A Hybridised Approach to Oxymethylene Ethers (OME) Synthesis – Designer Oxygenated Fuels and Solvents

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One of the most challenging sectors with regard to CO_2 emissions is mobility, which accounts for *ca*. 23% (6.7 Gt-CO_2) of energy-related Green House Gas Emissions (GHGE).[1] Regarding urban mobility there is also concern regarding combustion-related particulate matter (PM) and NO_x, as reflected in evolving legislation and emission standards (e.g. Euro VI).[2] It is important to note that liquid fuels (e.g. diesel) will continue to play a very important role as energy carriers for certain mobility modes (e.g. trucks, ships). Therefore, there is a need for alternative fuels with "designer" properties capable of addressing both GHGE legislation and emission norms. In a similar context, there is also increasing concern regarding environmental and health issues relating to "Volatile Organic Solvents" (VOC) use (e.g. dichloromethane, N-methyl-2-pyrrolidone *etc*.). Here as for fuels, legislation is promoting the adoption of "*green*" solvents with VOC-like solvation properties but with reduced environmental impact. In this regard, if synthetic or "designer" fuels or solvents are to be adopted, the following criteria must be fulfilled (1) CO_2 "quasi" neutrality (2) sustainability with regard to supply (3) as low an environmental/ecological impact as possible (4) economic viability and (5) compatibility with existing technologies and applications (e.g. "*Drop-in*" characteristics).[3] With this in mind, short chain "Oxymethylene Ether" oligomers (denoted here OME; $CH_3O-(CH_2O)_n-CH_3$ where n = 1 - 6) are considered promising. They are liquids and miscible with diesel, are non-hazardous to human health/environment, are weakly corrosive, have a high Cetane number, have promising intrinsic combustion properties and significantly reduced NO_x/PM/CO_2 emissions.[4] OMEs also have chain length dependent solvation properties (e.g. in CO_2 sorption applications) and appropriate vapour pressures.[5]

At Fraunhofer ISE, R&D focuses on OME synthesis based on a CH_3OH platform. This simplest of alcohols is sourced from the direct hydrogenation (e.g. H_2 from solar or wind powered H_2O electrolysis) of captured CO_2 (e.g. from steel/cement manufacture, biogas plants, or ultimately air).[6] CH_3OH can be converted to CH_2O

(Formaldehyde, FA) - a key building block in OME synthesis. This is commercially achieved via partial oxidation to yield an aqueous solutions with 37 - 55 wt.%(FA).[7] OME synthesis in the presence of H_2O in the feed however is thermodynamically unfavourable and reduces final product yield. However, as will be presented, a direct OME synthesis from CH_3OH + anhydrous FA has several CAPEX and OPEX saving potential in comparison with other reported processes.[6] This presentation will highlight the Fraunhofer ISE approach to process design based on a hybrid CHEMCAD®/VBA/Matlab® simulation platform. This approach promising allows single parameter optimisation of the main synthesis units followed by complete energy integration. Accordingly process "*Key Performance Indicators*" (KPIs) are identified and evaluated. A cost model for OME synthesis is also be presented, complimented by a preliminary Life Cycle Assessment (e.g. regarding emissions, resource depletion and material/energy demand), using the Umberto®/ecoinvent platform. The presentation therefore aims to demonstrate an efficient, sustainable and economically feasible OME synthesis process, which will enable identification of market entry points for these promising ethers.

References

1.(a) Rogelj, J.; K.; Meinshausen et al. M. *Nature* **2016**, *534* (7609), 631. (b) Change, I. P. on C. *Climate Change 2014: Mitigation of Climate Change*; Cambridge University Press, 2015; Vol. 3.

2.(a) *http://www.europarl.europa.eu/RegData/etudes/STUD/2016/578986/IPOL_STU%282016%2957 8986_EN.pdf (last accessed October 2017). (b) https://ec.europa.eu/clima/policies/transport/vehicles/cars_en (last accessed October 2017).*

3. Jacob, E.; Maus, W. *MTZ Worldw.* **2017**, *78* (3), 52.

4. (a) Burger, J.; Siegert, M.; Ströfer, E.; Hasse, H. *Fuel* **2010**, *89* (11), 3315; (b) M. Schappals, T. Breug-Nissen, K. Langenbach, J. Burger and H. Hasse, *J. Chem. Eng. Data*, **2017**

5. Himmel, D.; White, R. J.; Jacob, E.; Krossing, I. *Sustain. Energy Fuels,* **2017**.

6. (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, F. Mantei, M. Elmahlawy, R. J. White, H. Klein, S. Fateen, *Industrial & Engineering Chemistry Research.*, **2017** (submitted). (c) 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).

7. Reuss, Günther; Disteldorf, Walter; Gamer, Armin Otto; Hilt, Albrecht, Formaldehyde, Ullmann's Encyclopedia of Industrial Chemistry. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, **2000**.