

Project at glance

OBJECTIVE

FLEDGED project aims to develop a highly intensified and flexible process for DME production from biomass gasification.

WHY DME

DME is recognized as one of the most promising future biofuels, due to the easy adaptability of diesel engines and reduced life-cycle environmental impact.

OUTCOME

FLEDGED project will demonstrate at TRL5 sorption-enhanced gasification and sorption-enhanced DME synthesis and will assess the flexibility of the complete FLEDGED plant concept in:

- the conversion of different feedstocks
- the integration with electrolyzers for power-to-DME
- bio-CCS leading to a negative emission system.

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PROJECT NEWS

FLEDGED activities on biomass gasification are completed and in the last months the work focused on Sorption-Enhanced DME synthesis

- TRL5 experimental testing of the **complete SEDMES operating cycle** has been concluded at TNO, supported by SEDMES cycle modelling for operation mode design and optimization.
- Catalyst development** for direct DME synthesis in presence of sorbent for Sorption-Enhanced synthesis has been performed at ICP-CSIC laboratories in Madrid.
- A **2D + 1D heterogeneous dynamic model** of the reactor tube for design optimization has been successfully developed by POLIMI, validated and applied for defining operating parameters on thermal behavior and DME yield performances of the reactor.

Some aspects related with integration, economics, social and environmental impact are now under assessment:

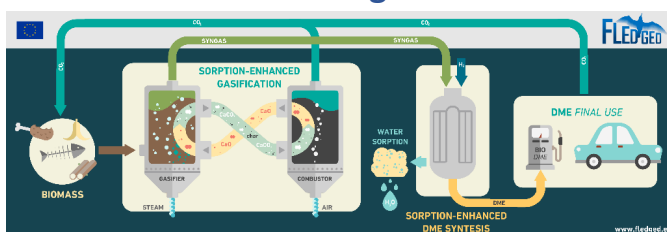
- Optimal plant operating conditions and process integration on the basis of the two operating points (with and without hydrogen addition) by **techno-economic analysis** and mathematical optimization of heat recovery network.
- Socio-economic analysis** including social and economic impact of FLEDGED technology, air quality and health impact modelling. Integration with **Life Cycle Assessment** results.
- Risk analysis** of the different configurations of FLEDGED process by means of hazards evaluation and materials characterization.

FLEDGED project has been presented during a webinar at eEUBCE 2020 and partners' presentations are available online



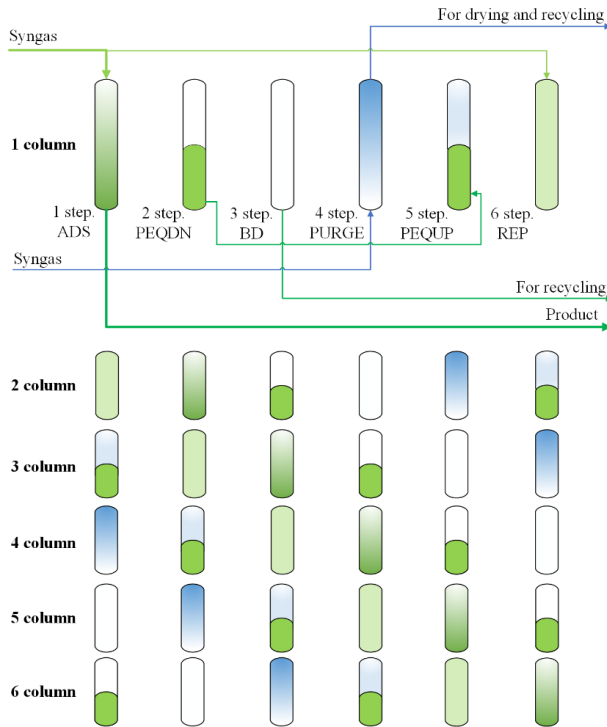
The webinar presentations and additional material on project activities and results are available on www.fledged.eu.

Several scientific publications now available and more are coming in the next months...



Find all the information and the Open Access documents in the [dedicated section of our website!!](#)

TRL 5 demonstration of Sorption-Enhanced DME Synthesis and modelling activities on cycle optimization (TNO)



Cycle design for six columns SEDMES unit with implemented pressure equalization system meets the following boundary conditions:

- 1) continuous feed stream;
- 2) continuous DME production;
- 3) continuous purge stream.

Six step pressure swing adsorption (PSA) cycle consists of:

- ADS** adsorption step (DME production);
- PEQDN** pressure equalization down (depressurisation);
- BD** blowdown (depressurisation);
- PURGE** purge (regeneration);
- PEQUP** pressure equalization up (pressurization);
- REP** repressurisation (pressurization).

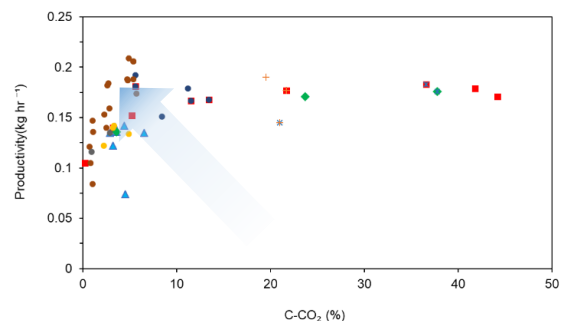
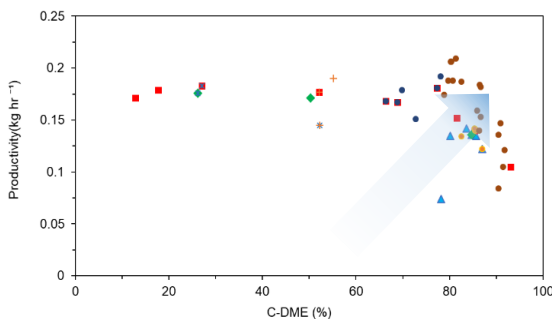
Cycle time is 45 min.

Column dimensions:

height	6 m
inner diameter	0.038 m
bed voidage	0.372
wall temperature	250 °C
operating pressure	25 bar _a

The data from the multiple simulations showed Pareto fronts, typical for PSA systems, for the defined key performance metrics C-DME, i.e. the single pass carbon selectivity to DME, and C-CO₂, i.e. the selectivity towards CO₂, and productivity, which allows to tune the process performance towards selectivity and productivity targets.

In good agreement with experimental results, high carbon selectivity to DME can be obtained (over 95%). Similarly, the carbon selectivity to CO₂ can be reduced to less than 1%, simplifying the downstream separation. However, both come at a cost in terms of productivity. Maximum productivity can be obtained for carbon selectivity to DME of over 80%. The average productivity for a single SEDMES tube is 0.17 kg hr⁻¹.



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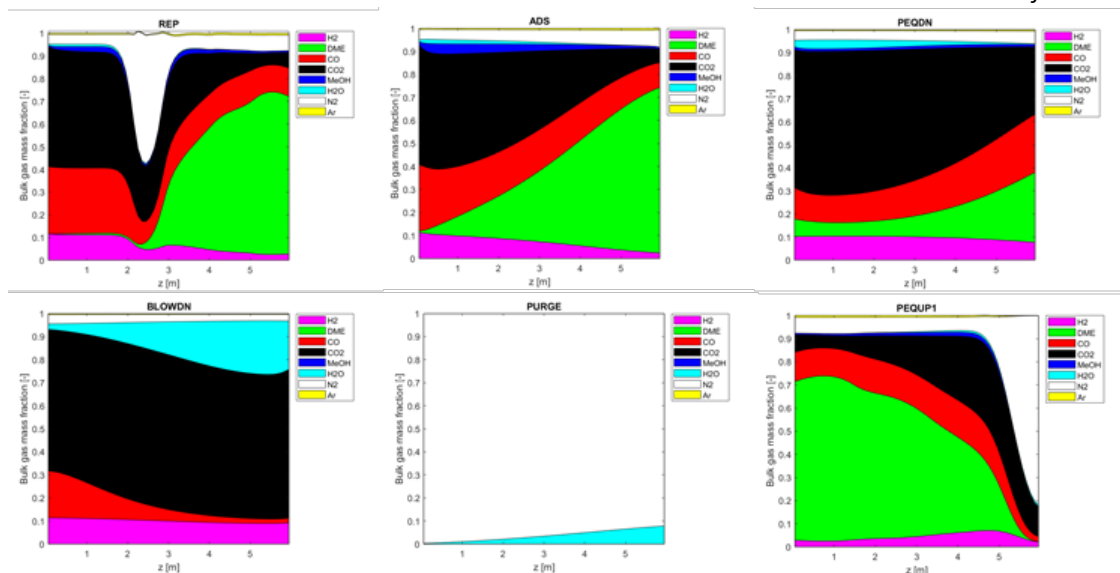
TRL 5 demonstration of Sorption-Enhanced DME Synthesis and modelling activities on cycle optimization (TNO)

Using the developed mathematical model it is possible to predict which process happens in the single reactor and how the components are distributed within the length of the reactor. This allows to select optimal process conditions in order to achieve maximal yield and purity of the product. For experimental validation, a 6 reactors test unit was operated at the same condition as the simulations, and the composition of the product was sampled in time.

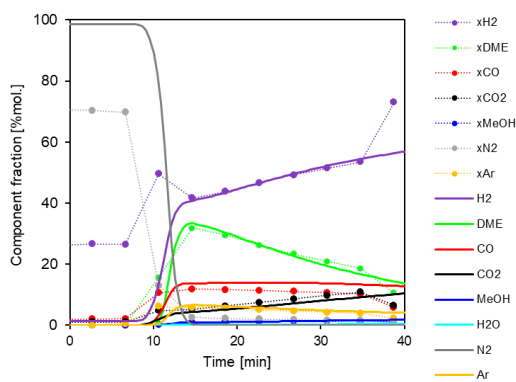
Using TNO's multi-column SEDMES reactor setup, the TRL 5 validation experiments were performed in the first half of 2020. The multi-column system allows to test complete cycle designs, e.g. including pressure equalisation steps. Besides model validation experiments at different temperatures in the range of 230-250 °C, specific conditions included CO-rich and CO₂-rich feed gas, up to a pure H₂-CO₂ feed gas.



Six-column SEDMES setup at TNO, 6 meter reactors each with 6 kg of bed materials



Concentration of the gas components after each step of the cycle: purple – hydrogen; green- dimethyl ether; red – carbon monoxide; black – carbon dioxide; blue – water; white – nitrogen; yellow – argon.



The model results (solid line) of the adsorption step at 250 °C vs. experimental results (dashed line)

Also different cycle timings were evaluated experimentally. Overall, material stability has been validated by testing for more than 500 full SEDMES cycles.

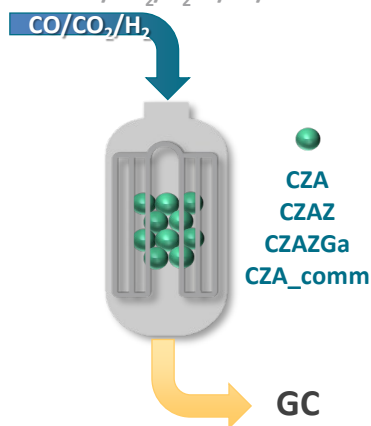
As shown, the experimental results are in close correlation with the simulated results. Therefore, the model can be used in the future prior to experiments to adjust the process parameters in accordance with a current target.

Catalyst development for indirect and direct DME synthesis (ICP-CSIC)

The Group of Sustainable Energy and Chemistry from the *Instituto de Catálisis y Petroleoquímica*, from CSIC, developed a series of Cu/ZnO based catalysts for the synthesis of methanol from CO₂-rich bio-syngas and acid catalysts for the production of DME from methanol.

The aim was to find the optimal catalyst composition to work under the optimum reaction conditions *Sorption Enhanced DME Synthesis (SEDMES)*, performing the reactions with a physical mixture of one of the methanol catalysts and commercial γ -Al₂O₃ and employing a sorbent zeolite, 3A type.

270 °C; 25 bar; 7500 h⁻¹; CO₂/CO=1.9;
CO/CO₂/H₂: 9/18/73



Fixed bed reactor for methanol reaction

The Cu/ZnO/Al₂O₃ catalysts were doped with ZrO₂ and Ga₂O₃ (see Table below). The catalysts were synthesized by coprecipitation of the metallic salts under controlled pH and evaluated in a fixed bed reactor using a syngas with CO₂/CO-ratio equal to 1.9.

Composition (wt.%) obtained by ICP-OES

	Cu	ZnO	Al ₂ O ₃	ZrO ₂	Ga ₂ O ₃	MgO
CZA	67	29	5	-	-	-
CZAZ	67	10	15	8	-	-
CZAZGa	63	16	13	6	1	-
CZA_Comm	59	27	11	-	-	2

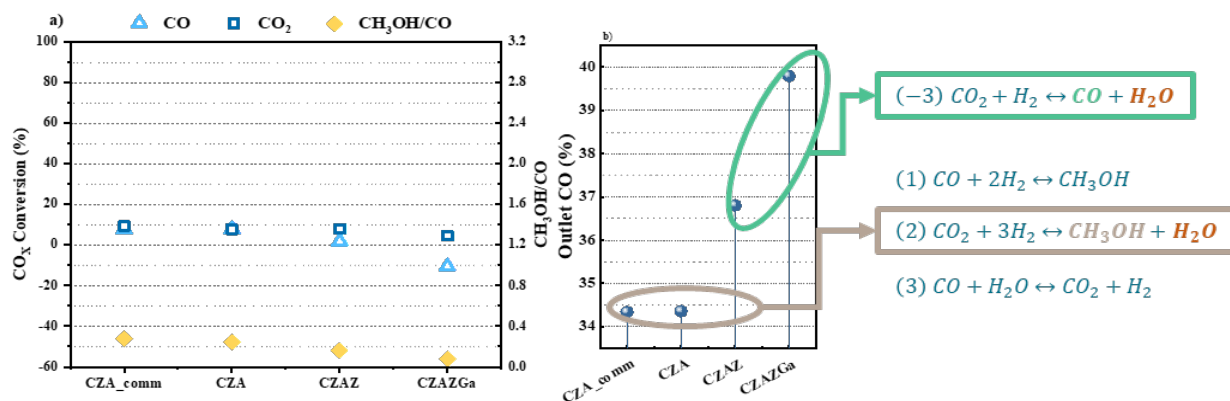


Figure 1. a) CO and CO₂ conversion and CH₃/CO outlet ratio over the catalysts, b) CO outlet concentration.

- Both CZA_comm and CZA record the highest CO and CO₂ conversions.
- Doping the catalysts with ZrO₂ decreases CO conversion to ca. 1.6 %, without affecting CO₂ conversion.
- Ga₂O₃ doping (CZAZGa) increases the CO/CO₂ ratio of the syngas (CO conversion of -10.6%)
- Negative conversion values indicate that CO is formed during the process via the r-WGS reaction, which is promoted by the addition of ZrO₂ and especially Ga₂O₃ to CZA.

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Catalyst development for indirect and direct DME synthesis (ICP-CSIC)

The Direct Synthesis of DME (DDMES) from biomass-derived CO_2 -rich syngas over a catalytic bed comprising a mixture of the Cu/ZnO catalysts and $\gamma\text{-Al}_2\text{O}_3$ was studied at TNO facilities. The effect of *in situ* water removal for the synthesis of DME was also studied under the same conditions using zeolite 3A as water sorbent. This approach is known as *Sorption Enhanced DME Synthesis* (SEDMES). Figure 2 illustrates how experiments were recorded. A catalytic bed containing the Cu/ZnO catalyst, $\gamma\text{-Al}_2\text{O}_3$ and zeolite 3A was used. The pre-breakthrough region, when zeolite 3A is capable to remove the H_2O produced, accounts to the SEDMES. After zeolite 3A saturation, the configuration is for the DDMES.

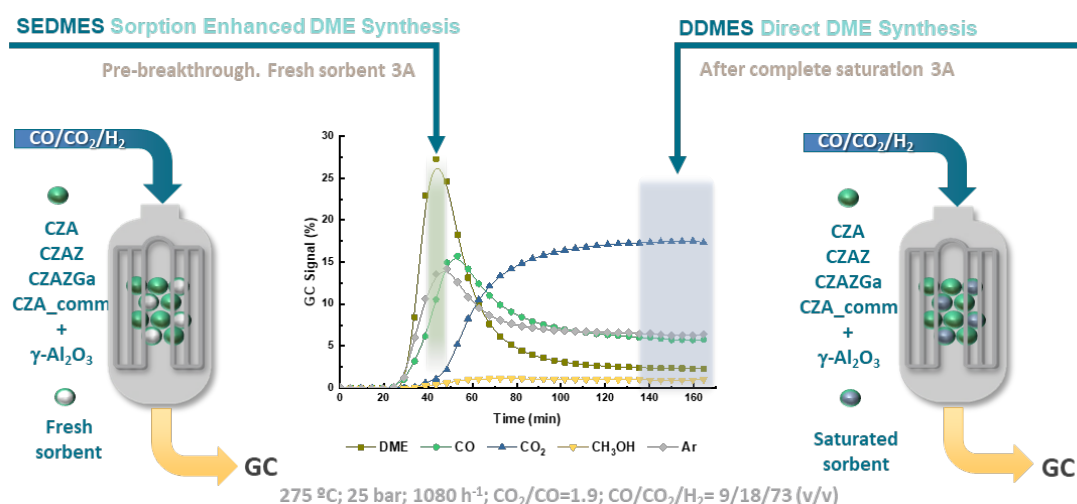


Figure 2. SEDMES and DDMES regimes for the synthesis of DME from CO_2 -rich syngas

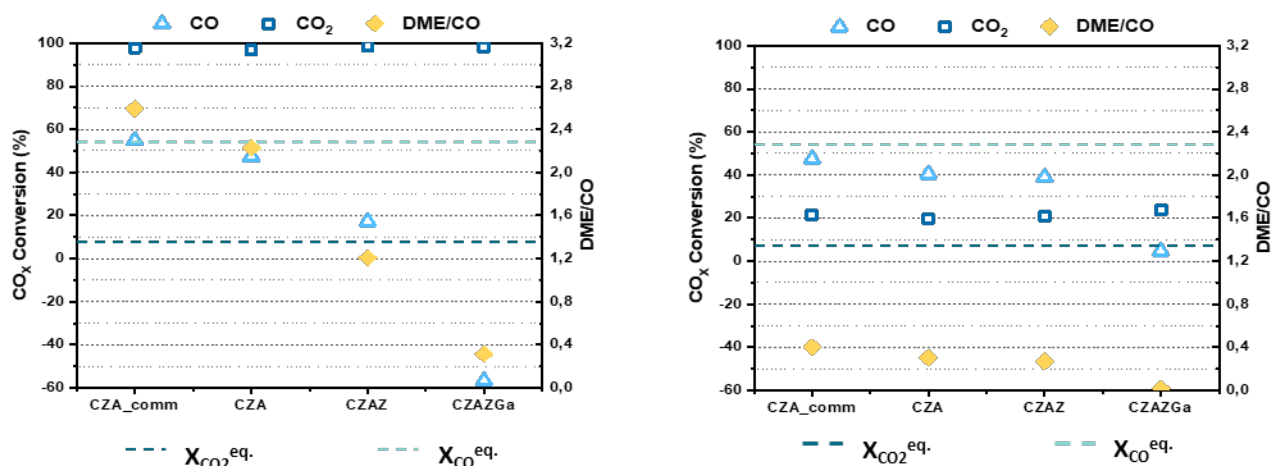


Figure 3. CO and CO_2 conversions and DME/ CO outlet ratios for the SEDMES (left panel) and DDMES (right panel) processes

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Catalyst development for indirect and direct DME synthesis (ICP-CSIC)

The carbon conversion and DME/CO outlet ratios are presented in Figure 3:

- The *in situ* removal of H₂O during the SEDMES process shows a marked effect, displaying higher CO and CO₂ conversions than conventional DDMES.
- Non promoted CZA catalysts (CZA_comm and CZA) display higher CO₂ conversions and DME production than the promoted catalysts in both SEDMES and DDMES regimes.
- The effect of ZrO₂ and Ga₂O₃ doping (CZAZ and CZAZGa), especially Ga₂O₃, is more obvious in the SEDMES process.

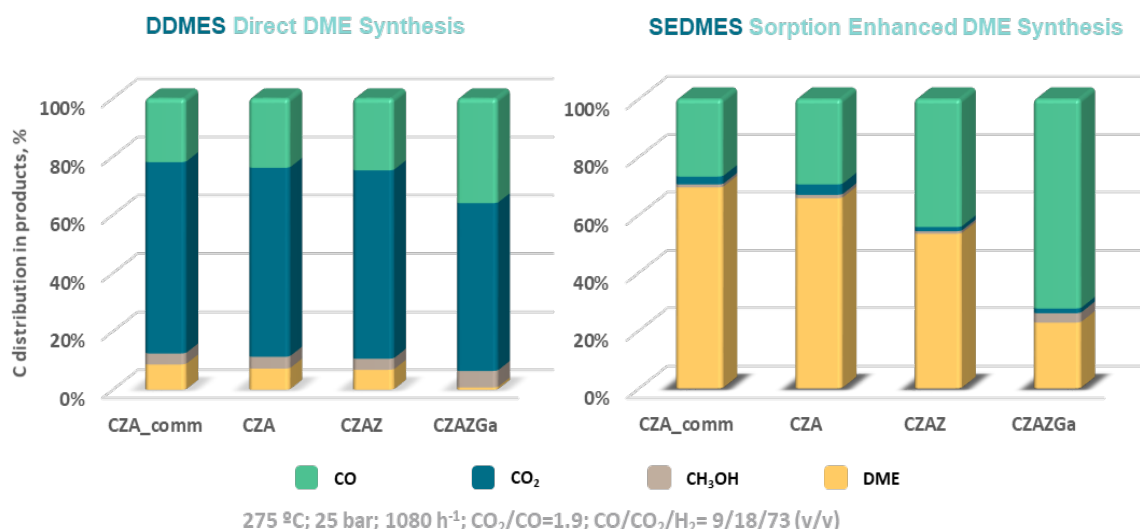


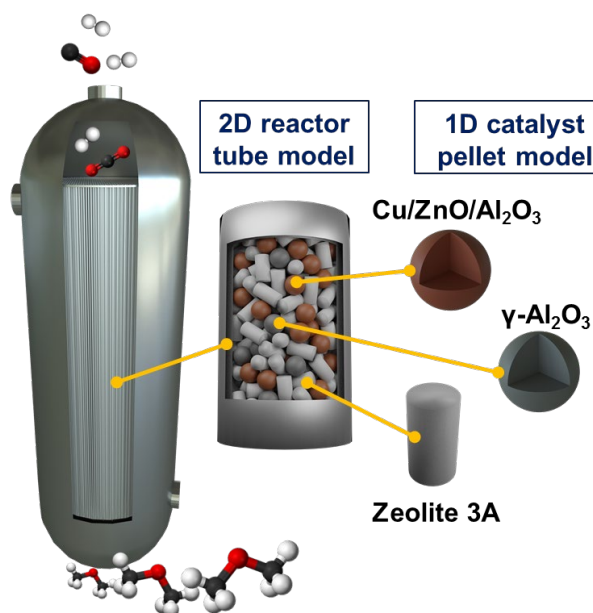
Figure 4. Products distribution obtained with the DDMES (left panel) and SEDMES (right panel) processes

As clearly shown in Figure 4, H₂O removal during the direct synthesis of DME from CO₂-rich syngas result significantly higher DME production, especially over non-promoted Cu/ZnO catalysts. However, the actual promotional effect is also affected by the catalyst, thus:

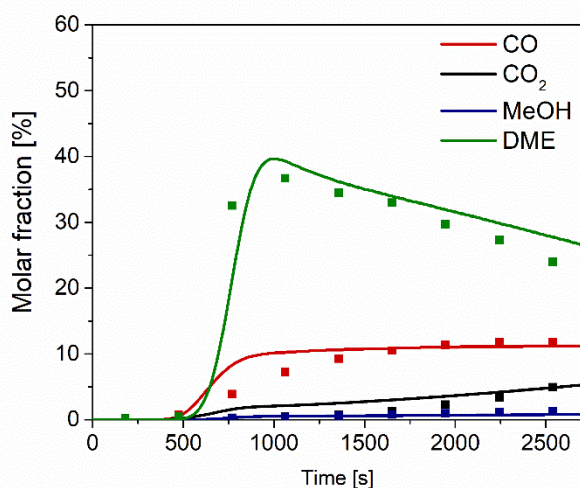
- Water removal during SEDMES over CZA catalysts promotes methanol production and dehydration reactions
- Water removal during the SEDMES over catalysts with high r-WGS activity promotes CO production

In summary, the promotional effect of the SEDMES approach for the direct synthesis of DME from biomass-derived CO₂-rich syngas has been demonstrated experimentally in the frame of FLEDGED project

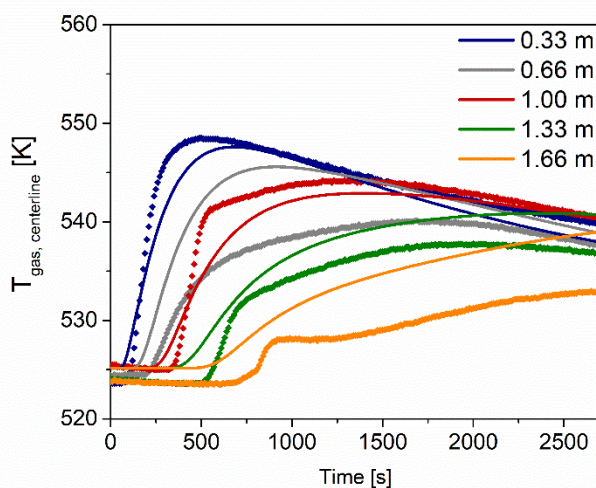
2D + 1D heterogeneous dynamic model of the SEDMES synthesis for reactor design and optimization (POLIMI)



The development of the mathematical 2D+1D dynamic model for SEDMES multitubular fixed bed reactor has been completed. The model has been implemented in gPROMS commercial language for the numerical solution and has been validated by a comparison with bench scale reactor experimental data obtained in the TNO facilities in Petten. The model shows the ability to capture the experimental dynamics of the outlet composition of reactants (CO , CO_2) and products (CH_3OH , DME) and also to describe the temperature trajectories in different points along the axial reactor coordinate.



Time evolution of outlet molar fraction experimental (■) vs. model (solid lines).

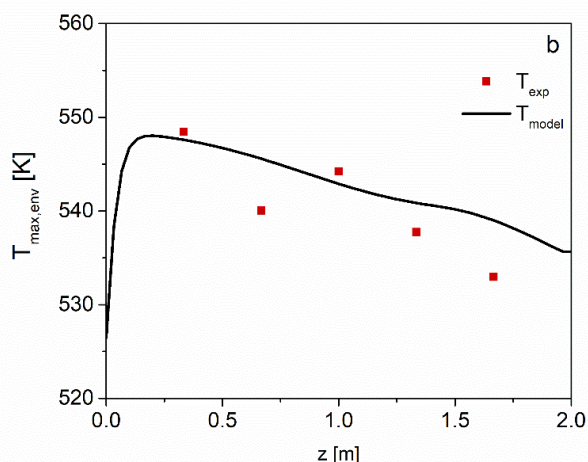


Time evolution of centerline gas temperature at different reactor coordinates. Experimental (◆) vs. model (solid lines).

From the local trajectories the envelope of the maximum temperatures along the axial coordinate is obtained. Comparison with the maximum values of temperature measured at the different axial locations during the adsorption/reaction step shows that the model is able to capture the catalyst temperature stress suffered during SEDMES operation, which is a key parameter in reactor design.

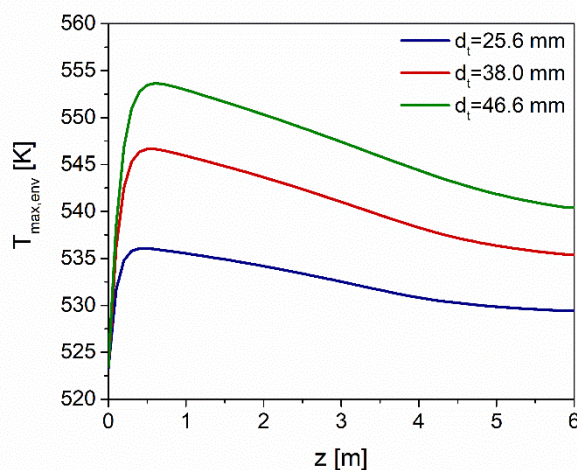
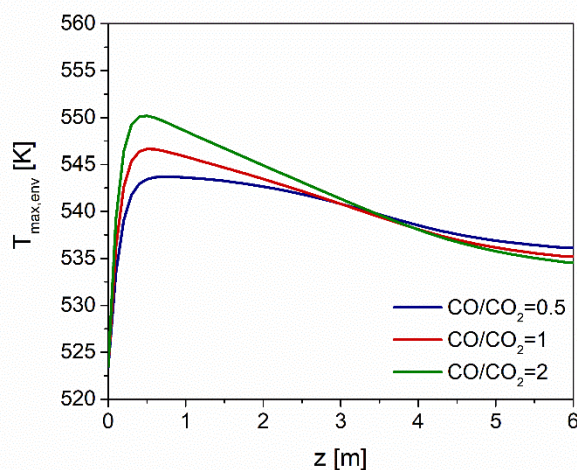
2D + 1D heterogeneous dynamic model of the SEDMES synthesis for reactor design and optimization (POLIMI)

The validated model has been used for the analysis and rational design of the industrial scale SEDMES reactor, focusing in particular on the DME yield performances and the thermal management of the exothermic process. The envelope of maximum temperatures achieved along the axial coordinate shows that catalyst thermal stresses in the hotter inlet zone of the reactor slightly increase with the CO content in the with due to faster kinetics of the DME production reactions.



Envelope of local maximum temperatures. Experimental (■) vs. model (solid line).

However, thanks to the dilution effect associated with the large amount of adsorbent material (catalyst:adsorbent=1:4 w/w), the maximum bed temperature keeps well below the limits reported in the literature (573 K) to preserve the CZA catalyst stability. Accordingly, larger tube diameters (up to 46.6 mm) than in conventional DME direct synthesis reactor can be adopted.

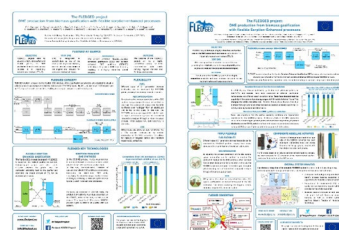


Axial profile of maximum gas centreline local temperatures at different feed CO/CO₂ ratios (d_t=38 mm) and with different tube diameters (CO/CO₂=1).

Project presentations, posters and deliverables

Posters, presentations and public deliverables of the project are available in the [download section of the website](#).

An infographic and a video are also available for less experienced people about sorption-enhanced processes and biofuel synthesis.



Scientific publications

Experimental investigation on sorption enhanced gasification (SEG) of biomass in a fluidized bed reactor for producing a tailored syngas (Martínez I., Kulakova V., Grasa G., Murillo R., *Fuel*, Volume 259, 2020)

Abstract

Synthetic fuel production from renewable energy sources like biomass is gaining importance driven by the ambitious targets for reducing greenhouse gas emissions worldwide. Sorption enhanced gasification (SEG) proposes carrying out the gasification of biomass in the presence of a CO₂ sorbent, which allows producing a syngas with a suitable composition for a subsequent synthetic fuel production step. This study aims at analysing the effect of different operating parameters (e.g. steam-to-carbon (S/C) ratio, CO₂ sorption capacity and sorbent-to-biomass ratio) in the syngas composition and char conversion obtained in a 30 kWth bubbling fluidized bed gasifier, using grape seeds as feedstock. The importance of reducing the formation of higher hydrocarbons through a high steam-to-carbon ratio and using a CO₂ sorbent with high sorption capacity is assessed. C₃-C₄ and unsaturated C₂ hydrocarbons contents below 1%vol. (in dry and N₂ free basis) can be achieved when working with S/C ratios of 1.5 at gasification temperatures from 700 to 740 °C. Varying the amount of the CO₂ separated in the gasifier (by modifying the temperature or the CO₂ sorption capacity of the sorbent) the content of H₂, CO and CO₂ in the syngas produced can be greatly modified, resulting in a module $M=(H_2-CO_2)/(CO+CO_2)$ that ranges from 1.2 to almost 3.

Sorption enhanced dimethyl ether synthesis for high efficiency carbon conversion: Modelling and cycle design (van Kampen J., Boon J., Vente J., van Sint Annaland M., *J. of CO₂ Utilization*, Volume 39, 2020)

Abstract

Dimethyl ether is one of the most promising alternative fuels under consideration worldwide. Both the conventional indirect DME synthesis and the improved direct DME synthesis process are constrained by thermodynamics, which results in limited product yield, extensive separations and large recycle streams. Sorption enhanced DME synthesis is a novel process for the production of DME. The in situ removal of H₂O ensures that the oxygen surplus of the feed no longer ends up in CO₂ as is the case for direct DME synthesis. As a result CO₂ can be converted directly to DME with high carbon efficiency, rather than being the main byproduct of DME production. The sorption enhanced DME synthesis process is a promising intensification, already achieving over 80 % single-pass CO₂ conversion for a non-optimized system. The increased single-pass conversion requires less downstream separation and smaller recycle streams, especially for a CO₂-rich feed. A key optimization parameter for the process performance is the adsorption capacity of the system. This capacity can be improved by optimizing the reactive adsorption conditions and the regeneration procedure. In this work, a detailed modelling study is performed to investigate the impact of various process parameters on the operating window and the interaction between different steps in a complete sorption enhanced DME synthesis cycle, and to compare its performance to other direct DME synthesis processes. The development of sorption enhanced DME synthesis, with its high efficiency carbon conversion, could play a significant role in the energy transition in which the carbon conversion will become leading.

Optimised production of tailored syngas from municipal solid waste (MSW) by sorption-enhanced gasification (Martínez I., Grasa G., Callén M.S., López J.M., Murillo R., *Chemical Engineering Journal*, Volume 401, 2020)

Abstract

Sorption-enhanced gasification (SEG) is a promising indirect gasification route for the production of synthetic fuels since it allows the H₂, CO and CO₂ content of the resulting syngas to be adjusted. This SEG process has been successfully demonstrated at pilot scale for lignocellulosic biomass and other agricultural and forest waste products, mainly focusing on H₂-rich gas production. Within this work, the potential application of the SEG process to a material derived from municipal solid waste (MSW) as feedstock is experimentally demonstrated in a 30 kWth bubbling fluidised-bed (BFB) gasifier. The influence of the sorbent-to-biomass ratio, steam excess and gasification temperature has been carefully analysed in order to understand their effect on SEG performance. Moreover, main conditions able to affect the resulting syngas composition, specifically in terms of H₂, CO and CO₂ content, have been indicated. Gasification temperature turned out to be the variable that most influenced syngas composition due to the limiting mechanisms associated with the carbonation of the CaO used as bed material. This operating variable also determined biomass conversion, together with solids residence time in the gasifier, resulting in a wide variation of fixed carbon conversion under the studied conditions. Finally, tar yield and composition were evaluated as a function of temperature and the sorbent-to-biomass ratio used, resulting in tar contents as low as 7 g/Nm³ (dry gas), consisting mainly of 1-ring aromatic compounds.

More in the [scientific publications section](#) of the website...

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Scientific publications

Model analysis of the effects of active phase distribution at the pellet scale in catalytic reactors for the direct dimethyl ether synthesis (Guffanti S., Visconti C.G., Groppi G., *Ind. Eng. Chem. Res.*, Volume 59, 2020)

Abstract

The direct synthesis of dimethyl ether (DME) from syngas is an exothermic process, which requires two different catalyst functions in the same reactor: methanol (MeOH) synthesis and dehydration to DME. The two functions can be intimately mixed in hybrid pellets, located on separated pellets or coupled in core@shell-engineered pellets. In this work, a multitubular fixed-bed reactor, loaded with the catalyst configurations mentioned above, has been investigated by mathematical modeling. It is shown that the different spatial distribution of the active phases has a drastic impact on reactor performance. Using the mechanical mixture of separated pellets, the DME yield is hindered by intraparticle diffusion limitations. The hybrid catalyst, minimizing the diffusion length between methanol synthesis and dehydration catalyst functions, provides better DME yield performances but higher hotspot temperatures and can suffer from deactivation issues due to the detrimental interaction between the two catalytic functions. The MeOH@DME configuration, which allows for a limited contact between the catalyst active phases, guarantees DME yields comparable to those of hybrid pellets while moderating the hotspot temperature.

Reactor modelling and design for Sorption Enhanced dimethyl-ether synthesis (Guffanti S., Visconti C.G., van Kampen J., Boon J., Groppi G., *Chemical Engineering Journal*, Volume 404, 2021)

Abstract

Sorption Enhanced DiMethyl Ether Synthesis (SEDMES) is a promising option to overcome thermodynamic limitations of conventional DME production processes. In this work a 2D + 1D heterogeneous dynamic model of the reaction/adsorption step in a tube of an externally cooled multitubular fixed bed SEDMES reactor is developed in order to investigate the effect of design and operating parameters on thermal behavior and DME yield performances of the reactor. The model is validated by comparison with experimental results from a bench scale unit, including the dynamics of the outlet composition and the temperature trajectories in different points along the axial coordinate. Simulations with the validated model address the effect of the CO/CO₂ ratio in the feed. The results confirm that, thanks to the effective in-situ H₂O removal, the DME yield performances (65–70% in this work) of SEDMES are poorly sensitive on the CO/CO₂ ratio. Accordingly, on increasing the CO₂ content in the feed, SEDMES provides larger advantages with respect to conventional DME direct synthesis. Calculations of maximum temperatures achieved along the axial coordinate show that catalyst thermal stress in the hottest inlet zone of the SEDMES reactor slightly increases with the CO content in the feed due to faster kinetics of the DME production reactions. However, thanks to the dilution effect provided by the adsorption material, maximum bed temperature keeps ~20–30 K below the catalyst stability limit reported in the literature (573 K). Accordingly, larger tube diameters (up to 46.6 mm) than in conventional reactors for the direct synthesis of DME can be adopted with less than 2% loss in DME yield.

Effects of support and reaction pressure for the synthesis of dimethyl ether over heteropolyacid catalysts (Peinado C., Liuzzi D., Ladera-Gallardo R.M., Retuerto M., Ojeda M., Peña M.A., Rojas S., *Scientific Reports*, Volume 10, 2020)

Abstract

Dimethyl ether (DME) is an advanced second-generation biofuel produced via methanol dehydration over acid catalysts such as γ -Al₂O₃, at temperatures above 240 °C and pressures above 10 bar. Heteropolyacids such as tungstosilicic acid (HSiW) are Brønsted acid catalysts with higher DME production rates than γ -Al₂O₃, especially at low temperatures (140–180 °C). In this work, we show that the performance of supported HSiW for the production of DME is strongly affected by the nature of the support. TiO₂ and SiO₂ supported HSiW display the highest DME production rates of ca. 50 mmolDME/h/ gHSiW. Characterization of acid sites via 1H-NMR, NH₃-isotherms and NH₃-adsorbed DRIFT reveal that HSiW/X have Brønsted acid sites, HSiW/TiO₂ showing more and stronger sites, being the most active catalyst. Methanol production increases with T until 200 °C where a rapid decay in methanol conversion is observed. This effect is not irreversible, and methanol conversion increases to ca. 90% by increasing reaction pressure to 10 bar, with DME being the only product detected at all reaction conditions studied in this work. The loss of catalytic activity with the increasing temperature and its increasing with reaction pressure accounts to the degree of contribution of the pseudo-liquid catalysis under the reaction

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