Experimental validation of process modeling in methanol synthesis using the CAMARE process: influence of byproducts on selectivity and conversion

Inés Alejandra Carbajal Ramos[1]*, Quido Smejkal[2], Arash Bagherzadeh[2], Sergey Sokolov[1], Sebastian Wohlrab[1]

[1]*Leibniz-Institut für Katalyse e.V., Albert-Einstein-Str. 29a, 18311 Rostock, Germany;* [2]*EnProCo Berlin GmbH, Volmerstr. 7A, 12489 Berlin, Germany*

**Corresponding author: alejandra.carbajal@catalysis.de*

Highlights

- Validation is necessary for the optimization of recycling steps.
- Laboratory experimental results are essential for successful design of pilot plants.
- Byproducts affect the size of compressors and reactors.

1. Introduction

A contemporary strategy to reduce greenhouse gases emissions in the mobility sector relies on advances in H_2 storage, e-mobility, and creation of cleaner synthetic fuels with lower carbon footprint. The latter is achieved by converting to bio-feedstock for fuel production and by improving fuel burning efficiency. Years of research on fuel additives identified numerous organic molecules that make the burning process cleaner and more efficient. Methyl formate (MeFo) and dimethyl carbonate (DMC) are examples of such additives that also have low health and environmental hazard [1]. DMC is also used as an electrolyte in lithium-ion batteries which makes its ample supply of pivotal importance for e-mobility.

The aim of our project is to create a pilot-scale demonstration plant for MeFo and DMC production from renewable sources. Figure 1 illustrates the planned process flowsheet. The CO_2 produced from biomass via pyrolysis reacts in reverse water gas shift reactor (RWGSR) with electrolytically produced H_2 to yield syngas which then turned into methanol (CAMERE [2]). Next, one part of the methanol is transformed to MeFo [3] and the other is reacted with CO and O_2 to form DMC [4]. The pilot plant will include recycling of gases and liquids to achieve maximal feed conversion. Validation of model assumptions through real experiments is essential, especially when recycling steps are involved [5].

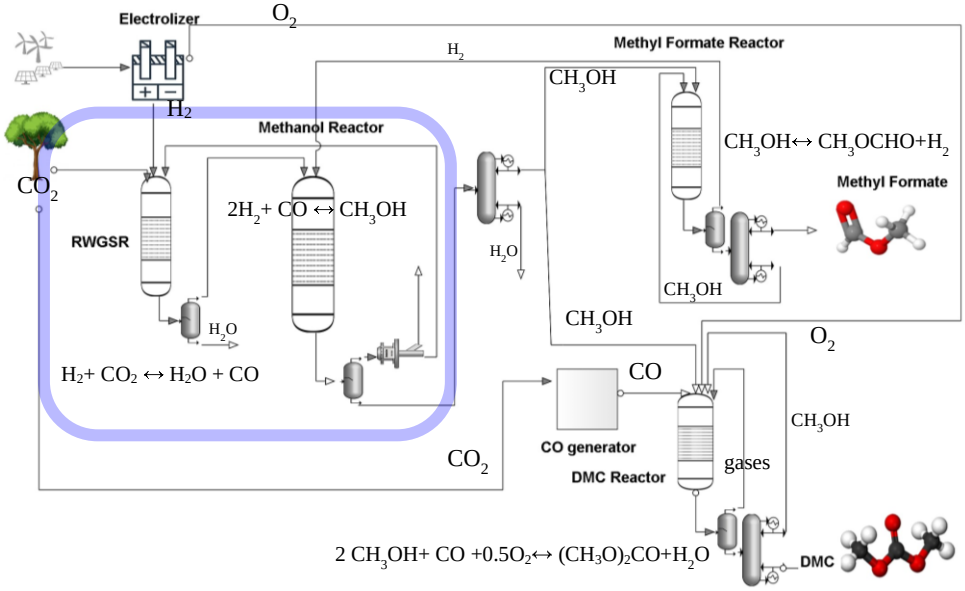

Figure 1. Scheme of pilot plant for DMC and MeFo synthesis with methanol as intermediate reactant.

Methanol synthesis from syngas is a thermodynamically limited reaction. To maximize conversion of educts, recycling of unreacted gases is implemented. Methanol catalysts need a minimum amount of

CO_2 in the feed to be activated, but the rate of CO_2 consumption is lower than that of CO. Thus, CO_2 accumulates in the feed via recycling. In our case, the recycled gases are fed not to the methanol reactor, but to the RWGS reactor where CO_2 is converted to CO and its accumulation is avoided. The main source of CO_2 for RWGS reactor is biomass pyrolysis. Even after purification, CO_2 contains some CH_4 and CO. Both gases can affect RWGS reaction, e.g. via coke formation. The material of the reactor has also a great influence on this reaction [6]. Hence, laboratory scale experiments accounting for these variables are necessary prior to moving to the pilot scale. In this work, we will study the influence of the byproducts and impurities in the feeds as well as the reactor materials on RWGS and methanol synthesis reactions. Obtained key process parameters will be a basis for a calculation design of main processing parameters of the reactors and compressors (size, volumes, safety, power demand). Achieved experimental results are used in systematic process modeling with the aim to predict and to design the technology layout for the upscaled capacity, under consideration of recycling flows.

2. Methods

The reaction mixtures in the catalytic experiments had compositions chosen based on the simulations. A fixed-bed quartz or stainless-steel reactor was used for the RWGSR (650 °C, 1 bar). Gases were analyzed by GC (Shimadzu-2010 Plus) with HP Plot Q, DB-Wax columns, FID and TCD. A fixed-bed stainless-steel reactor was used for the methanol synthesis (230 °C, 53 bar). Gases were analyzed by GC (Shimadzu-2010 Plus) equipped with Plot Q, MolSieve 5A columns and FID and TCD. The process simulations were made with the software HSC from Metso [7] and verified later by Simulate 365.

3. Results and discussion

The cumulative production of MeFo/DMC in the pilot plant was set at 1 kg/h. It requires 1.53 kg/h of methanol, which was a value assumed for simulations. The modelling description was based on our own experimental data from the lab scale screening. Two scenarios were considered: in the first feedstock was CO_2 and H_2 only, in the second a more realistic mixture of CO_2, CO, H_2 and CH_4 (concentration based on pyrolysis of biomass) was used.

Table 1 - Comparison of different models and their influence on the volume of the reactor and size of the compressors.

	First case	Second case
Feedstock (Nm^3/h)	CO_2:H_2/1.09:2.78	CO_2:H_2:CO:CH_4/0.75:2.44:0.35:0.075
Recycled flow (Nm^3/h)	6.5	8.5
RWGS Reactor Volume (dm^3)	1.4	1.7
Methanol reactor Volume (dm^3)	1.1	1.3

The results of process modelling demonstrate some crucial indicators for further development of the technology. Among other results of the process sensitivity, the recycled flow (compressor), is 30% bigger in the second case and the reactors are at least 16 % bigger. These preliminary results demonstrate the effect of the feed quality on process design and highlight the importance of having good experimental data before scaling to pilot plant. A systematic overview of achieved data will be given in detail.

4. Conclusions

The validation of the model of the RWGS and methanol synthesis reactors and the influence of the educts on the system and reactor materials are studied in this work. These results will be used to optimize the design of a pilot plant for DMC and MeFo production.

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Keywords
RWGS; Methanol; validation; byproducts; recycling.