

Deckblatt

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Related Own Publications

¹ (a) M. Ouda, G. Yarce, R. J. White, M. Hadrich, D. Himmel, A. Schaadt, H. Klein, E. Jacob, I. Krossing, React. Chem. Eng., 2017, 2, 50. (b) M. Ouda; G. Yarce; K. Hesterwerth; M. Hadrich; A. Schaadt; R. J. White; H. Klein; E. Jacob, DGMK-Tagungsbericht 2016-3 (ISBN 978-3-941721-66-1). (c) **M. Ouda**, F. Mantei, R. J. White, M. Elmehlawy, S. K. Fateen, H. Klein, I & EC Research, **2017**, Submitted.

Using Renewable Energy for Thermochemical Catalytic Synthesis of Sustainable Designer Fuels – A Short-term Solution for the Mobility Sector

Introduction and Background Context

Within the global challenge of establishing a sustainable society, the desired properties of future fuels have recently been discussed. In this regard, global fossil fuel consumption is predicted to decrease over the coming decades, although the short term consumption of diesel fuel is expected to increase till the middle of the current century. Conversely the global expansion of sustainable but intermittent electrical energy sources necessitates the need for storage on a large scale (TWh) over extended periods. This expansion is aimed at dramatically reducing greenhouse gas emissions (e.g.. \geq 80% relative to 2011 in Germany). In this context, liquid fuels will continue to play a very important role as energy sources and potentially as storage media, as for certain heavy load transport modes (e.g. trucks, ships, aviation) there will be demand for high energy density, easy to handle liquid energy carriers. One of the most challenging sectors in this context is (e.g. urban) mobility, which represents an ever growing share of global energy-related GHGE arising from transport (ca. 23%: 6.7 Gt-(CO₂). Furthermore, there is also an increasing awareness of the health hazards arising from combustion of fuels (e.g. diesel) and the concurrent release of particulate matter (PM (soot)) and nitrous oxides (NO_x) to the urban environment, with evolving legislation and emission standards (e.g. Euro VI) reflecting this. In Germany, road freight (trucks, lorries, heavy duty vehicles) have the lion share of energy consumption in transportation sector and consequently in emissions (Figure 1).



Figure 1. Mobility sector share from the total transport sector energy consumption

The growth rate in private cars is estimated at 9,000 cars/h with 61 M cars in total (DE). For the last century the diesel engine has been the favoured drive-train due to its high efficiency and the better market price of diesel fuel. On the other hand, short term sustainable solutions are urgent for the mobility sector which is facing difficulties to meet the emissions regulations. E-mobility and bio-based diesel are foreseen solutions but with broad limitations. The former is limited for urban mobility due to driving range limitations and the lack of infrastructure. The latter is facing the dilemma of food or tank and its contribution to the reduction of net emissions (NO_x , PM, VOCs and CO_2) is highly sensitive regarding the biomass source. Other solutions are also of interest (e.g. H₂-based mobility) but with other limitations and infrastructural barriers which will lead to mid- or long-term development and introduction. Therefore, there is a need to bring alternative fuels particularly for the mobility sector to the market that generates reduced emissions in both an urban health and global context. This must also be achieved to support the expected growth in mobility demand (e.g. with population growth) whilst performing in a superior manner (e.g. regarding combustion properties) to conventional fuels and also complex/expensive exhaust gas treatment systems. In the context of this discussion, alternative, synthetic or "designer" fuels must fulfil the following criteria (1) CO₂ "guasi" neutrality (2) Sustainability with regard to unlimited availability (3) as low environmental/ecological impact as possible (4) Economic efficiency and (5) functionality and best possible integrity with existing technologies.

To fulfil these criteria, synthetic "designer" fuels can be produced based on the following approach, often referred to within the German research landscape as "Power-to-Liquid" (PtL). In this approach H_2 (e.g. from renewable electricity powered H_2O electrolysis) is employed in the hydrogenation of CO_2 (e.g. sourced from steel/cement manufacture, biogas plants, *etc.* or ultimately air) to produce a range of liquid energy stores, fuels and chemical industry platform molecules including CH_3OH (methanol) and H_3COCH_3 (dimethyl ether), which can in turn act as precursors in the synthesis of "Poly-Oxymethylene Dimethyl Ethers" (POMDE), or for short chain oligomers "Oxymethylene Ethers" (OME). **OME** are receiving increasing interest *as potential*

diesel substitutes or additives. They are known to be miscible with diesel at any ratio, are non-hazardous to human health or the environment, are weakly corrosive, have a high Cetane number (relative to conventional diesel), whilst, due to their chemical structure, have promising interesting intrinsic combustion properties and leading to reduced or no emissions of soot, NO_x, PM and CO₂. Due to similar physical properties as diesel, OME blends with diesel or pure OME mixtures could be applied in current diesel combustion engines with no or with slight modifications (mainly sealing). Also the infrastructure for diesel fuel (transport, storage, tank, *etc.*) can be directly used for OME. When OME is sustainably produced (e.g. based on a PtL approach), it represents a **short- to mid-term** solution meeting the designer fuels criteria and developing mobility sector demand. OME are also being considered with regard to solvent applications) and appropriate vapour pressures. Therefore, based on this PtL approach, it would also be possible if desired to produce a range of greener, more environmentally friendly alternative solvents (e.g. based on OME chain length control), which have potentially reduced environmental impacts in comparison to existing, large volume industrial solvents (e.g. dichloromethane).

There is a prospective market demand for OME within several sectors including fuels, solvents *etc.* but as yet, a technically and economically feasible **synthesis process** is the **bottle neck** for this value chain. State-of-the-Art OME synthesis process is at capacities 30 – 40 ktons per year with low efficiency and mainly based on fossil based methanol production in China (CtL, GtL). In EU and particularly Germany, another process (OME-technologies GmbH/TU Kaiserslautern) is addressed which enhance the synthesis efficiency but not showing economic feasibility (relative to fossil based diesel) due to the expensive feedstock and several synthesis steps.

A key building block in OME synthesis is CH_2O (Formaldehyde - denoted hereon as FA). FA is commercially produced via partial oxidation of methanol to yield an aqueous solution of concentrations in the range 37 – 55 wt.%(FA). OME synthesis in the presence of **water** in the feed is thermodynamically unfavourable and reduces the final product yield (Equation 1). However, a direct OME synthesis from methanol and anhydrous FA shows several CAPEX and OPEX saving potential in comparison with other purposed processes in literature based on different feed systems. Ouda *et. al* demonstrated the potential of this synthesis path and concluded that a anhydrous FA feed with a ratio of FA/MeOH *ca.* 2 leads to high yield of OME with chain length n = 3 - 5 (candidate chain as diesel additive) and favourable process economics.

2 CH₃OH + n CH₂O ⇒ CH₃O-(CH₂O)_n-CH₃ + H₂O
$$Δ_r$$
H^{298K} = -25 kJ/mol (1)

Within our department the goal is to conceptualise and develop an efficient, sustainable and economically feasible OME synthesis process, which will enable market entry of these promising ethers; thus closing **the gap** between an envisioned growing and developing supply and demand. In addition to the technological aspects, the PtL process chain is evaluated in terms of economic and ecological efficiency. The goal in this regard is to find production pathways and scenarios which are the most favourable regarding the environmental and monetary costs.

Contributions & prominent Results:

1- Process Simulation Platform

Our intended process concept for OME synthesis is based on green methanol and proceeds through an initial anhydrous FA synthesis (via endothermic methanol dissociation). This initial step enables a synthesis approach where the whole process framework is defined by the interactions with the surrounding environment. With a preliminary market analysis, the production capacities based on an expected demand can be defined. A process simulation model based on our concept is then constructed and through experimental results the model can be validated. Since OME are relatively new candidates, the thermodynamic, thermal and physical properties need also to be implemented through the use of a simulation software platform. CHEMCAD[®] is used in this context, with in-house designed reactors developed based Matlab® integrated via the Visual Basic for Applications (VBA) interface. This so-called "A Hybrid approach" enables the whole process to be described in a holistic manner (Figure 2).

The synthesis of OMEs represents a complex, multicomponent reactive system based on a range of different reactions, leading to the formation of *ca*. 30 compounds at equilibrium. A Newton Raphson systematic solver (NR) and Stochastic Global Optimizer with Cuckoo Solver (SGO-CS) have been both applied in this context to converge the equilibrium of OME synthesis. The FA synthesis reactor is integrated as a kinetic reactor with performance defined from experimental results obtained within the frame of this work. The rest of the unit operations and auxiliaries are simulated with algorithms in CHEMCAD[®]. With the whole process described on the platform (Figure 2), optimum operating parameters are identified, material and energy balance are defined and process Key Performance Indicators (KPIs) can be established and evaluated.



Figure 2. Hybrid simulation CHEMCAD® platform with own developed Matlab reactors models (SCDS – rigorous tray distillation columns)

2- Experimental

The two main synthesis reactors are built in a test rig that was developed in the frame of this work. For anhydrous FA synthesis, an endothermic reaction is addressed in literature and several catalysts have been tested. One aspect is to find a stable and sufficient active catalyst capable of operating at high temperatures (500 - 900 °C) under a strong reducing environment, with H_2 as main side product. Since the target product FA is highly unstable in anhydrous monomeric form, innovative reactor design is required to achieve a feasible operation. Fast educt heating, stable and rapid reaction (very low retention time of about 0.01 s) and fast product quenching (ca. 120 °C) are **pre-requisites** for such reactors. Our own innovative, in-house developed Annular-Counter-Current-Reactor ACCR has been employed for this purpose and more than 40 h of continuous steady state duration runs have been observed. Conversion and selectivity of target products in the vicinity of the desired performance (FA Selectivities > 90 % and MeOH conversion > 60 %) defined from simulation platform was achieved. However there is still much research required for the stability aspect of the catalyst in such harsh operational conditions.

For the OME synthesis step, batch experiments were done with different feed approving the capability of our reaction equilibrium model over a broad operational range. The results of these experiments are published elsewhere (Ouda et al. React. Chem. Eng., 2017, 2, 50.)

3- Techno-Economic Evaluation

With a defined process, the following step is the evaluation of the economic feasibility relative to State-of-the-Art processes. The first step of the cost calculation is the determination of the Capital Expenditures (CAPEX), giving a sum of each long term asset cost with its delivery and installation. In a second step the Operational Costs (OPEX) are calculated, based on a functional running plant. CAPEX is evaluated using CHEMCAD[®] built in tools with 2017 EU price Indexing and including depreciation and market proven interest rates. OPEX is evaluated based on variable (energy, raw materials) and fixed components (maintenance, personnel, overhead costs, *etc.*). The raw material cost represents the major cost contribution with 74% share followed by the energy cost (15%) and the investment capital (8%). A comparison of the economics of our discussed process with other processes discussed in literature shows a significant cost reduction potential (Figure 4; *ca.* 7% reduction than the most inexpensive <u>theoretical</u> process (DE), *ca.* 19% reduction than the only technically realized process in China). A sensitivity analysis can also be performed to demonstrate showing the most strongly influencing parameters to be methanol feedstock cost and the CAPEX.



Figure 4. OME production cost from different processes (Burger et al.: OME-technologies GmbH/TU Kaiserslautern; FhG ISE: process described in this work; Chinese process feed with fossil based methano; bbl: Barrel)

4- Preliminary LCA

For a holistic evaluation of any new production process it is very important to also account for the environmental impacts. Especially in case of a process' declaration as being potentially "sustainable", an assessment of its life-cycle emissions, resource depletion, material and energy demand becomes obligatory. In this context, we evaluate the environmental aspects of the PtL concept using a comprehensive approach via a Life-Cycle-Assessment (LCA), considering not only the amount of CO_2 which is chemically bound in the synthesised molecule. The origin of the CO_2 (e.g. fossil vs. biogenic) is also investigated as is the amount of CO_2 avoided by substitution of fossil-based production by the proposed new pathways. Furthermore, the appropriateness of the emission allocation resulting from the multi-output PtL process is also considered. The results of the LCA-PtL-model will complement the techno-economic feasibility of the PtL chain by assessing combined KPIs. KPIs offer possibilities to value different complex PtL-process-alternatives in terms of their economic and ecologic efficiency. One central KPI is the CO_2 avoidance cost ($CO_{2, AC}$), accounting for the global warming potential of the sustainable PtL and the fossil product (GWP_f; GWP_e) as well as their respective production costs (PC_f; PC_e).

$$CO_{2,AC} = \frac{PC_{e_i} - PC_{f_i}}{GWP_{f_i} - GWP_{e_i}}; \left[\frac{\epsilon}{t \ CO_{2eq}}\right]$$
(2)

For also assessing future development of $CO_{2, AC}$ a decreasing investment cost for water electrolysis technologies is also considered due to (expected) progress in R&D and further market penetration (e.g. H₂ as a feedstock for sustainable OME). Also ever reducing prices for renewable electricity (presently already first projects (China, Abu Dhabi, Chile) with RE generation prices below $3.0 \in ct/kWh_{el}$) as well as possibly rising fossil production are also considered. This leads for example in the case of PtL methanol production to

significantly falling $CO_{2, AC}$ from presently 400 \notin /t(CO_2 avoided) to prospected cost of ca. 87 \notin /t(CO_2 avoided) in 2030 and becoming negative in the following 2-5 years.

For PtL products applied as liquid fuels in the mobility sectors their environmental impacts in a well-to-wheel approach are assessed. This means that not only emissions arising during fuel production but also the impacts due to production of the respective vehicle and its utilization phase are considered. Although there has to be special attention to the depletion of raw materials which can vary between the possible PtL routes it is made clear that PtL-fuels offer the chance for a significant decrease of CO_2 emissions (Figure 5).



Figure 5. CO₂-equivalent emissions per km of driving distance for PtL and conventional fuels: PtL-Methanol and –OME via Wind-/PV-electricity mix and CO₂ derived from biogas, PtL-Methanol/Petrol-Mix (90 Vol% MeOH), fossil MeOH via steam-reforming of natural gas, conventional fuels; specified deviations originate from different production



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Motivation – Sustainable Fuels for Cleaner Mobility



Figure 1: German CO₂ emissions from the mobility sector and the German Federal Government reduction targets till 2050 (UBA 2016, Agora 2017)

Figure 2: Development of primary energy consumption in the mobility sector: largest share is private and freight transportation (BMVI 2013)

Figure 3: *left*: EU1-6 regulations for g/km-emissions of CO₂, NO_x and particulate matter; *right*: Illustration of the cleaner combustion properties of the non-toxic diesel-substitute OME (G. Wachmeister (2017) MTZ Worldw 78 (3), pp. 52–57)

- Mobility as the only sector without any net CO_2 -reductions between 1990 2015 (Energy sector: -27%;
- Industry: -34%; Buildings: -40%; Agriculture: -21% relative to 1990 emissions level); Without a 'Verkehrswende' there cannot be a 'Energiewende'
- Private and freight transport with highest energy consumption (Diesel engine is the preferred drive-train with predicted consumption growth rate (EIA 2014)) : Offering clean
 - fuels for this mobility sector holds high potential for sustainable mobility
- Liquid Oxymethylenethers (OME) as clean diesel substitute and drop-in solution for instant reductions in NOx, Particulate Matter and well-to-wheel CO_{2eq}-emissions

Research Scope

- The <u>bottle-neck</u> for sustainable OME-synthesis is an efficient and feasible **synthesis process**
- State-of-The-Art for synthesis processes (30 40 ktons/a capacity) based on methanol as feedstock with several reaction and separation steps, overall synthesis efficiency (40 – 52%) with potential for (21) improvement and a suffering economic feasibility (figure 5)
- A novel process concept (<u>FhISE process</u>) based on methanol endothermic dissociation to <u>anhydrous Formaldehyde</u> followed by OME synthesis step represents a direct and efficient synthesis (ca. 60%) route (Figure 4).
- Process hybrid simulation platform is implemented, KPIs are defined, techno-economic & preliminary LCA evaluation are pursued showing high potential of this novel process to facilitate OME market entry ^{a,b}



Figure 4: FhISE Hybrid Process Model on CHEMCAD[®] Platform with reactor units modelled in Matlab[®] and interfaced using VBA-Excel units.

Preliminary Life Cycle Assessment





Methanol [USD/t] OME production cost [USD/t]

Figure 5: Production costs of OME and proportion of MeOH costs. Cost model for FhISE process implemented in CHEMCAD[®], OME-technology GmbH/TU Kaiserslautern **route A**: With Methylal (OME1) and Trioxane feed, route B: With Methanol and aqueous Formaldehyde feed, production capacity for both processes is 1 mio t/a; Jiansou Kaimao Co. Ltd. (China) : Methanol and aqueous Formaldehyde feed and production capacity 40 kt/a



Figure 6: CO₂-equivalent emissions per km of driving distance for PtL and conventional fuels: PtL-Methanol and –OME via Wind-/PV-electricity mix and CO₂ derived from biogas, PtL-Methanol/Petrol-Mix (90Vol%) MeOH), Fossil MeOH via steam-reforming of natural gas, conventional fuels; specified deviations originate from different production parameters.

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