FACULTY OF ENGINEERING AND ARCHITECTURE

DEPARTMENT OF MATERIALS, TEXTILES AND CHEMICAL ENGINEERING

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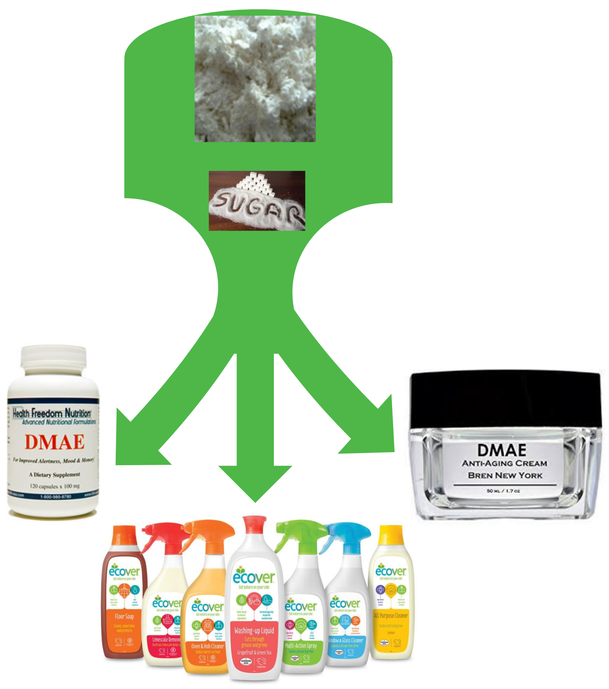
# KINETICS OF THE REDUCTIVE AMINOLYSIS OF GLUCOSE WITH DIMETHYLAMINE BELOW 400 K

## RENEWABLE RESOURCES AS A MEANS TO INHERENT SAFETY




Cellulose pulp as a renewable resource for the production of aminoalcohols (N,N-dimethylaminoethanol, DMAE) and diamines (N,N,N',N'-tetramethylethylenediamine, TMEDA). These chemicals are currently made from ethylene oxide and dichloroethane.



**Specific research goal:** Development of a **competitive** , **greener** and **inherently safe** production process for **DMAE** and **TMEDA** by means of an **experimental** and **kinetic modeling** investigation of the **reductive aminolysis** of glucose, as a model component, with DMA as aminating agent

## EXPERIMENTAL INVESTIGATION

fed-batch reactor

| | | |
|---|---|---|
| $W_{cat}$ | 2.9 – 7.4 | $g_{cat}$ |
| T | 383 – 398 | K |
| P | 6.0 – 7.5 | MPa |
| $n_{glucose}^0$ | 0.2 – 0.4 | mol |
| $n_{H2}/n_{glucose}^0$ | 4.7 – 9.6 | mol mol$^{-1}$ |
| $n_{DMA}/n_{glucose}^0$ | 11.9 – 23.6 | mol mol$^{-1}$ |
| $F_{glucose}$ | 5 - 30 | $10^{-5}$ mol s$^{-1}$ |
| Glucose concentration | 500 | $g_{glucose}$ $l_{H2O}^{-1}$ |

**narrow range of operating conditions** possible, given the **complex chemistry**, resulting in an **unstrained dataset** of 7 experiments and 36 data points

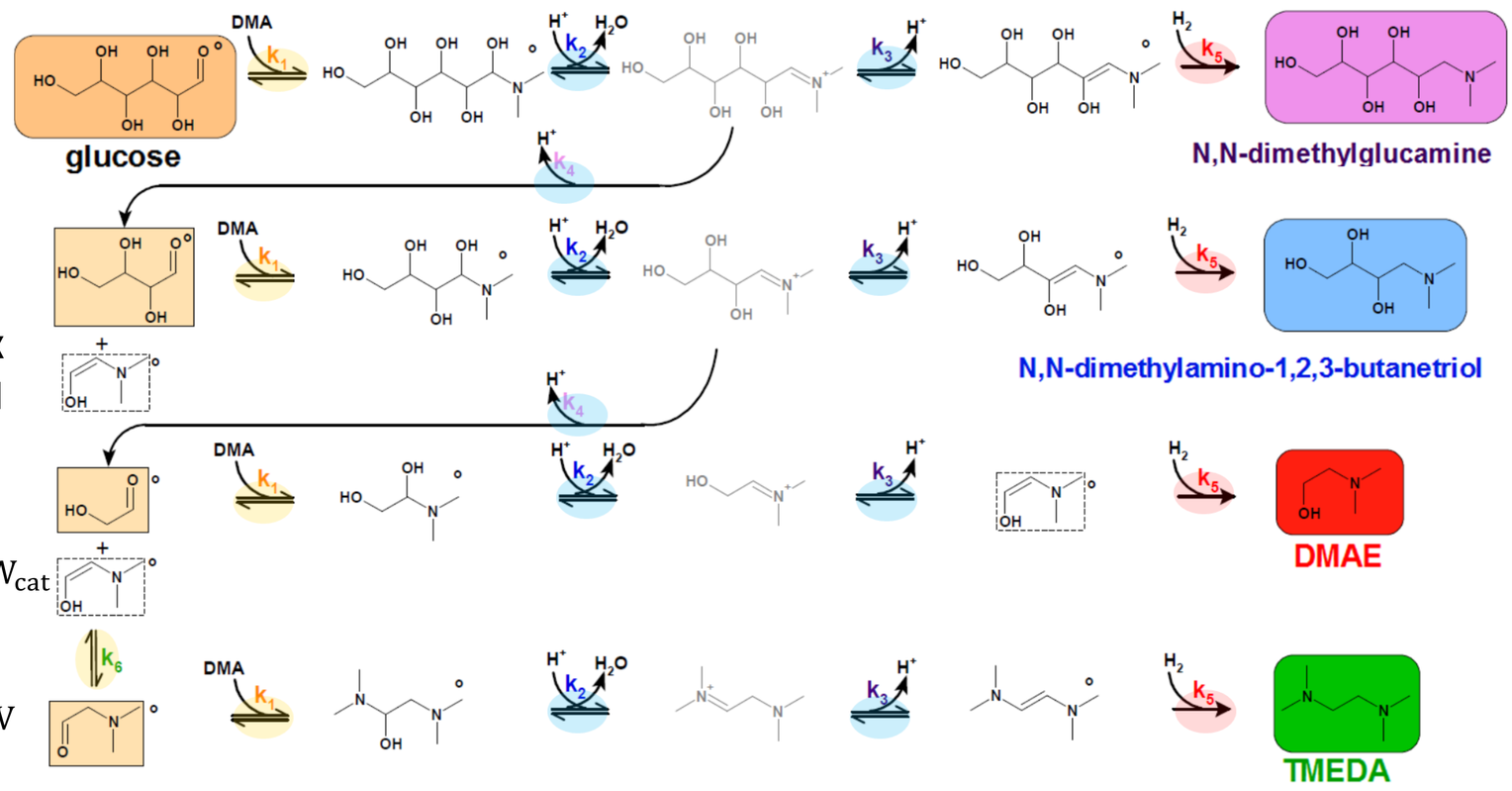
## REACTION NETWORK: 3 TYPES OF CATALYSIS

homogeneous base catalysis: 1. amination step; 6. keto-enol tautomerism

heterogeneous acid catalysis ◊: 2. iminium ion formation; 3. enamine rearrangement; 4. retro-aldol

heterogeneous metal catalysis *: 5. enamine hydrogenation

° 7. susceptible to homogeneous degradation




## RATE EQUATIONS

$$r_1 = \left(k_1 a_{DMA}^2 a_{glucose} - k_{-1} a_{DMA} a_{hemiC_6}\right)\varepsilon V$$

$$r_2 = \left(k_2 \theta_{\Diamond,hemiC_6} - k_{-2} \theta_{\Diamond,imC_6^+} a_{H_2O}\right) W_{cat}$$

$$r_3 = \left(k_3 \theta_{\Diamond,imC_6^+} - k_{-3} \theta_{\Diamond,enamC_6}\right) W_{cat}$$

$$r_4 = k_4 \theta_{\Diamond,imC_6^+} W_{cat}$$

$$r_5 = k_5 \theta_{\Diamond,enamC_6} \theta_{*,H}^2 W_{cat}$$

$$r_6 = \left(k_6 a_{DMA} a_{enamC_2} - k_{-6} a_{DMA} a_{C_4H_9NO}\right)\varepsilon V$$

$$r_7 = k_7 a_{glucose} \varepsilon V$$

## KINETIC MODEL

| Estimated average rate coefficient | | | | Estimated activation energy ( kJ mol$^{-1}$) | | |
|---|---|---|---|---|---|---|
| $k_{Tave,1}$ | $6.3\ 10^{-10}$ | $\pm 0.5\ 10^{-10}$ | $m_L^6$ mol$^{-2}$ s$^{-1}$ | $E_{a,1}$ | 78.1 | ± 7.2 |
| $k_{Tave,2}$ | $2.1\ 10^{4}$ | $\pm 0.6\ 10^{4}$ | mol $kg_{cat}^{-1}$ s$^{-1}$ | $E_{a,2}$ | 49.9 | ± 4.9 |
| $k_{Tave,3}$ | $7.0\ 10^{-2}$ | $\pm 1.3\ 10^{-2}$ | mol $kg_{cat}^{-1}$ s$^{-1}$ | $E_{a,3}$ | 47.5 | ± 7.9 |
| $k_{Tave,4}$ | $3.9\ 10^{-1}$ | $\pm 0.7\ 10^{-1}$ | mol $kg_{cat}^{-1}$ s$^{-1}$ | $E_{a,4}$ | 59.9 | ± 9.9 |
| $k_{Tave,5}$ | $5.0\ 10^{1}$ | $\pm 0.7\ 10^{1}$ | mol $kg_{cat}^{-1}$ s$^{-1}$ | $E_{a,5}$ | 8.8 | ± 2.5 |
| $k_{Tave,6}$ | $8.9\ 10^{-4}$ | $\pm 1.2\ 10^{-4}$ | $m_L^3$ mol$^{-1}$ s$^{-1}$ | $E_{a,6}$ | 1.6 | ± 0.3 |
| $k_{Tave,7}$ | $2.8\ 10^{-3}$ | $\pm 0.2\ 10^{-3}$ | s$^{-1}$ | $E_{a,7}$ | 141.7 | ± 13.0 |

| Estimated average adsorption equilibrium coefficient ($m_L^3$ mol$^{-1}$) | | | Estimated adsorption enthalpy ( kJ mol$^{-1}$) | | |
|---|---|---|---|---|---|
| $K_{Tave,C6}$ | $5.7\ 10^{-5}$ | $\pm 1.0\ 10^{-5}$ | $-\Delta H_{ads,C6}$ | -30.3 | ± 9.1 |
| $K_{Tave,C4}$ | $6.7\ 10^{-2}$ | $\pm 0.6\ 10^{-2}$ | $-\Delta H_{ads,C4}$ | -13.7 | ± 1.9 |
| $K_{Tave,C2}$ | $7.0\ 10^{-3}$ | $\pm 0.3\ 10^{-3}$ | $-\Delta H_{ads,C2}$ | -26.0 | ± 4.6 |
| $K_{Tave,H2}$ | 1.1 | ± 0.3 | $-\Delta H_{ads,H2}$ | -2.9 | ± 0.3 |

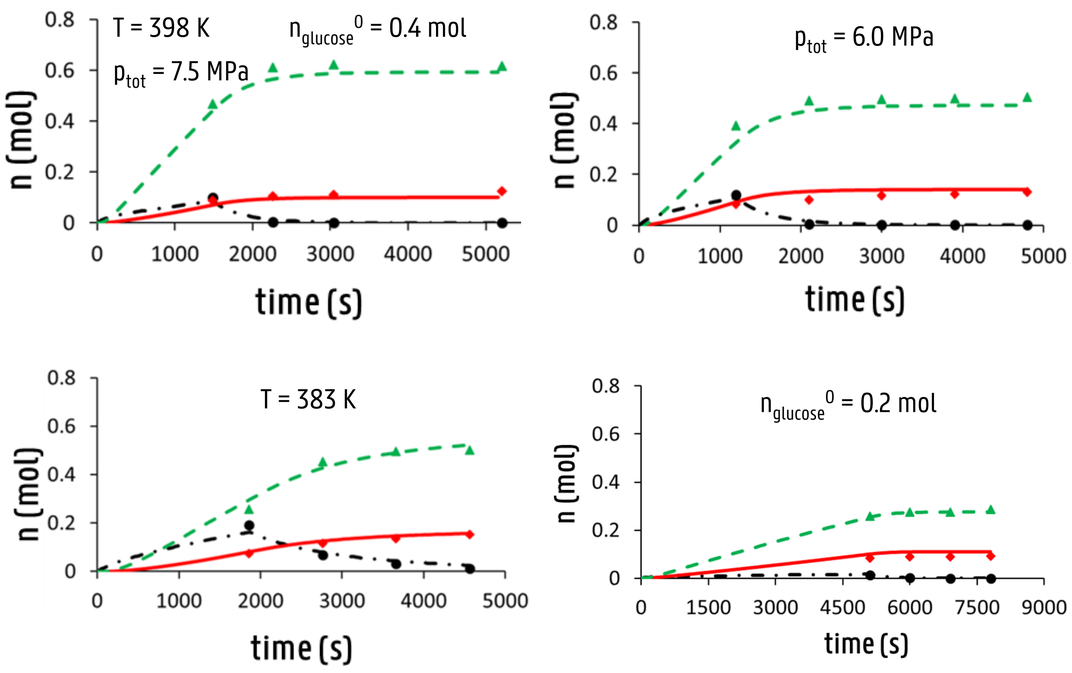
statistically significant model: $F_{test} = 160 > F_{tab} = 2.79$

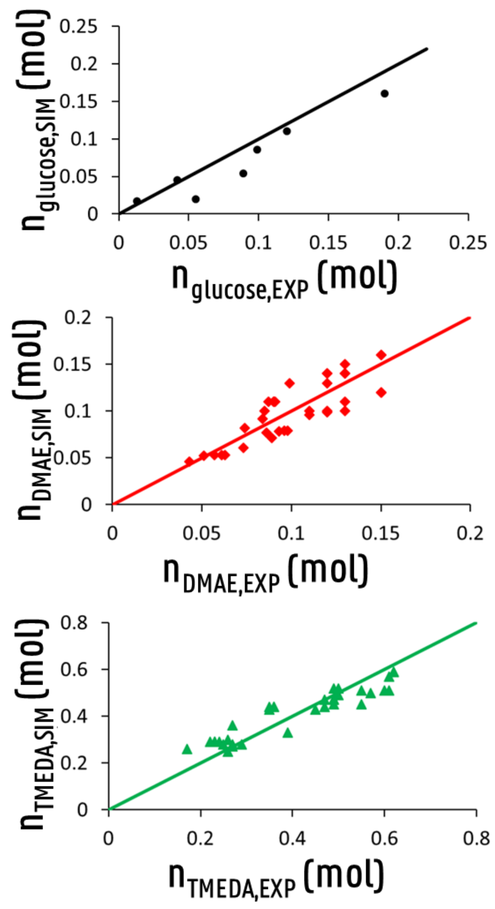
higher temperatures favor retro-aldol cleavage and thus DMAE and TMEDA formation

$E_{a,4}$ significantly lower than typical retro-aldol ~ 140 kJ mol$^{-1}$ → retro-aldol below 400K

selectivity tuning between DMAE and TMEDA not possible by varying the temperature

too high temperatures result in almost exclusively degradation products




## CONCLUSIONS

**renewable** and **safe** production route for DMAE and TMEDA **without excessive degradation**

activation energy for retro-aldol ($E_{a,4}$) is significantly reduced by the presence of a nitrogen atom →retro-aldol occurs at temperatures below 400 K

statistically significant **kinetic model** manages to **simulate and explain experimentally observed trends**

## ACKNOWLEDGMENTS

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