A Hybrid Description and Evaluation of Oxymethylene Dimethyl Ethers Synthesis based on the Endothermic Dehydrogenation of Methanol

Electronic Supplementary Information

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Keywords
Oxymethylene Ethers; anhydrous formaldehyde; Gibbs minimisation; Process design and optimisation

Experimental results for equilibrium constant evaluation for Na_2CO_3 catalyst at 690 °C

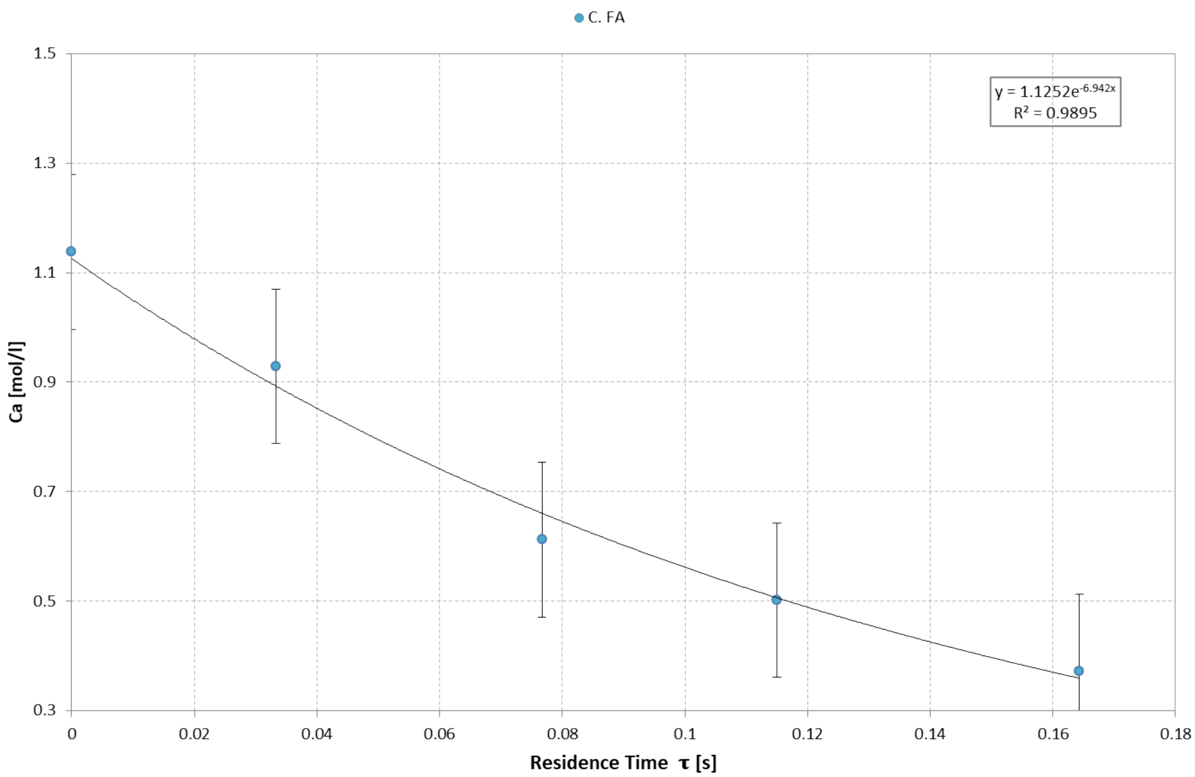

Fig. S1 Dependency of MeOH concentration consumed for FA production on residence time at 690 °C, a first order reaction fitting is illustrated

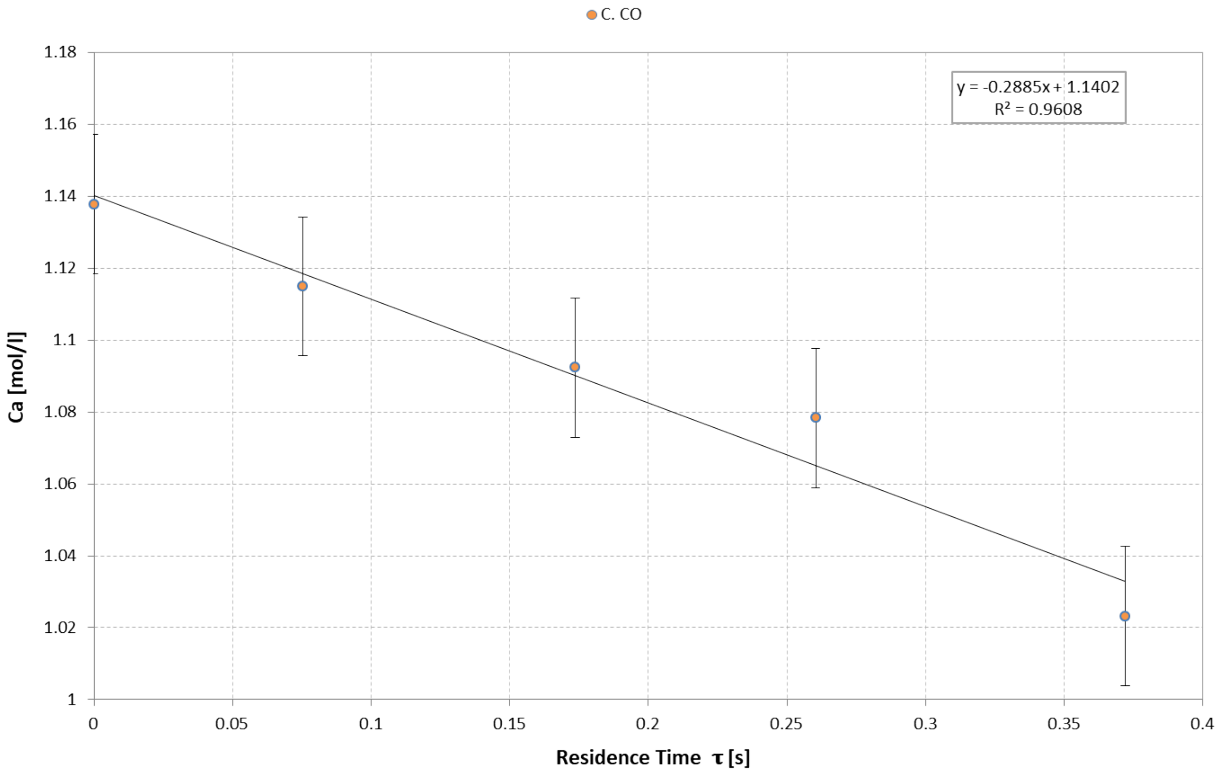

Fig. S2 Dependency of MeOH concentration consumed for CO production on residence time at 690 °C, a zero order reaction fitting is illustrated.

Kinetic model results for endothermic selective methanol dehydrogenation to formaldehyde reaction over Na_2CO_3 catalyst

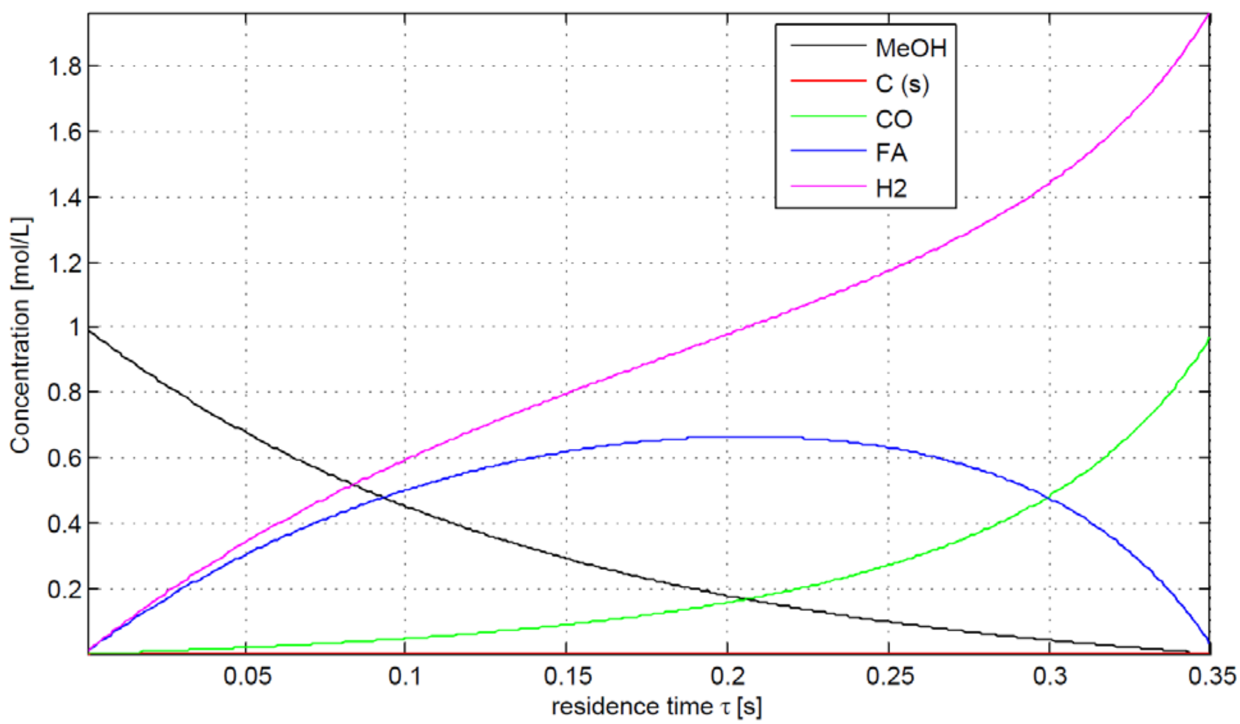

Fig. S3 Concentration curves of MeOH, C, CO, FA and H_2 over residence time for C_{A0} = 1 mol/L, T = 690 °C from kinetic FA reactor model

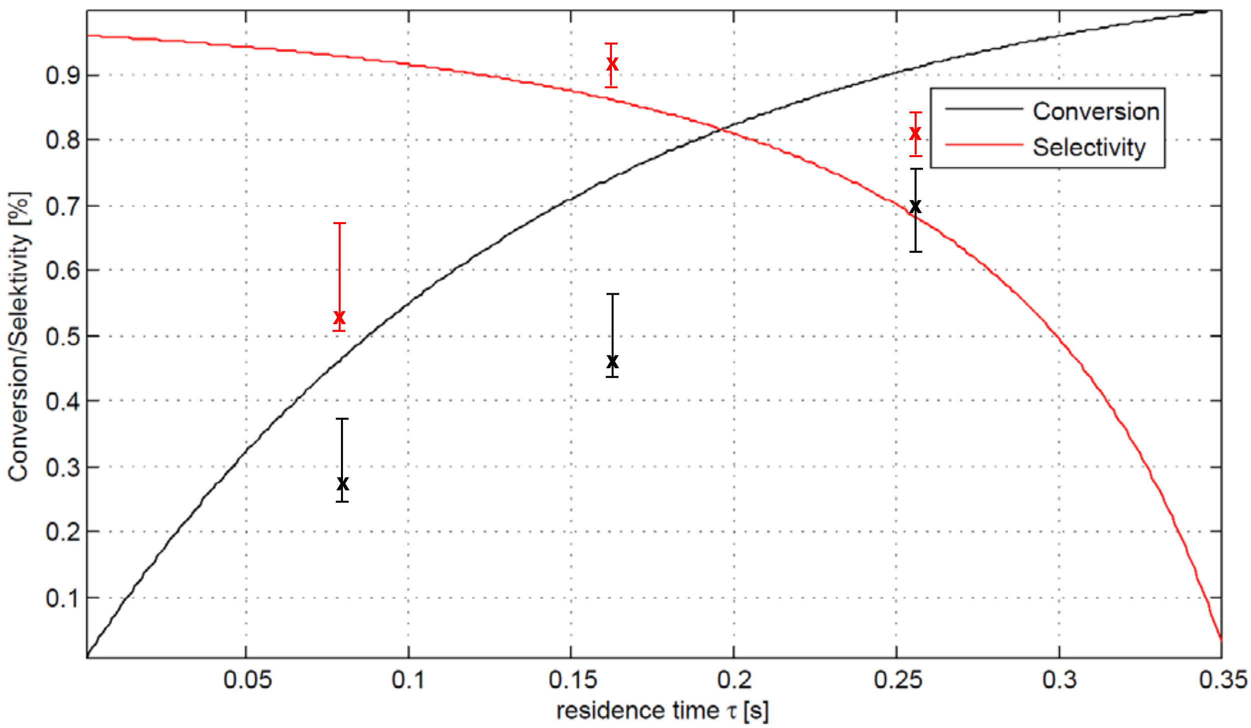

Fig. S4 Conversion of MeOH and Selectivity of MeOH regarding FA over residence time for C_{A0} = 1 mol/L, T = 690 °C from kinetic FA reactor model**. X:** measured conversion; **X:** measured selectivity.

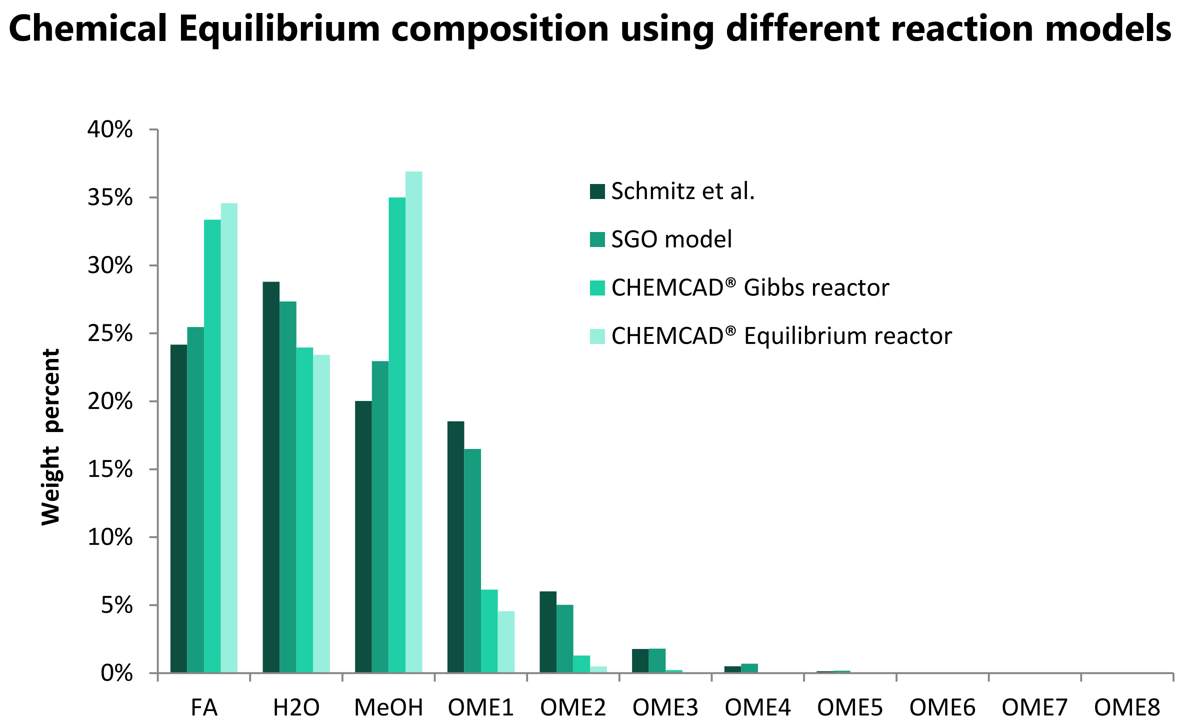

Fig. S5 Comparison of chemical equilibrium composition of experimental results from Schmitz *et al.*[1] at T = 348 K, P = 2 bar with a feed composition of FA/MeOH = 0.89 and H_2O/MeOH = 0.54, with the results obtained from the Stochastic Global Optimizer model and the CHEMCAD®, Gibbs and equilibrium reactors modules

Results and HEN from PinCH 2.0

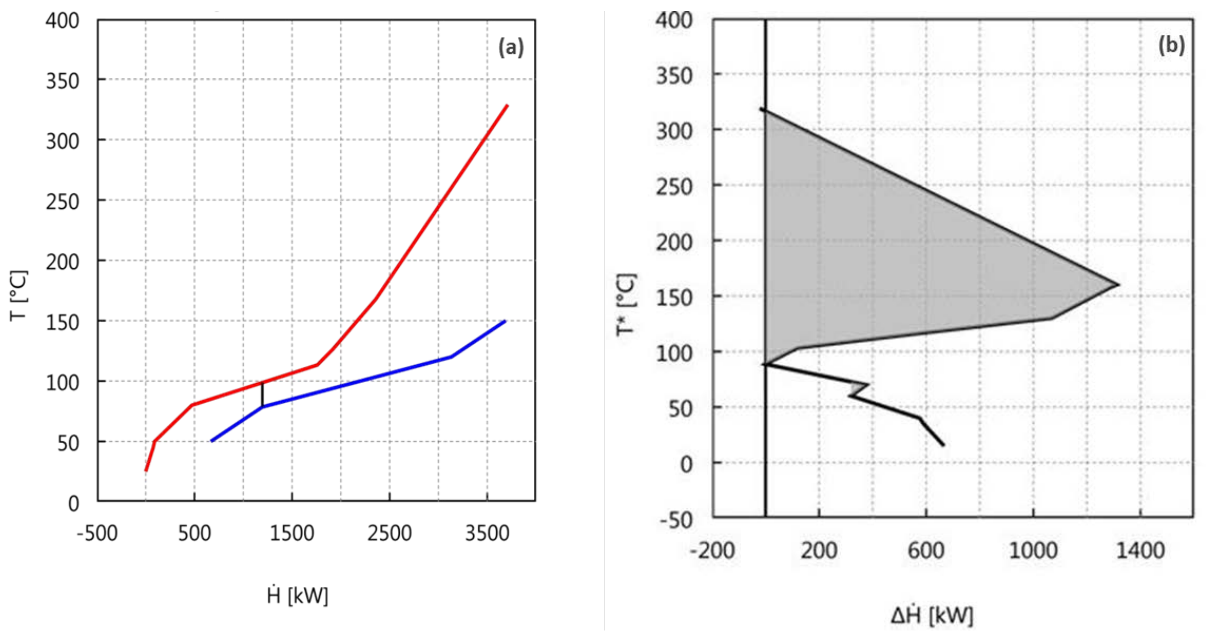

Fig. S6 (a) Composite curves and (b) Grand composite curve from PinCH 2.0 for generating the HEN

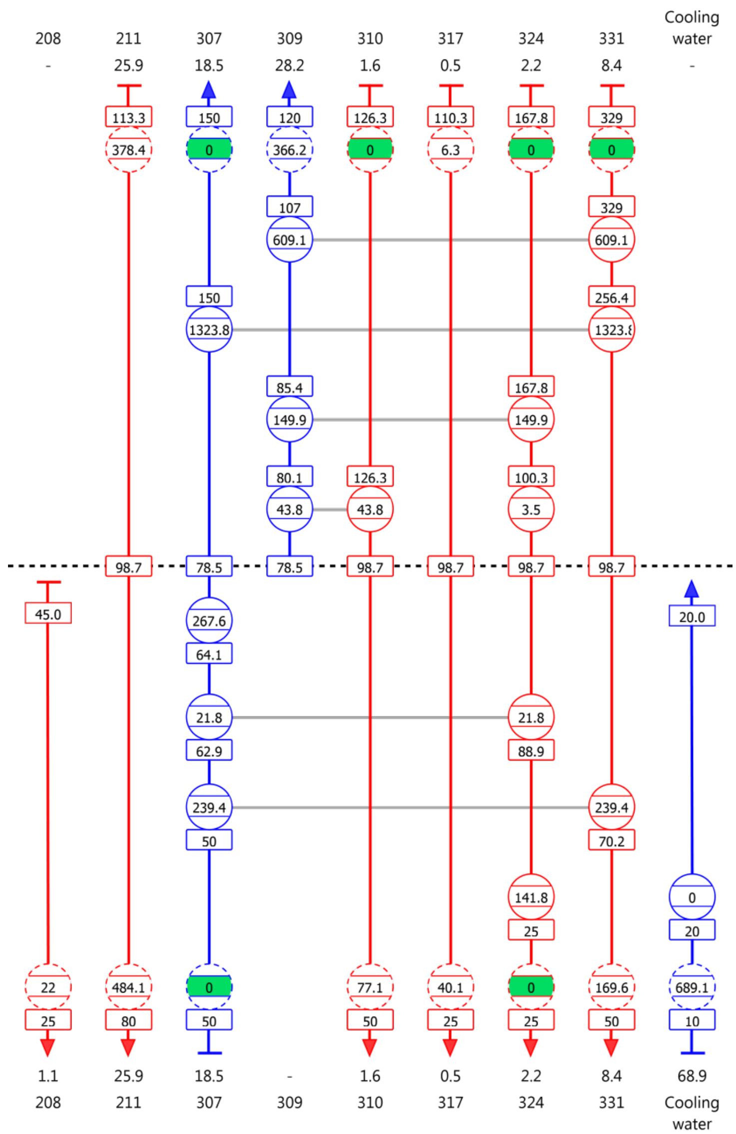

Fig. S7 HEN designed using PinCH 2.0 for the OME_{3-5} production process

Test stand for endothermic MeOH catalytic dehydrogenation to FA

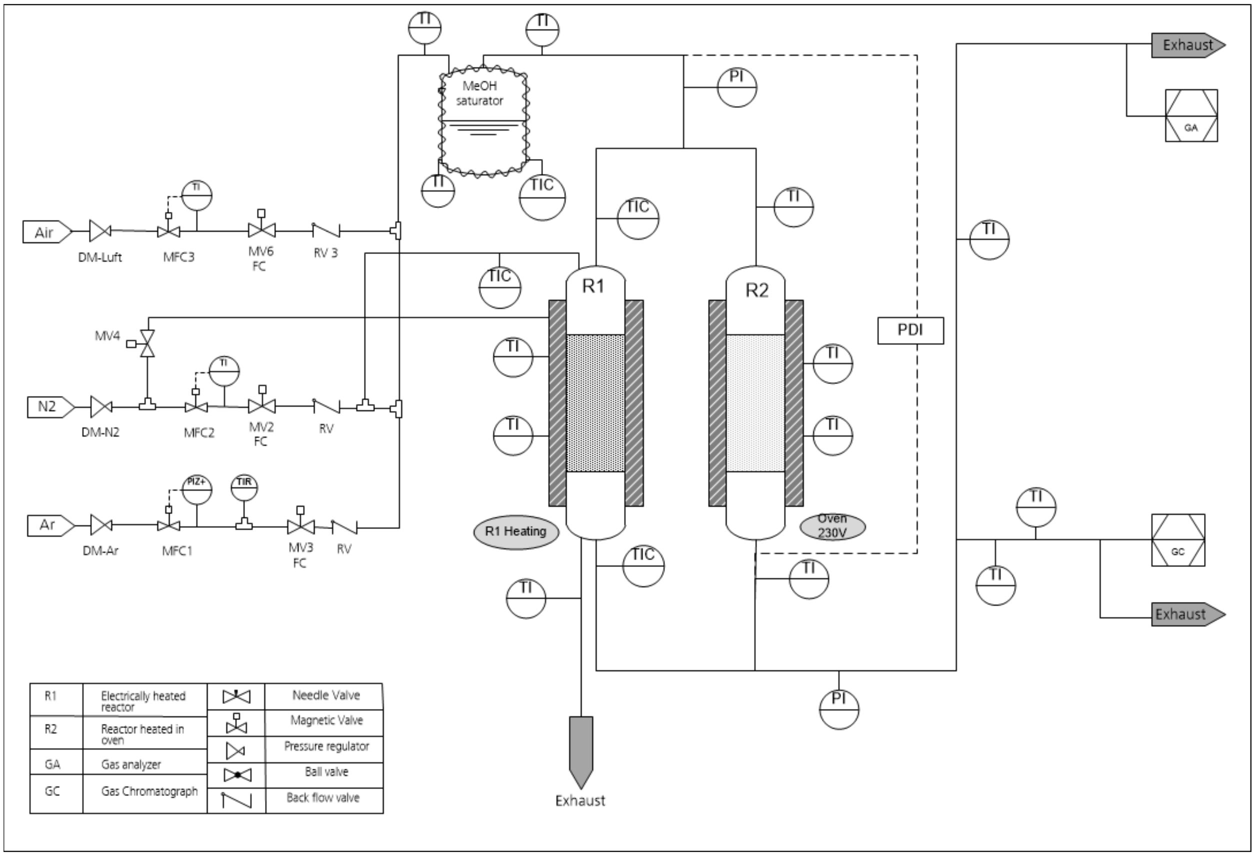

Fig. S8 Simplified Process Flow Diagram for the laboratory test stand used for anhydrous FA synthesis.

Ergun's Equation for pressure drop evaluation in ACCR[2]

$$P = P_0 \times (1 - \frac{2\times\beta_0\times z}{P_0})^{0.5}$$ *Equation S1*

With $$\beta_0 = \frac{G(1-\Phi)}{\rho_0 D_P \Phi^3} \times [\frac{150\times(1-\Phi)\times\mu}{D_P} + 1.75 \times G]$$

P = pressure [Pa]

z = Length of the catalyst bed [m]

G = Superficial velocity [kg/(m min)]

Φ = Porosity

ρ = Density [kg/(m^3)]

D_p = Lower limit of catalyst particle size [m]

μ = Viscosity [kg/(m min)]

Photographs of the ACCR with relative dimensions

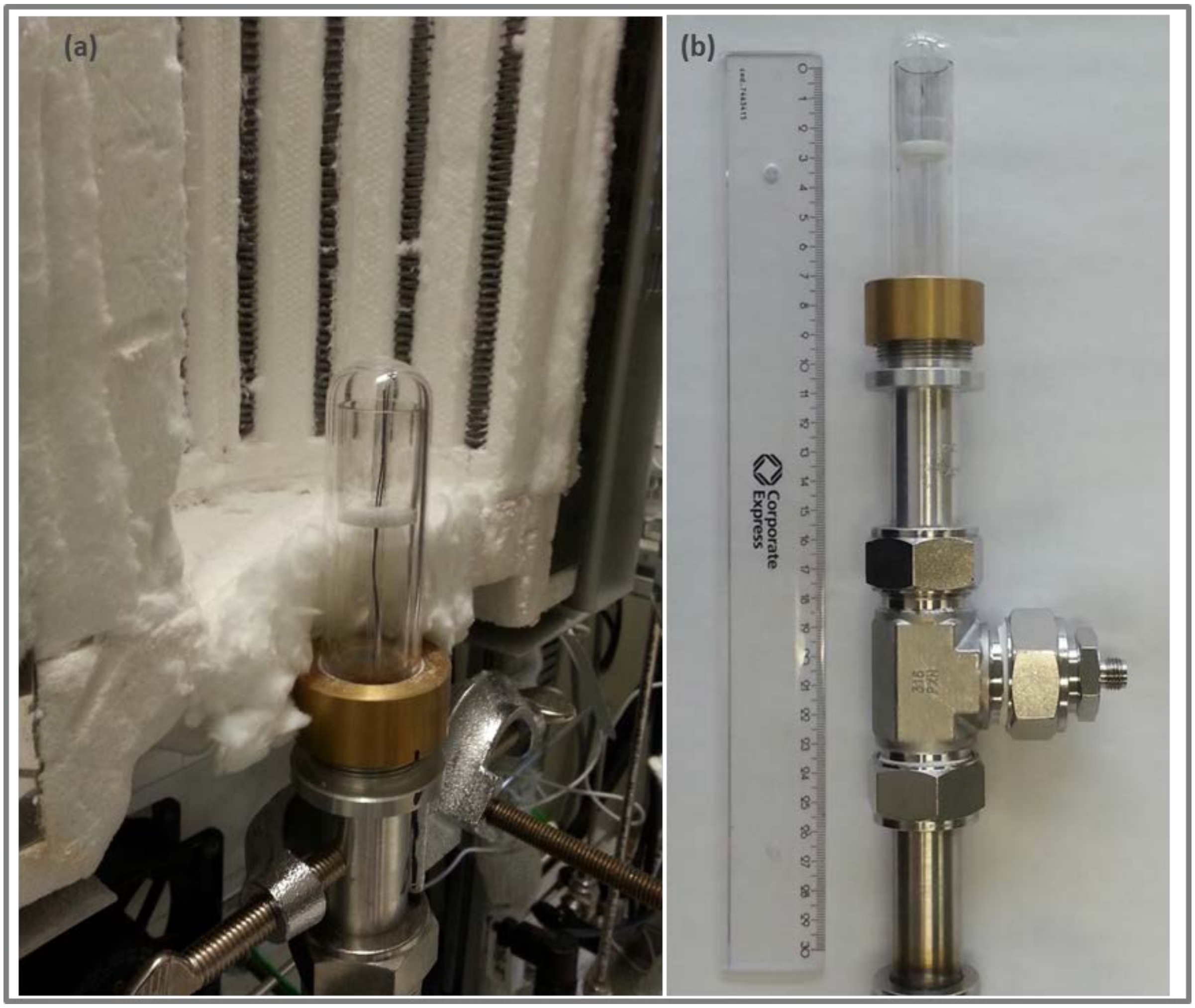

Fig. S9 Demonstration of the ACCR as installed in the electrically heated oven (a) and with relative dimensions as shown in (b)

Na_2CO_3 Catalyst Characterization

(a) (b)

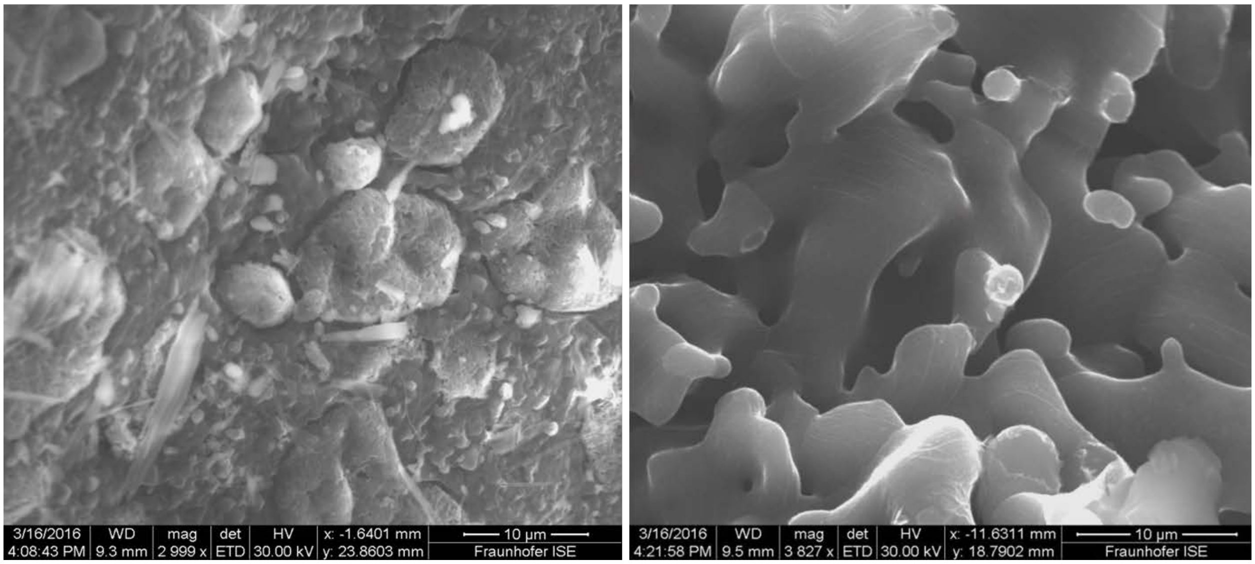

Fig. S10 SEM analysis for Na_2CO_3 catalyst with D_p = 400-800 μm (a) before test; (b) After test

References

1. N. Schmitz, F. Homberg, J. Berje, J. Burger and H. Hasse, *Ind. Eng. Chem. Res.*, 2015, **54**(25), 6409.
2. K. Schwister and V. Leven, eds., *Verfahrenstechnik für Ingenieure*, 2012.