

Flexible Dimethyl ether production from biomass gasification with sorption enhanced processes

Newsletter #3 – March 2019

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:

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

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PROJECT NEWS

FLEDGED project - one year of results



The FLEDGED consortium at the third project meeting hosted by University of Stüttgart (Stüttgart, Germany). The participants visited the 200 kWth dual fluidized bed facility where SEG is being demonstrated at TRL5.

FLEDGED project is moving ahead! During this second phase of the project experimental activities have intensified to demonstrate the technologies in an industrially relevant environment. Preliminary calculations of efficiency and economics of a reference FLEDGED plant have been carried out, highlighting the areas of improvements. In the meantime, simulation tools for the SEG and SEDMES processes are being refined. Risk and sustainability analysis are ongoing and the first results are expected in the next phase.



The following activities performed in the last months are presented in the next pages:

- ullet Experiments of wood **biomass gasification** in the 200 kW_{th} dual fluidized bed facility at the University of Stuttgart
- **SEDMES testing** in lab-scale test facilities, the so-called "Spider" and "CaTe" facilities, at ECN part of TNO
- Simulations of DME synthesis reactor considering different catalysts configurations
- Preliminary techno-economic analysis of the complete FLEDGED plant
- Development and test of two series of catalysts for methanol and DME synthesis at CSIC ICP
- characterization of materials for risk assessment by INERIS



The FLEDGED consortium: 10 partners from 7 EU countries including academic, R&D and industrial expertise

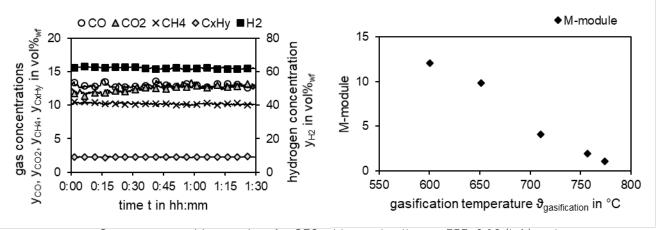
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N° 727600.





Experiments in the pilot scale facility at USTUTT

In the 200 kW_{th} dual fluidized bed facility at USTUTT, tests of the sorption enhanced gasification (SEG) of wood pellets have continued. Experiments were conducted at different gasification temperatures and different steam-to-carbon ratios. It was possible to modify the M-module in a range between 12 and 1, showing the flexibility of the process. Also the target value for DME production (M=2) has been reached. Some of the results from these tests are presented in the diagrams below.



Syngas composition vs. time for SEG with wood pellets at 757±8 °C (left) and M-module vs. gasification temperature (right)

The experimental experience showed that the process can be operated stably in the pilot scale facility at gasification temperatures between 600 °C and 774 °C. Syngas composition and M-module strongly depend on gasification temperature due to the influence on the equilibrium carbonation reaction, which influences the amount of ${\rm CO_2}$ removed from the syngas.



In addition to the experiments with wood pellets, the first experiments with biogenic waste material from the Ecohispanica plant have been successfully conducted. During the last campaign the team of the University of Stuttgart led by Selina Hafner (center) was supported by Isabel Martínez (CSIC, left) and Juha Palonen (Sumitomo SHI FW, right).

The abovementioned results have been presented at FBC23 (International Conference on Fluidized Bed Conversion, May 13-17, 2018, Seoul, Korea). The presentation is available for download in the dedicated section of the website.





SEDMES lab-scale testing and scale-up at ECN po TNO

Continued SEDMES testing at lab-scale test facilities, the so-called "Spider" and "CaTe" facilities, has led to progress in terms of the further delay of steam breakthrough. The time for SEDMES operation, i.e. the period of high concentration of DME, is extended by the reduction of the applied space velocity as well as the fine tuning of operating conditions, specifically the regeneration conditions (pressure, temperature). Also different catalyst formulations (commercial samples) have been tested. Corroboration of the results with different catalyst formulations shows the applicability of the different catalysts for the SEDMES process.

Preparations for SEDMES scale-up are in full swing. In these next experiments a single column reactor, the so-called "SEWGS-1" facility, containing about 2 kg of sorbent and catalytic material will be used for testing the SEDMES process. Besides validation under industrially relevant conditions, these tests give further input for reactor and process modelling, and are a first guidance for the full cycle validation ("SEWGS-7") planned in a later stage of the project.











SPIDER

CATE

SEWGS-1

SEWGS-7

DME synthesis simulation tool is ready at POLIMI

The parametric analysis of the conventional reactor for direct DME synthesis has been extended considering different catalysts configurations in order to study the effects of intraparticle diffusion phenomena on the process. Meanwhile, a dynamic heterogeneous model of a single tube of the SEDMES converter has been developed. The model, similarly to the one developed for the conventional reactor, consists of i-species mass, energy and momentum balances written in 2D cylindrical coordinates for the gas phase, coupled with i-species



mass and energy balances for the catalyst phase and for the adsorbent phase. The model has been used to get some preliminary results and now it should be assessed and validated on experimental data.



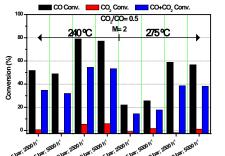


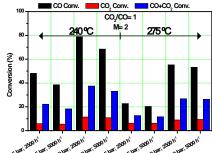
Catalyst development at CSIC-ICP

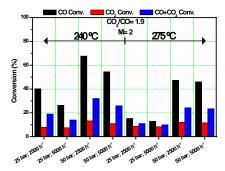
The CSIC Institute of Catalysis and Petrochemistry, developed two series of catalysts: one series for the methanol synthesis from bio-syngas and one for DME synthesis from methanol dehydration. The of this work was to find the optimal reaction conditions to obtain the direct synthesis of DME from bio-syngas by performing the reactions with a physical mixture of the two series of catalysts. The physicochemical properties of the synthesized materials were thoroughly analyzed.

Methanol production from bio-syngas

A series of $\text{Cu/ZnO/Al}_2\text{O}_3$ catalysts with different Cu loading was studied, including the commercial $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst for methanol production. The effect of the reaction pressure, temperature, contact time and bio-syngas composition was analyzed, as well as the use of promoters: Pd, Zr and Ga. Here we show the results of the experimental matrix developed to study the reaction conditions using the commercial catalyst.



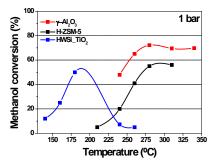


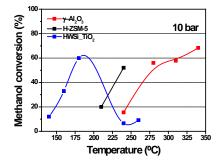


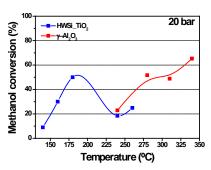
Reaction conditions study with Cu/ZnO/Al₂O₃ commercial catalyst

DME production from methanol

The experimental results for synthesis, characterization, and catalytic performance of supported HPA, HZSM5 and γ -Al $_2$ O $_3$ catalysts for methanol dehydration are presented. Heteropolyacids are very active for methanol dehydration reaction. When supported onto inorganic solids they show very high methanol conversion to DME at temperatures as low as 140 °C with 100% selectivity to DME under undesired hydrocarbon by-products. HZSM5 and γ -Al $_2$ O $_3$ are used as acid benchmark catalysts to compare the methanol dehydration performance with supported HPA catalysts.







Studied catalysts for DME production reaction from methanol at different conditions. LHSV=1.11 h⁻¹.

Results are summarized in public deliverables available in the dedicated section of the website.

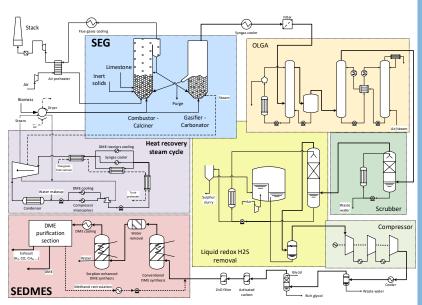




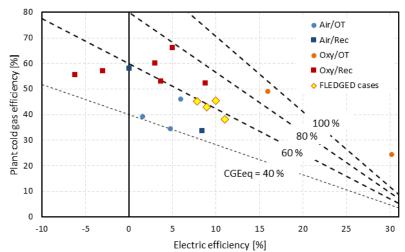
Preliminary techno-economic analysis of the complete FLEDGED plant released by POLIMI

POLIMI developed an Aspen Plus model to calculate the heat and balances of a reference complete FLEDGED plant, including: i) a biomass drying and preparation unit, ii) the SEG process, iii) the syngas cleaning units for removal of tar (OLGA). soluble contaminants (water scrubber), bulk sulfur removal (liquid redox process) and residual contaminants and H₂S (activated carbons and ZnO bed), iv) syngas compression, ٧) DME reactors and vi) DME separation unit.

The model allowed calculating the key performance indicators such as biomass-to-DME conversion efficiency and the electric efficiency. The calculated overall "equivalent" cold gas efficiency CGE_{eq} (i.e. taking the primary energy credits/debits associated to the electric balance) is in line with those reported in the literature for other biomass to DME processes based on air-blown gasification systems. An economic analysis of a plant with 100 MW_{LHV} biomass input was performed. With a biomass unit cost of 125 €/t. the calculated DME cost ranges between 46 and 55 €/GJ, largely associated to the cost of (57%)biomass and to the investment cost (40%).



Reference FLEDGED plant configuration.



Comparison of performance indexes between the reference FLEDGED process calculated with different process parameters and selected literature, considering different technologies for biomass gasification (Air = air-fed gasfier, Oxy = oxy-fed gasifier) and DME synthesis (OT = Once-through, Rec = Products recirculation)

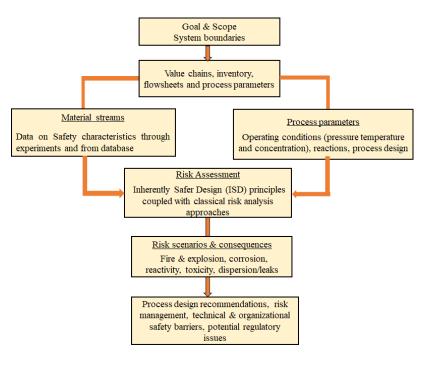
This preliminary techno-economic analysis allowed identifying the critical plant units and the governing process parameters. Lessons learned will be used in the second half of the project to explore solutions capable to increase the economic competitiveness of the process.

The preliminary techno-economic study with a detailed description of the model and of the results obtained is available as <u>public deliverable on the project website</u>.





Risk assessment in the FLEDGED project (INERIS)



Increased public awareness of industrial safety issues and regulatory demands as response to accidents has led to the integration of risk assessment studies at the early stages of innovative process design and development. Risk assessment carried out in the FLEDGED project aims at eliminating or minimizing identified from the process rather than incorporating add-on controls and safety barriers at a later stage. A stepwise methodology implemented to study the risks related to process steps and materials all along the value chain, making use of Inherently

safer Design (ISD) approach for the safe and sustainable development and deployment of the FLEDGED technology. One of the tasks in progress is the safety characterization of the material streams for the physico-chemical properties related to hazards (e.g flammability, explosibility) and related risks (fire, explosion sensitivity, self-heating...). Dedicated experiments will focus on the wood biomass, refuse derived fuels and catalysts. The risk assessment will focus on comparison of process configurations with respect to safety (e.g. hydrogen integration and storage, reforming and CCS options), identification of accident scenarios, evaluation of ATEX zones, choice of equipment, safe handling and storage of biomass and proposition of technical and organizational safety barriers. The results will contribute to the safe development and deployment of the FLEDGED technologies.

Experimental facilities for safety characterization of material streams



DTA/ATG for pre-screening of self heating of solids

Isothermal oven test

20-liters sphere apparatus for explosibility characterization





FLEDGED Project presentations at conferences and events

Results achieved has been presented at national and international events and conferences in the last months. POLIMI and TNO part of ECN represented the project at the *DME Sustainable Workshop*, presenting the FLEDGED process for flexible and intensified DME synthesis. Preliminary results of experimental campaign on SEG and modelling of gasification in the dual fluidized bed process have been presented by University of Stuttgart and Lappeenranta University at FBC23. ECN and POLIMI presented at ISCRE 25 the preliminary experimental campaign on SEDMES regeneration strategies and reactors modelling activities.

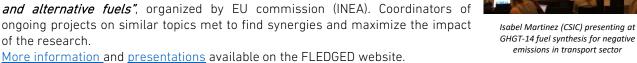


Selina Hafner (USTUTT) presenting at FBC23 the experiments on biomass gasification

Thermodynamics of CO/CO₂ conversion to liquid fuels and different options for Sorption Enhanced DME Synthesis have been presented at the 16th International Conference on Carbon Dioxide Utilization. CSIC, POLIMI, USTUTT and QUANTIS presented a joint work on the performance comparison of FLEDGED process and CH_A production from biomass with CO₂ capture at the 14th International Conference on Greenhouse Gas Control Technologies (GHGT-14).

The preliminary results of the FLEDGED process have been also presented at 12th ECCRIA, GIC 2018, 8th International DME Conference, 13th SDEWES and CHEM REACTOR 23 conferences.

FLEDGED project participated also in the meetings on "Bioenergy, Advanced Biofuels and Renewable Fuels", "Biofuels and Alternative fuels" and "CCS, CCU and alternative fuels", organized by EU commission (INEA). Coordinators of ongoing projects on similar topics met to find synergies and maximize the impact of the research.





GHGT-14 fuel synthesis for negative

Where to find us - Next events

The project and its outcomes will be presented at the following upcoming events:

- International Symposium on Green Chemistry (ISGC 2019) on 13-17th May 2019 at La Rochelle (France).
- 12th European Congress of Chemical Engineering in Florence (Italy) on 15-19th September 2019.
- 27th European Biomass Conference and Exhibition (EUBCE 2019) on 27-30th May 2019 in Lisbon (Portugal).
- 14th European Congress on Catalysis Europacat 2019 in Aachen (Germany) on 18-23rd August 2019.
- Conference of the Spanish Society of Catalysis (SECAT 19) on 24-26th June 2019 in Cordoba (Spain)











Find more on the website

Scientific publications

Reversible deactivation of γ -alumina by steam in the gas-phase dehydration of methanol to dimethyl ether (Boon J., van Kampen J., Hoogendoorn R., Tanase S., van Berkel F.P.F.,van Sint Annaland M., Catalysis Communications, Volume 119, 2019)

Abstract

Acidic \(\gamma - Al2O3 \) is an active catalyst for the dehydration of methanol to dimethyl ether (DME). However, the produced steam reduces the activity. In this work, the influence of the exposure of γ -Al2O3 to steam on the catalytic activity for methanol dehydration has been determined. At 250 °C and increasing stream partial pressure the conversion of γ-Al2O3 into γ-AlO(OH) is observed at a p(H2O) of 13-14 bar. As a consequence, the catalytic activity decreases, reducing the rate of methanol dehydration to around 25%. However, this conversion is reversible and under reaction conditions γ-AlO(OH) converts back to γ-Al2O3, recovering its catalytic activity.

Open access full paper on Zenodo

