



## ARRMAT

# Attrition Resistant Reactive Bed Materials in Fluidised Beds

## Development, in situ investigations and application

### Scope of project

This project proposal deals with the manufacturing of attrition resistant reactive bed materials with desired properties for the application in fluidised beds, with the experimental testing of these materials to identify optimal operation conditions as well as with the in situ investigation of such materials to derive design rules for improved bed materials.

The aim of this proposal is to contribute to significant improvements along the process chain in the production of Synthetic Natural Gas (SNG) from dry biomass, the SNG-from-wood process which is already investigated within the CCEM project «2<sup>nd</sup>GenerationBiogas».

### Summary of project

The process from wood to methane includes four major process steps. Wood has to be gasified; the producer gas from the gasifier then needs to be cleaned to remove dust, impurities and potential poisons to the catalyst that is applied in the third step, the methane synthesis (methanation). The raw-SNG from the methanation needs to be conditioned, i.e. water, carbon dioxide and unreacted hydrogen have to be removed to meet the gas quality required for feeding into the natural gas grid.

A closer look into the first three steps (gasification, gas cleaning and methanation) reveals that in all three steps gas has to be brought in contact with a solid reactive material (e.g. a catalyst). Therefore, optimisation efforts for the three first steps of the process chain have to be based on an optimal combination of reactor type, reactive material and operation conditions.

From the gas solid reactors suited for high temperatures, fluidised bed reactors are a good choice for the SNG-from-wood process as e.g. the particles are continuously mixed and the temperature is uniform. If reactive bed materials such as catalysts are applied in fluidised bed reactors, they have to fulfil certain requirements to avoid failure of the process step:

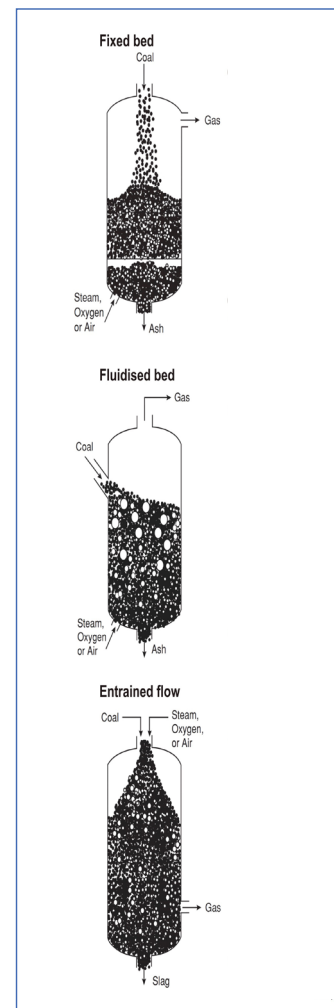
- The materials have to be mechanically stable, i.e. attrition resistant, as the particles are always moving.
- The active species of the material must not be separated from the carrier to avoid (selective) transport out of the reactor into the filter. As in the fluidised bed, the gas phase is changing along the travel of the particles, the state of the catalyst and therefore the chemical stability might change as well.
- Depending on the reaction rates and the particle diameters, a macro-porous carrier material might be favourable to avoid limitations due to long diffusion length from the gas phase into the middle of the particle.

A detailed understanding of the up-stream processes and the operation conditions such as pressure, temperature, degree of mixing (hydrodynamics) in the process step is necessary to avoid catalyst deactivation by poisoning (e.g. by sulphur) or fouling (e.g. due to carbon deposition) and process failure.

In the SNG-from-wood process, potential for improvements is given by improved bed material for the gasification, the gas cleaning and the methanation.

This project started in 2009.

Figure 1: Reactors designed for gas-solid reactions and their temperature profile for strong endothermic and exothermic reactions: example of coal gasification.



### Main Investigator

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### Project Partners

Empa  
PSI

The actually used commercial nickel based catalyst for the methanation has proven in a 1000 hours duration test to be active, mechanically and chemically stable enough. To avoid the costly loss of about half of the material during grinding, an especially manufactured material that has some macro porosity and is directly extruded in the required size without need of further grinding would improve the material flows.

Therefore there is a need for the development of improved methods to manufacture reactive bed materials for the use in fluidized bed reactors. Based on previous results, macro-porous carrier materials of high mechanical stability will be loaded with ruthenium or nickel by e.g. wet impregnation. Moreover, a method is developed to sinter such macro-porous granulates at lower temperatures what would allow the direct incorporation of active catalyst powder.

These new materials as well as commercial samples of ruthenium based catalysts will be tested in a micro-fluidized bed for screening of their activity and for identification of optimal operation conditions. The most promising candidates of modified (so called 2<sup>nd</sup>) ruthenium and nickel catalysts will be tested in a bench scale reactor to test their performance under more realistic conditions.

As all these materials will be applied in fluidized bed reactors, it is necessary to understand how the movements of the particles through the reactor and through changing gas concentrations affect the performance, the deactivation behavior and the catalysts state. Therefore in-situ experiments with suited spectroscopic methods have to be carried out. To properly represent the conditions a particle is confronted with inside a fluidized bed adequate experimental methods have to be developed within this project.

From field experiments on a fluidized bed, it was found that under special circumstances, beside methane also ethane can be formed. Ethane is increasing the lower heating value of the SNG and is therefore desired. Investigating the reaction mechanism in detail with a suitable spectroscopic tool will help to understand the conditions of ethane formation and help to transfer the knowledge by optimizing the design and the operation conditions in a commercial SNG plant accordingly.

Results of this project are expected on several levels such as materials with improved performance, new methodical competences and validated next generation technology concepts for the process «SNG-from-wood».

- Standard operation procedure for the manufacturing of attrition resistant reactive bed materials.
- Improved methanation catalysts.
- Procedures for in situ material investigation with XAS and DRIFTS for the so called moving observer.
- Mechanistic approach of state of the art materials (methanation catalyst, Olivin).
- Experimental proof-of-principal for next generation concepts for the process «SNG-from-wood», i.e. gasification, sulphur removal, methanation section.

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