogenous H<sub>2</sub> produced from renewable electricity. The TBR was scaled up to pilot scale and it was successfully operated with firstly artificial and afterwards real syngas produced from the gasification of wood pellets in an allothermal fluidized bed gasifier.

### **Materials and Methods**

The key component of the TBR was the trickle bed column where syngas was converted to biomethane from the MMC in the biofilm (Fig. 1) (Asimakopoulos et al., 2019). Then the biomethane entered the headspace of a liquid reservoir and exited the setup through a gas flowmeter. Simultaneously, the liquid phase was continuously recirculated in order to wet the biofilm and provide it with the necessary nutrients.



Figure 1. Trickle Bed reactor configuration

The comparison between mesophilic and thermophilic conditions was performed at 37 °C and 60 °C, respectively. The TBR was operated in 5 steady states, at empty bed residence times (EBRTs) of 3 h, 1.5 h, 1 h, 0.75 h and 0.6 h, and the conversion efficiency of the substrate (syngas) and the productivity of methane were calculated in each of them. The composition of the artificial syngas was 45% H<sub>2</sub>, 25% CO<sub>2</sub>, 20% CO and 10% CH<sub>4</sub>.

Syngas produced from biomass gasification contains a high stoichiometric excess of carbon and thus additional reducing power is required to convert the remaining CO<sub>2</sub> and produce natural gas grade biomethane. This was studied by supplying high purity hydrogen in the TBR. Five steady states were selected at electron donors per carbon donors molar ratios of  $R = \frac{H_2 + CO}{CO + CO_2} = 1.44, 2.93, 3.67, 4.00$  and 4.78 at a stable EBRT of 3 h and thermophilic conditions.

Finally, a scale-up (28 x) study of the TBR was performed and the pilot scale reactor (PSTBR) was connected in series with an allothermal fluidized bed gasifier fed producing syngas from wood pellets.

## **Results and Discussion**

The reactor performance in thermophilic conditions was significantly better at all tested steady states (Table 1). At the lowest EBRT the conversion efficiency of CO and the productivity of  $CH_4$  were more than 2 times higher at 60 °C compared to 37 °C. Since the gas solubility decreases when the temperature is increased, it is can be concluded that the kinetics under thermophilic conditions outcompeted the kinetics under mesophilic conditions.

	Conversion Efficiency of H <sub>2</sub>		Conversion Efficiency of CO		Methane Productivity	
	(%)		(%)		$(\text{mmol·l}_{\text{bed}}^{-1} \cdot \mathbf{h}^{-1})$	
EBRT (h)	Mesophilic	Thermophilic	Mesophilic	Thermophilic	Mesophilic	Thermophilic
3.00	95	99	92	99	1.5	1.7
1.50	71	98	68	96	2.7	3.8
1.00	58	95	56	88	3.1	5.9
0.75	75	92	42	85	3.2	7.2
0.60	60	89	34	73	3.6	8.5

Table 1. Comparison between the mesophilic and the thermophilic TBR

Additional pure  $H_2$  was supplied in the TBRs due to the fact that the syngas used could not be fully converted to methane due to stoichiometric limitations (high CO<sub>2</sub> content, 25%). The obtained results showed that when the ratio R took a value of 4 the conversion efficiency of  $H_2$ , CO and CO<sub>2</sub> were 99.8 %, 99.2% and 98.0%, respectively, resulting to an effluent gas containing 97.2% CH<sub>4</sub> (Table 2). Such a gas complies with the criteria for injection in the natural gas grid of Denmark.

Table 2. Conversion efficiency of the substrate and CH<sub>4</sub> outlet content with respect to the ratio R

	Convers	CH <sub>4</sub> in		
		the		
R	$H_2$	CO	$CO_2$	outlet
1.44	99.2%	99.3%	30.5%	55.9%
2.93	99.9%	99.6%	70.7%	84.5%
3.67	99.9%	100.0%	91.3%	94.2%
4.00	99.8%	99.2%	98.0%	97.2%
4.78	81.3%	56.6%	99.8%	51.6%

The PSTBR achieved higher conversion efficiency of the substrate and better  $CH_4$  productivity in all tested EBRTs (Table 3) compared to the lab scale (LSTBR). The  $CH_4$  productivity of 10.6 mmol·l<sub>bed</sub><sup>-1</sup>·h<sup>-1</sup> achieved in this study with the PSTBR at an EBRT of 0.6 h is, to our knowledge, the highest achieved so far in the literature for syngas biomethanation. Moreover, when the PSTBR was connected in series with a gasifier, full conversion of  $H_2$  and CO was achieved up to an EBRT of 0.6 h without any sign of inhibition.

Table 3. LSTBR vs PSTBR results. E: conversion efficiency, Q: productivity, green: LSTBR and red: PSTBR

	EBRT (h)					
	1.5	1.0	0.86	0.75	0.60	
$\mathbf{E} = (0/1)$	96	88	86	84	73	
ECO (%)	100	100	100	100	98	
$\mathbf{E}$ (0/)	98	95	93	92	89	
EH2 (70)	100	100	100	100	100	
Осн4	3.8	5.8	6.5	7.2	8.5	
(mmol·l <sub>bed</sub> <sup>-1</sup> ·h <sup>-1</sup> )	4.3	6.4	7.5	8.4	10.6	

## Conclusions

This study showed that thermophilic conditions favour syngas biomethanation and that with the additional supply of  $H_2$  at the proper flowrate a natural gas grade effluent can be produced. Furthermore, 28x scale-up of the TBR was successfully performed and wood pellet syngas was converted to biomethane without any sign of inhibition.

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### References

K. Asimakopoulos, H.N. Gavala, I. V. Skiadas, Reactor systems for syngas fermentation processes: A review, Chem. Eng. J. 348 (2018) 732–744.

K. Asimakopoulos, H.N. Gavala, I. V Skiadas, Biomethanation of Syngas by Enriched Mixed Anaerobic Consortia in Trickle Bed Reactors, Waste and Biomass Valorization. (2019), doi: 10.1007/s12649-019-00649-2