In situ CO_2-rich syngas pre-treatment to promote the methanol production rate over CZA catalysts

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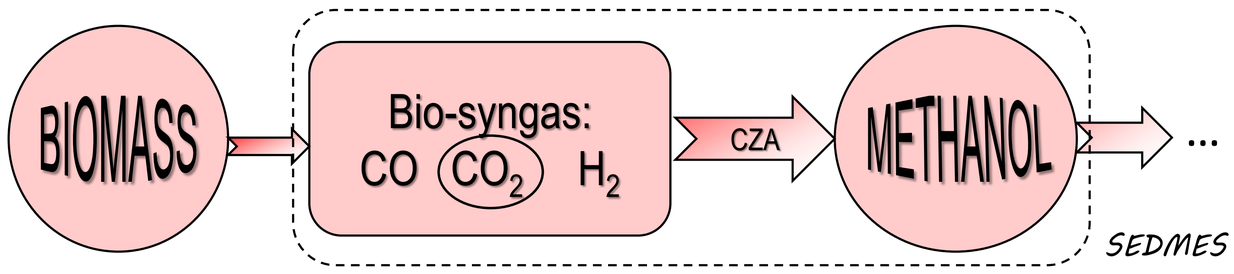
Introduction

Typical high CO_2 concentrations in the bio-derived syngas decrease productivity of CZA catalysts for methanol

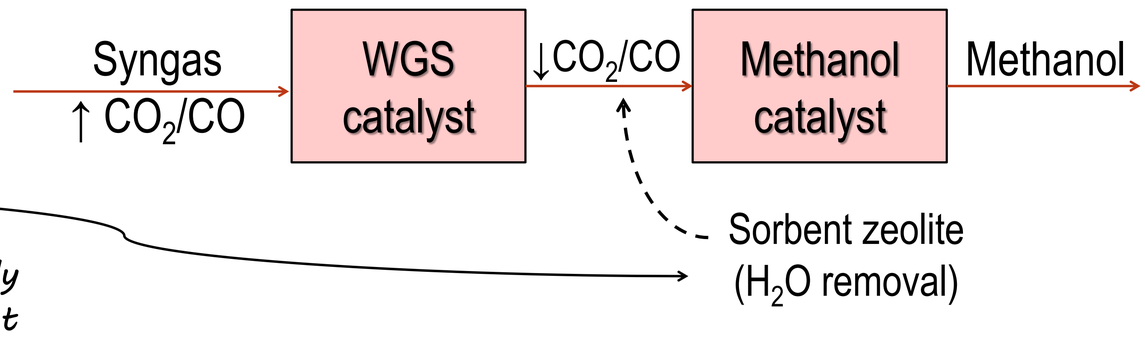


R-WGS reaction decreases CO_2/CO ratio in the syngas...

$$CO_2 + H_2 \rightarrow CO + H_2O$$

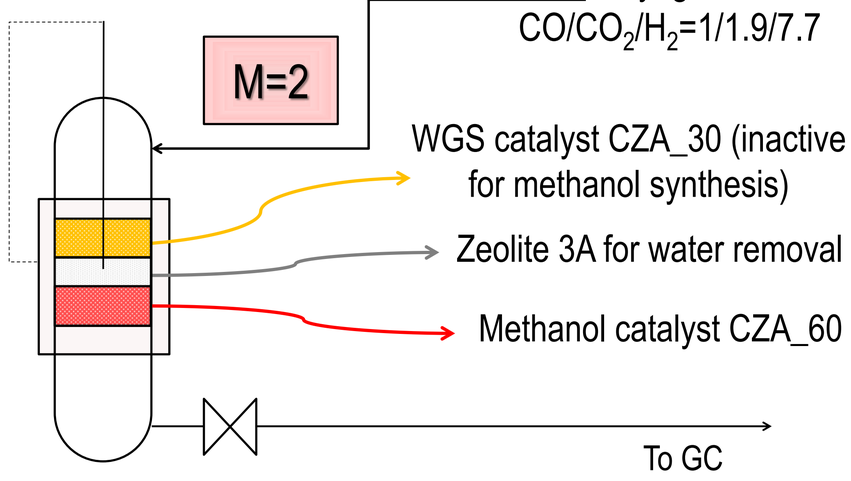
...but water is a product in the CO_2 hydrogenation (thermodynamically disadvantageous) and can deactivate the methanol catalyst

Objective: in-situ increasing the CO/CO_2 ratio of biomass-derived CO_2-rich syngas feed via RWGS before syngas reaches the syngas-to-methanol catalyst to enhance syngas conversion per pass:



Experimental

Fixed bed reactor



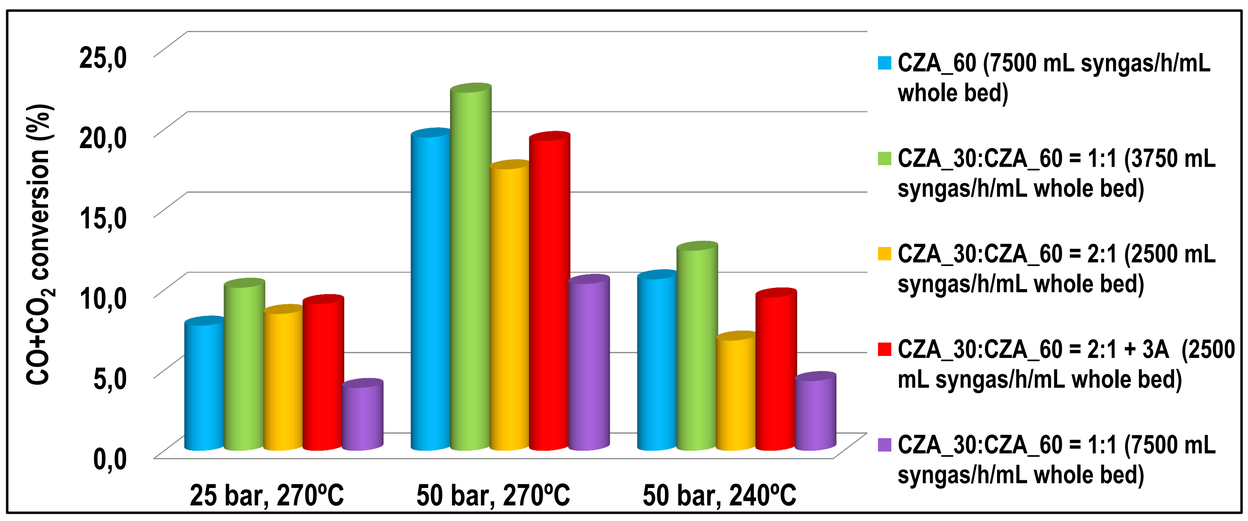
Operating conditions:

240°C, 50 bar
270 °C, 25 bar
270 °C, 50 bar

GHSV was maintained either along the CZA_60 or the whole bed

Catalytic bed configurations studied	GHSV	
	mL syngas h^{-1} mL^{-1} **CZA_60**	mL syngas h^{-1} mL^{-1} **whole bed**
CZA_60	7500	7500
CZA_30/CZA_60 = 1	7500	3750
CZA_30/CZA_60 = 2	7500	2500
CZA_30/CZA_60 = 2 + 3A	7500	2500
CZA_30/CZA_60 = 1	15000	7500

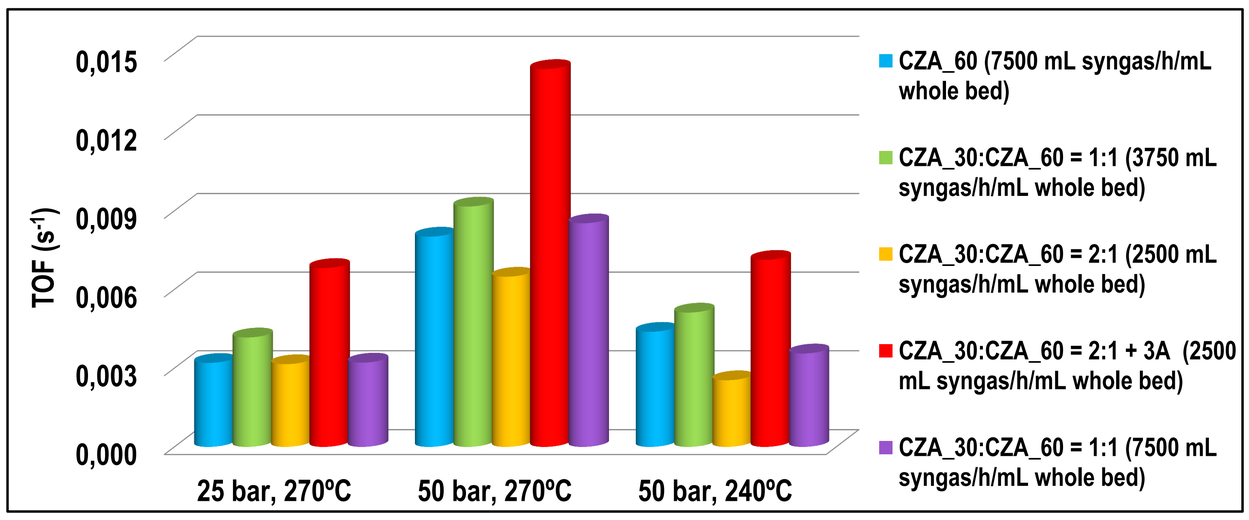
Results



The use of CZA_30/CZA_60 = 1 increases the conversion of C per pass in comparison with the single CZA_60 bed when GHSV is maintained over the CZA_60.

The comparison between CZA_30/CZA_60 = 1 and 2 reveals that the former leads to a higher C conversion.

The use of the sorbent zeolite 3A increases the C conversion, avoiding, at least in part, the unfavourable effect of the formed water.



Both the pre-treatment and the water removal increase the activity of the CZA_60.

Comparing CZA_60 and CZA_30/CZA_60 = 1 beds maintaining the GHSV in the whole bed it is observed that the TOF remains practically constant despite the formed water.

C conversion (top) and TOF (bottom) referred to the surface Cu in the CZA_60 for the different bed configurations and operating conditions

The only catalyst over which methanol is produced

Conclusions

- *A pre-treatment of a CO_2-rich syngas through r-WGS prior to the methanol synthesis process increases the activity of the CZA methanol catalyst in comparison to the same process without pre-treatment.*
- *The configuration of the double catalytic bed (WGS catalyst/methanol catalyst ratio and addition of water sorbent) can be optimized depending on the composition of the syngas.*

Acknowledgements

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