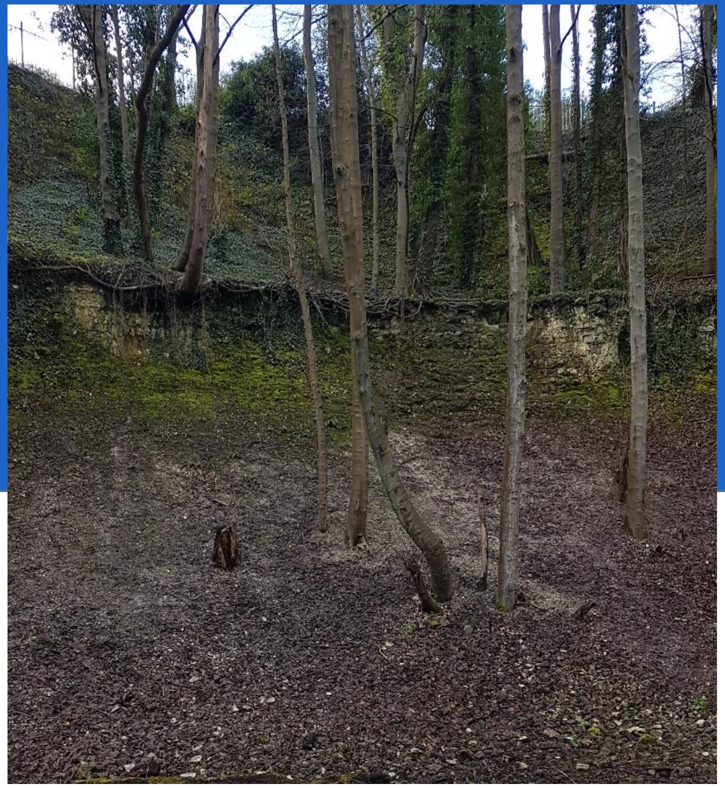
EUROKIN WORKSHOP, FEBRUARY 26, 2020, HULL UK

# Mastering the interplay between homogeneously and heterogeneously catalyzed reactions: kinetic modeling and scale-up of glucose aminolysis

Jeroen Poissonnier and Joris W. Thybaut



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# Motivation

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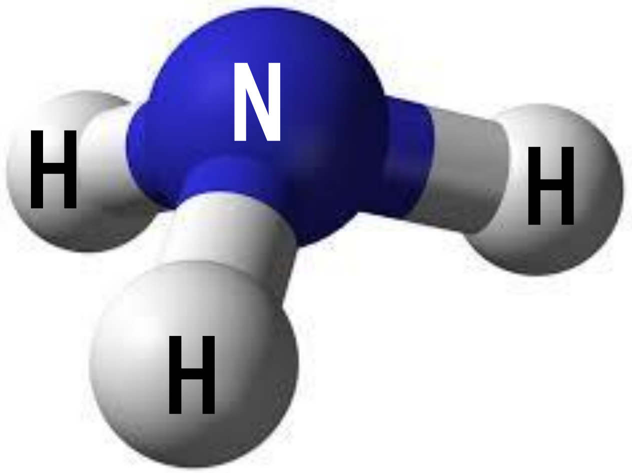
# aminolysis

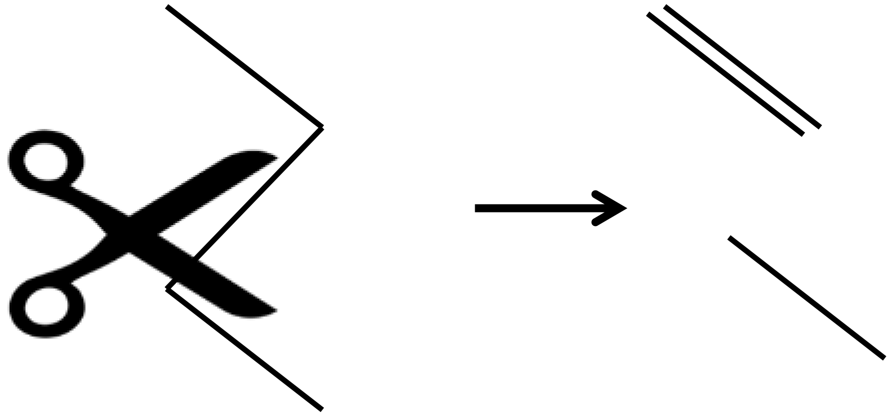
## Mastering the interplay between homogeneous and heterogeneously catalyzed reactions: kinetic modeling and scale-up of glucose aminolysis

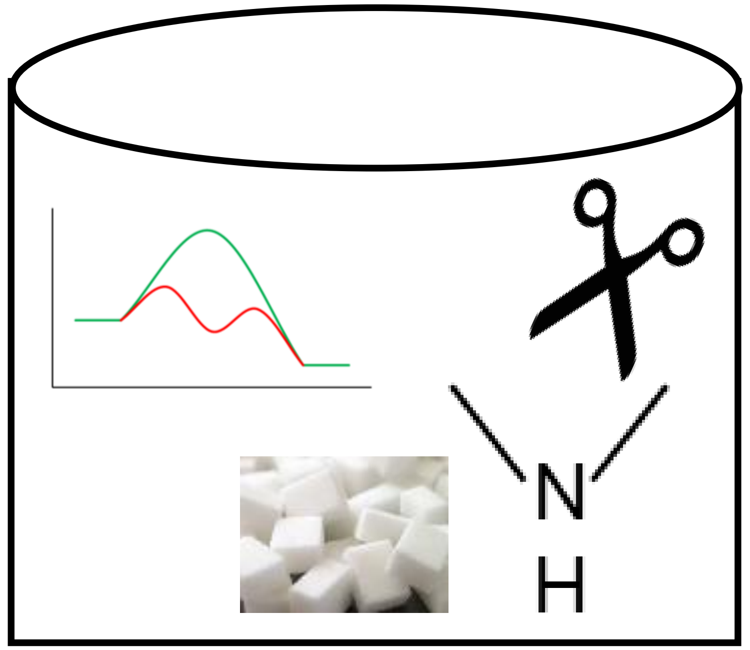
AMINO

7
N
nitrogen



LYSIS





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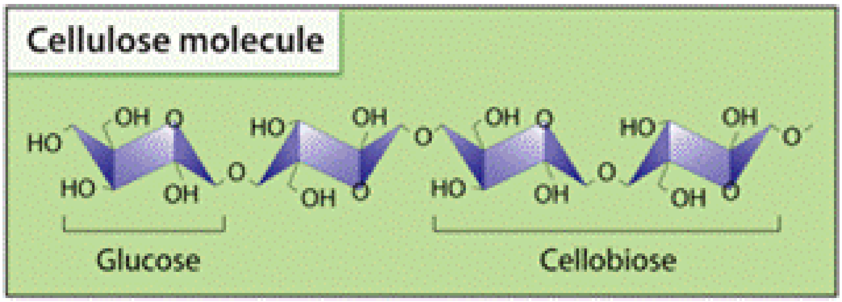
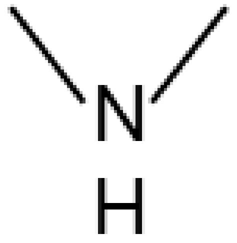
# project overview

cellulose pulp

Cargill

complex structure of cellulose

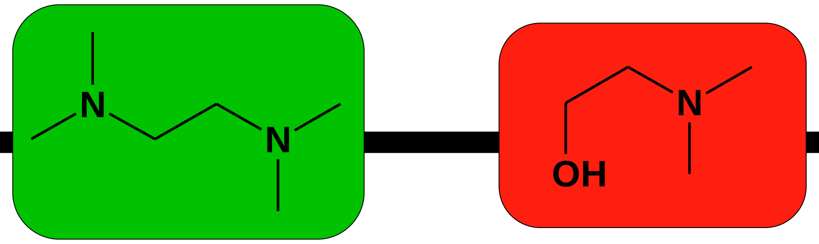




EASTMAN

**glucose aminolysis**

target molecules

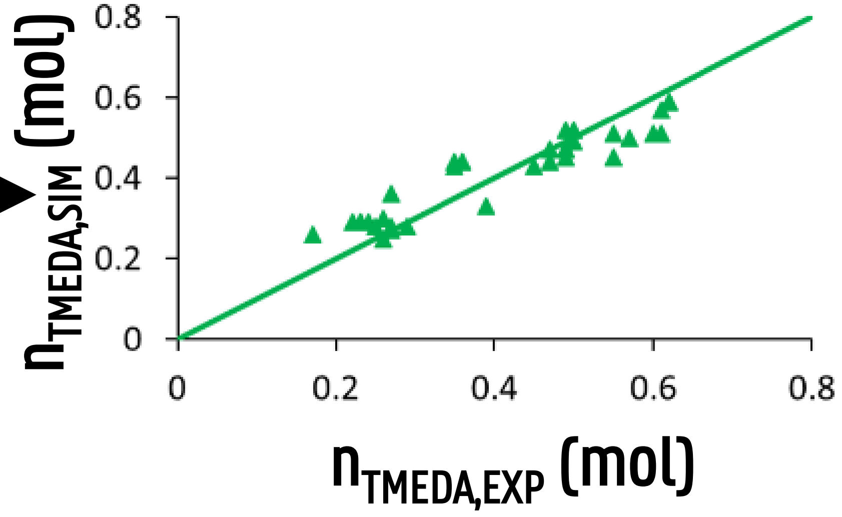


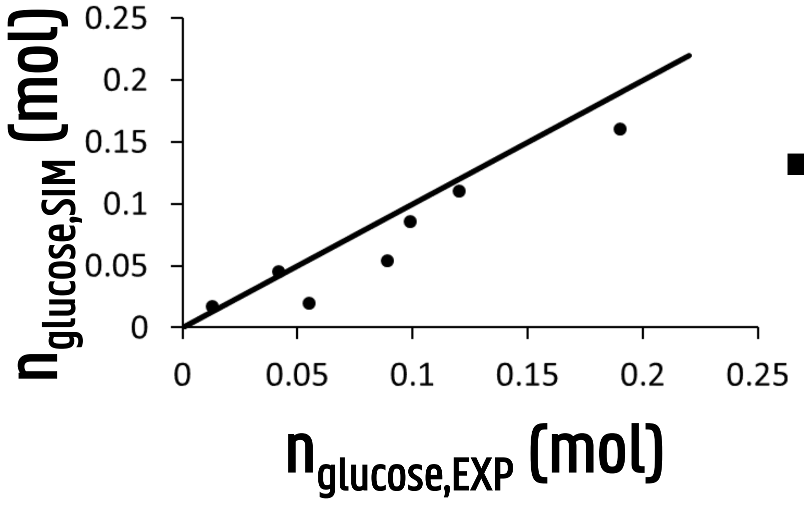
detergent

ECOVER

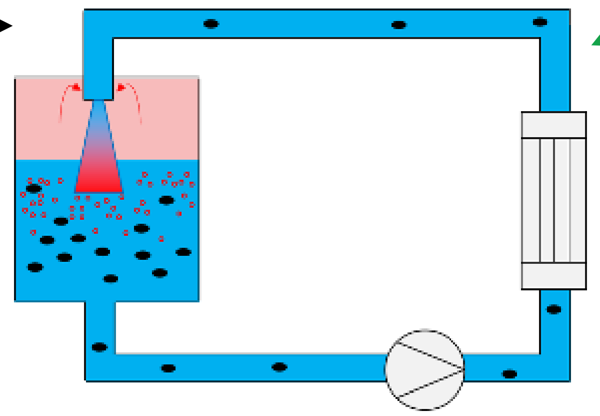
experimental assessment

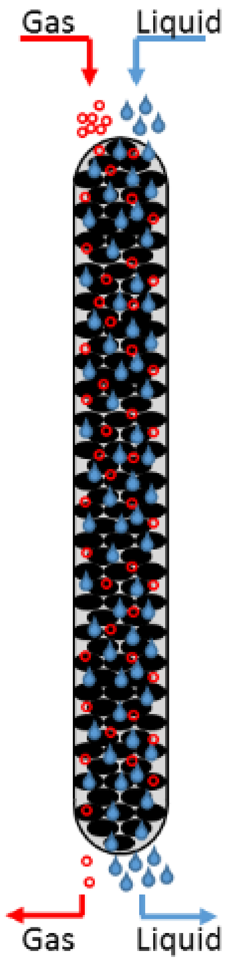
kinetic model construction





industrial reactor simulation





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# overview

experimental assessment

- batch reactor experiments
- fed-batch reactor experiments

kinetic model construction

industrial reactor simulation

conclusions

# batch reactor experiments: operating procedure

## start-up

1. load (dissolved) glucose and catalyst and close reactor
2. flush the reactor
3. perform pressure test
4. load DMA
5. load $H_2$ ($p^0$)
6. start heating
7. maintain pressure with He ($p_{tot}$)

## shutdown

8. cool down the reactor
9. vent and flush the reactor
10. remove reactor contents and clean

| property | symbol | range | units |
|---|---|---|---|
| initial pressure | $p^0$ | 4.5 – 6.4 | MPa |
| total pressure | $p_{tot}$ | 4.0 – 7.5 | MPa |
| glucose feed | $n_{glucose}^0$ | 0.3 – 0.5 | mol |
| DMA to glucose ratio | $n_{DMA}/n_{glucose}^0$ | 9.0 – 15.0 | mol mol$^{-1}$ |
| catalyst mass | $W_{cat}$ | 3.0 – 4.5 | $g_{cat}$ |

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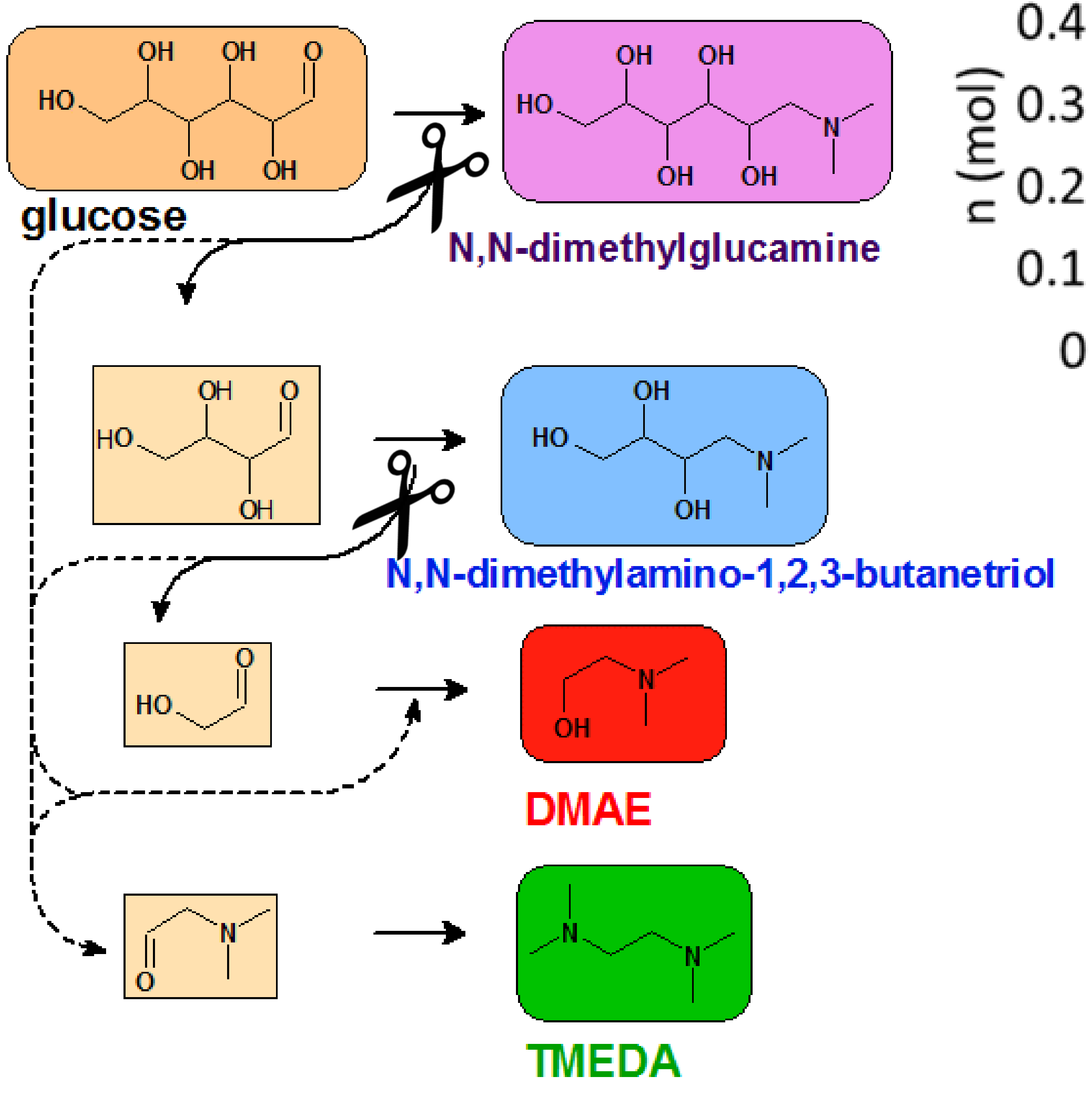
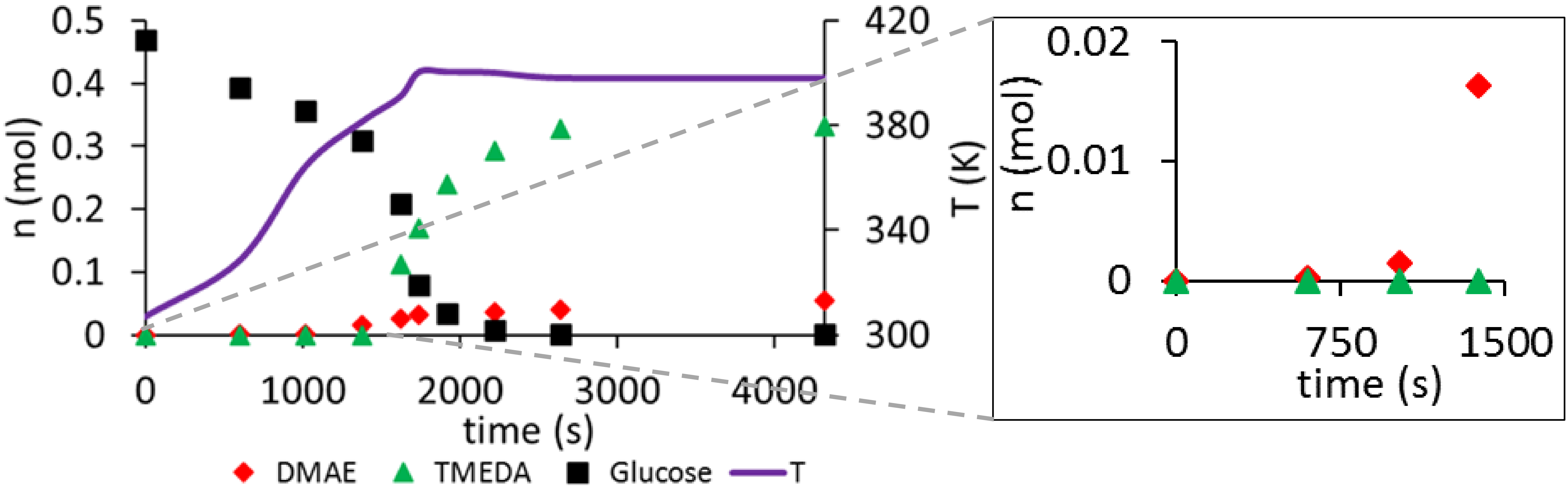
# reaction profile





TMEDA main product (Yield: 35 %), DMAE byproduct (Yield: 4 %)

✂ occurs at **lower temperatures than expected** (>423 K = > 150°C)

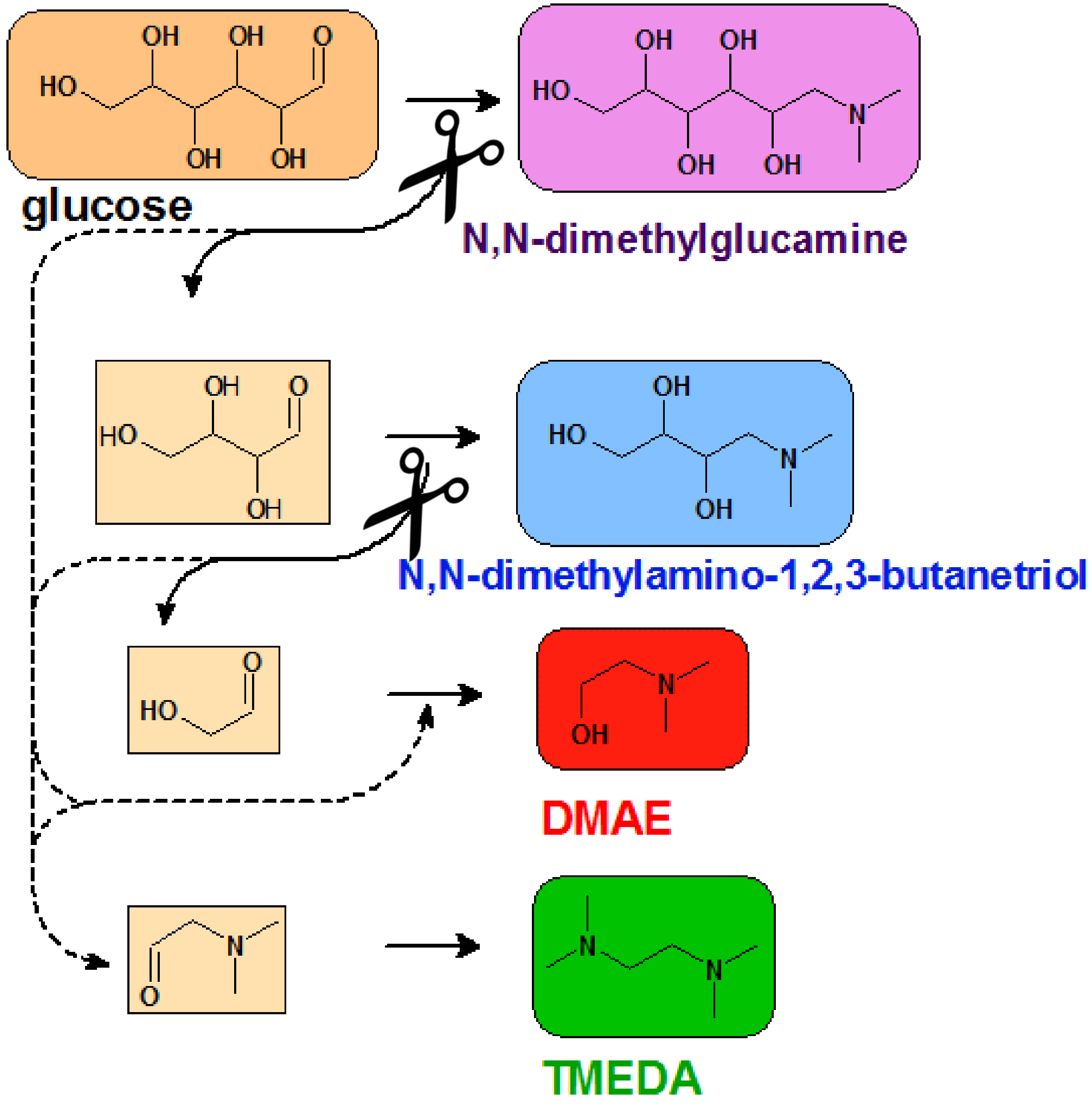
both TMEDA and DMAE are stable

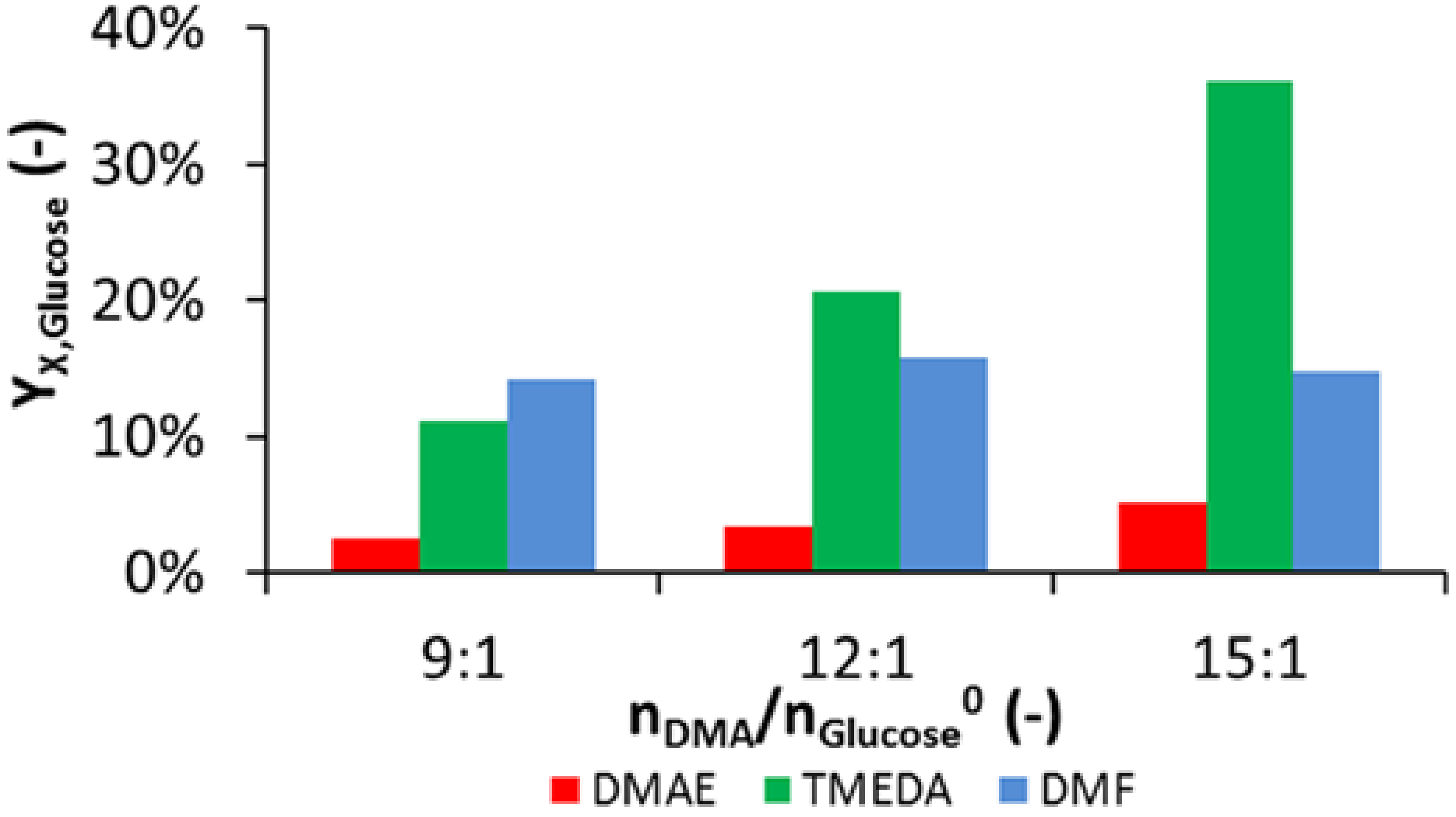
DMAE formed earlier than TMEDA

glucose conversion during heating

→ **operating conditions not well defined and not suited for kinetic modelling**

# effect of DMA to glucose ratio





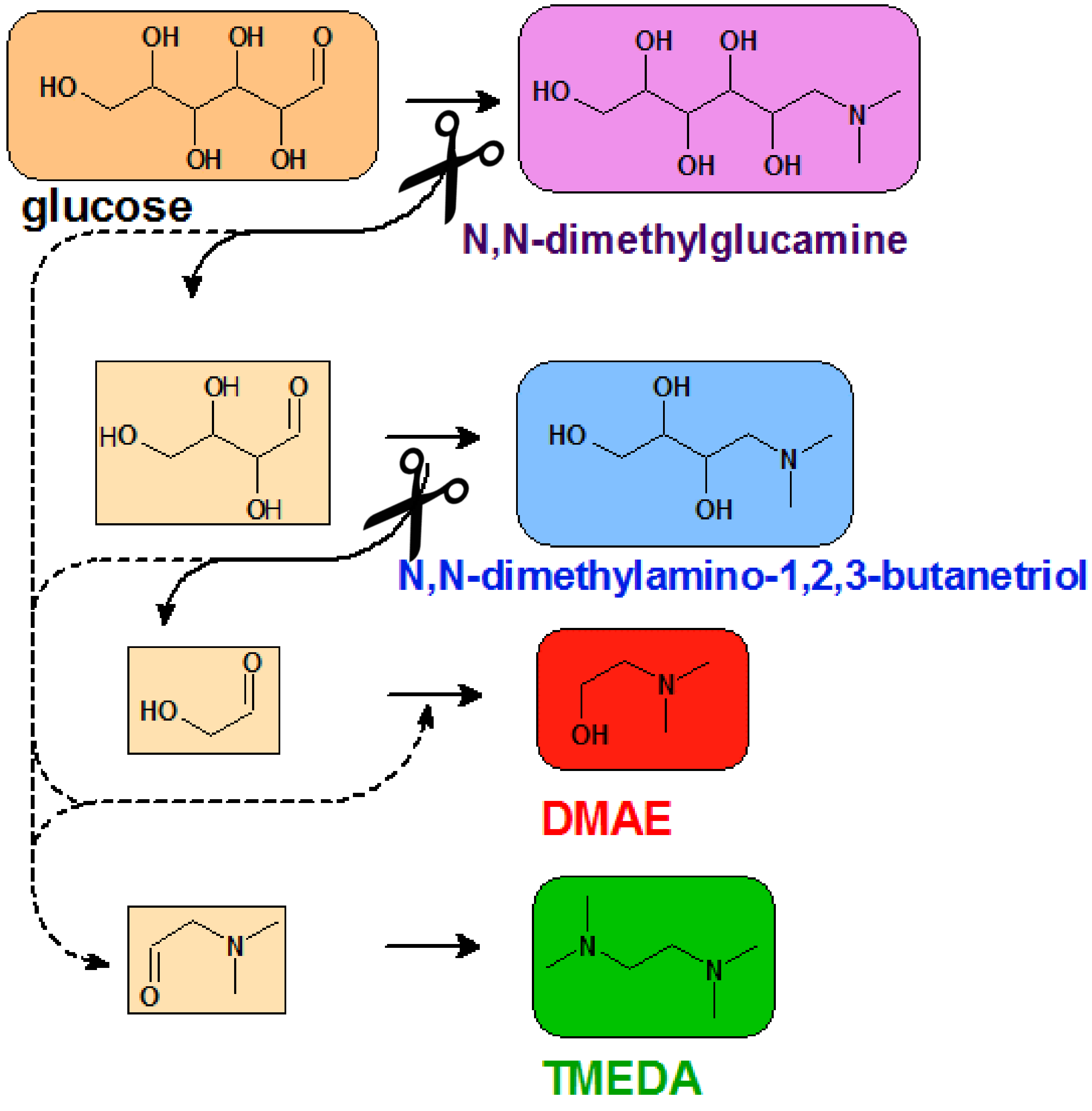
when $n_{DMA}/n_{glucose}^0$ increases:

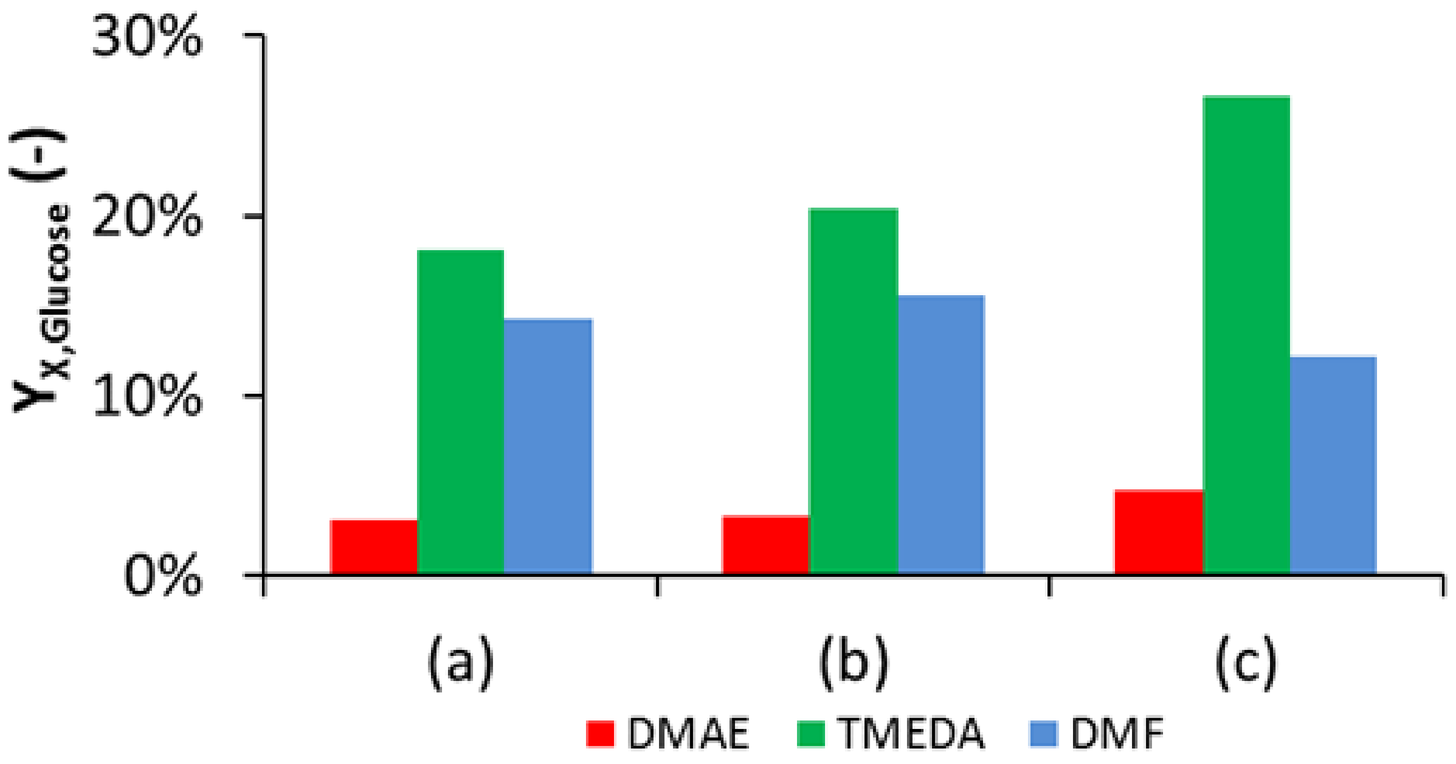
DMAE yield increases

TMEDA yield greatly increases

DMF yield remains the same

# effect of $H_2$ and total pressure





| | $H_2$ | total pressure |
|---|---|---|
| (a) | $p^0$: 4.5 MPa | $p_{tot}$: 6.0 MPa |
| (b) | $p^0$: 4.5 MPa | $p_{tot}$: 7.5 MPa |
| (c) | $p^0$: 6.2 MPa | $p_{tot}$: 7.0 MPa |

$p_{tot}$ increases: slightly more TMEDA

$p^0$ increases: more DMAE and much more TMEDA, less DMF

effect $p^0$ more pronounced than $p_{tot}$:

**hydrogen availability is key!**

# conclusions, challenges and opportunities

experimental assessment of glucose aminolysis at temperatures below 400 K

- DMAE formed first, TMEDA main product
- higher DMA to glucose ratio beneficial, especially for TMEDA
- higher total pressure and, especially, higher initial amount of hydrogen beneficial

trends can be observed but not modelled because

- operating conditions are not sufficiently well specified
- reaction and main product loss during heating

➔ fed-batch experimentation

- feed glucose when desired temperature is reached
  → temperature specified
  → properly asses the effect of the temperature
  → avoid losses during heating phase
- maintain pressure with $H_2$ instead of He

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# fed-batch reactor

batch reactor

fed-batch reactor

## advantages of fed-batch reactor operation:

- controlled addition of key reactant when other reaction conditions are reached
  - operating conditions are well specified (T, p)
  - no product loss during heating phase → higher yields
- possibility to adapt the feed rate
  - opportunity slow down or speed up reaction on purpose

## disadvantages of fed-batch reactor operation?

- very challenging to assess conversion in case of fast reactions at controlled feeding rates

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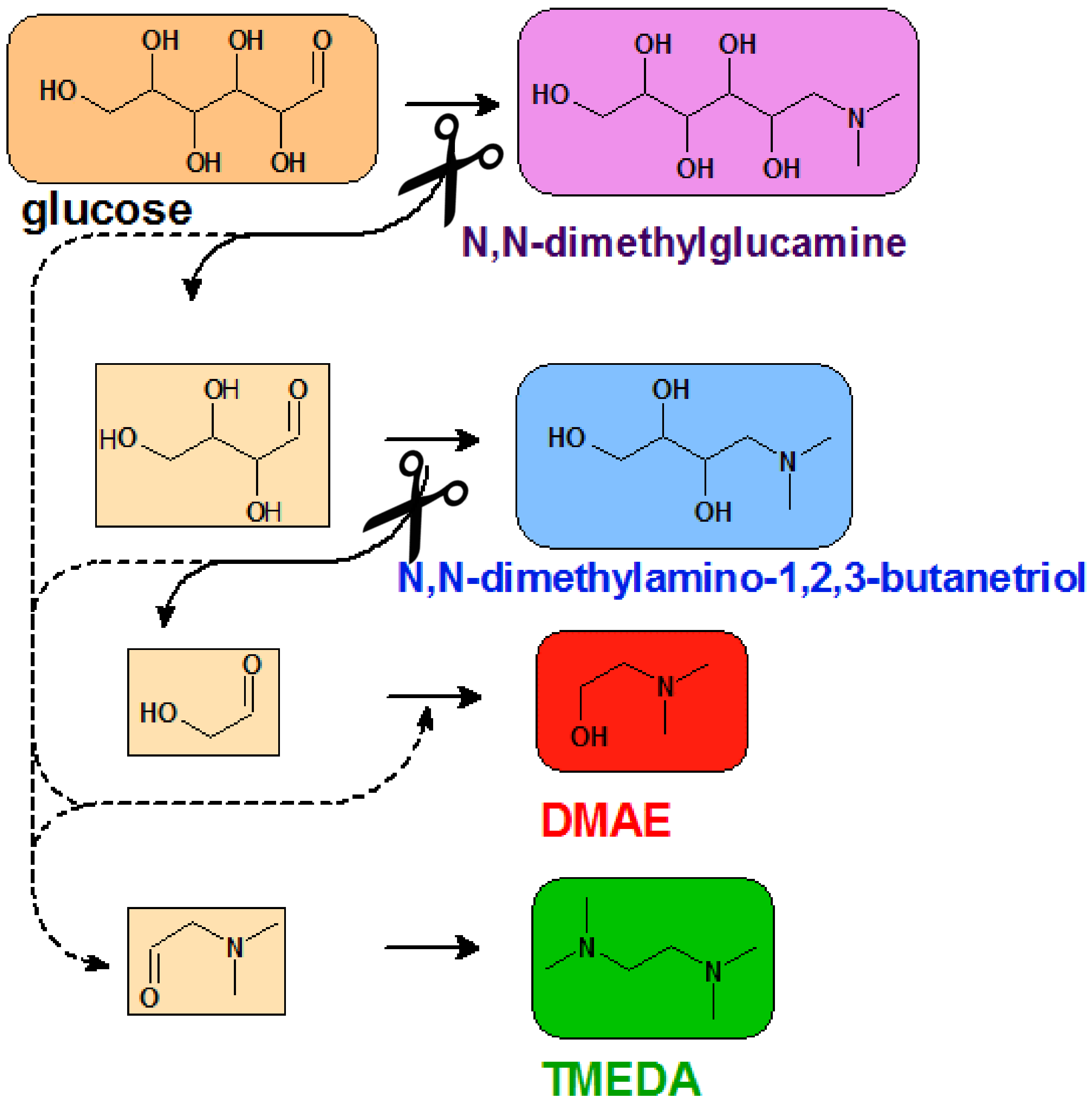
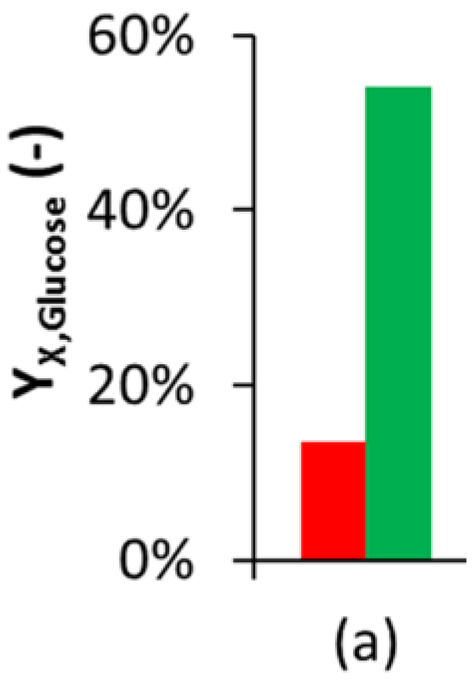
# fed-batch reactor experimentation





(b) T = 383 K

(c) $p_{tot}$ = 6.0 MPa

(d) $W_{cat}$ = 7.4 g,

$n_{DMA}/n_{glucose}^0 = 19$

(e) $n_{DMA}/n_{glucose}^0 = 16$

(a) reference: T = 398 K, $p_{tot}$ = 7.5 MPa, $W_{cat}$ = 3.6 g, $n_{DMA}/n_{glucose}^0 = 12$

higher desired product yields in fed-batch operation compared to batch operation:

$Y_{DMAE}$: 5% → 14%, $Y_{TMEDA}$: 36% → 54% ($Y_{DMF}$: 10% → 1 – 4%)

lower temperatures: slightly more DMAE, less TMEDA, more N,N-dimethylglucamine

lower total pressure: slightly less TMEDA, not very pronounced

higher $W_{cat}$: less TMEDA, much more N,N-dimethylglucamine (Y = 28% compared to 10% in (a) )

higher $n_{DMA}/n_{glucose}^0$: more TMEDA ← highest amount of DMA required!

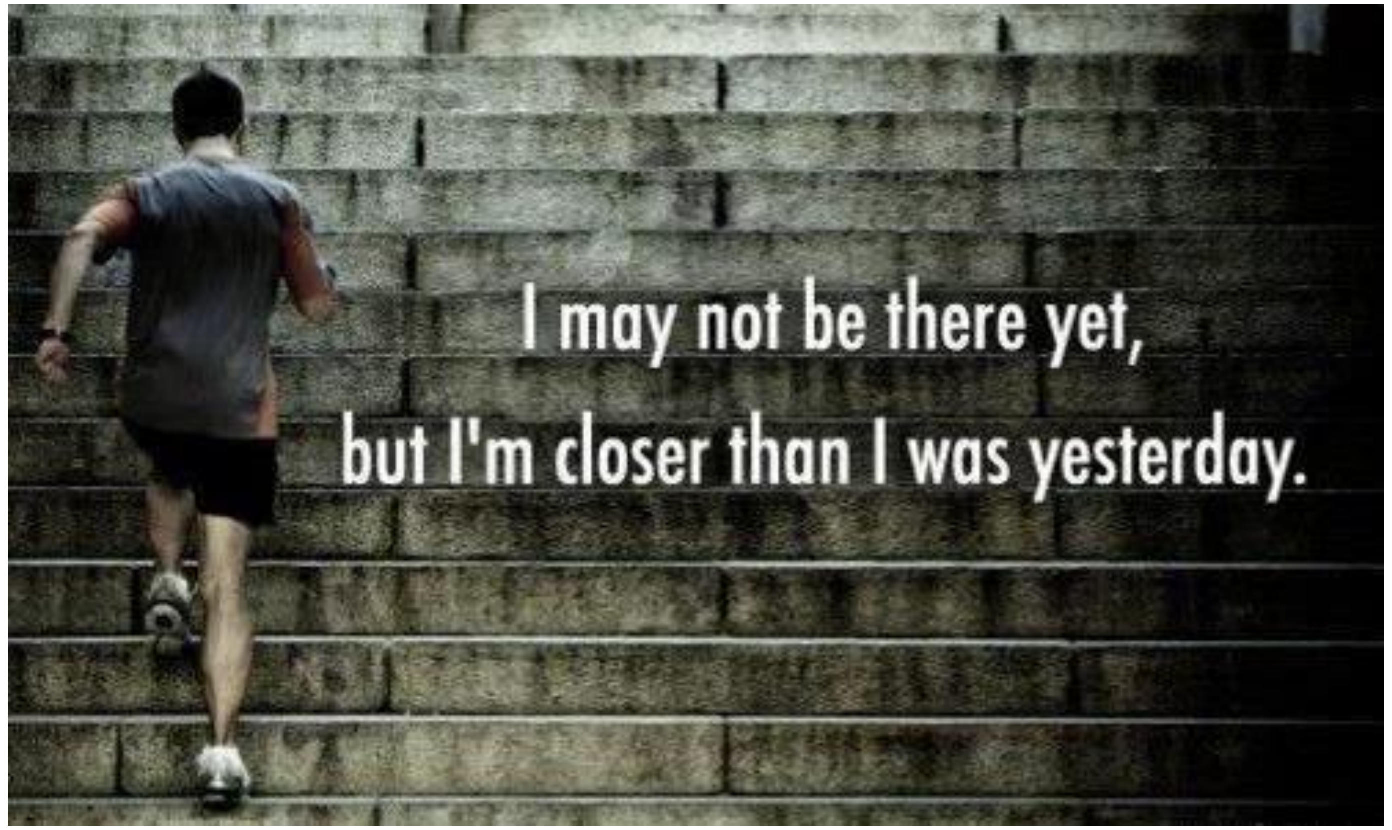
# experimental assessment: conclusions

## batch experimentation

+ aminolysis occurs at lower temperatures than expected
+ DMAE formed first, TMEDA main product
+ higher DMA to glucose ratio beneficial, especially for TMEDA
+ higher total pressure and, especially, higher initial amount of hydrogen beneficial
- observed trends can not be modelled

## fed-batch experimentation

+ proper assessment of temperature effect
+ operating conditions much better specified
++ higher DMAE and TMEDA yields, less degradation



# overview

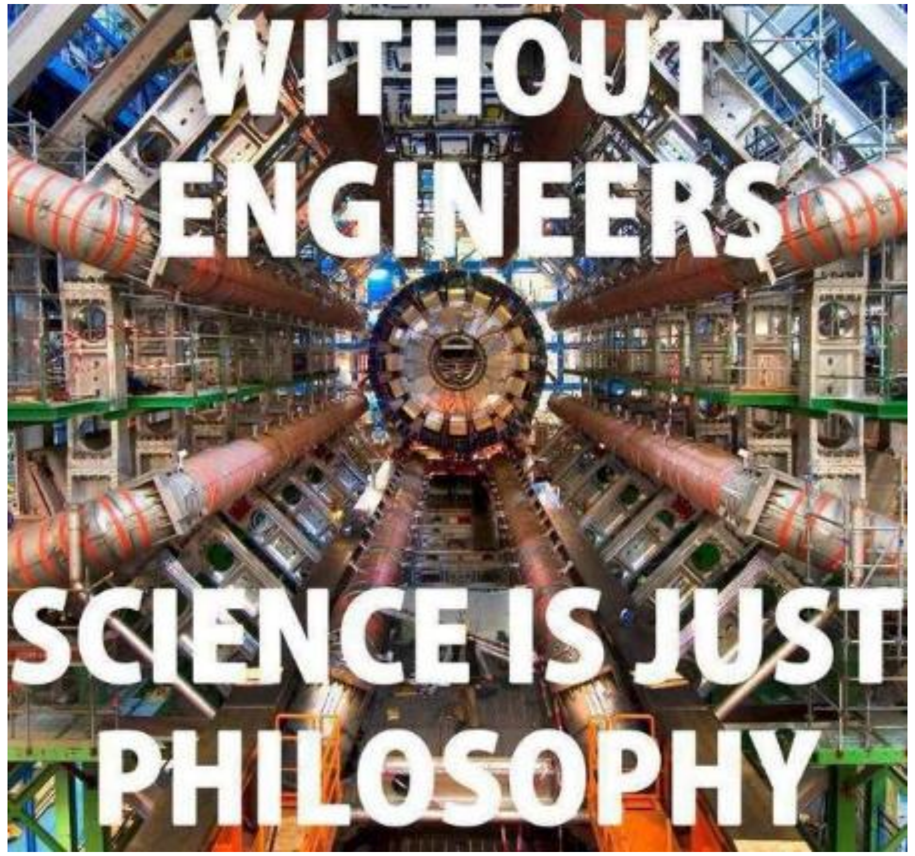
experimental assessment

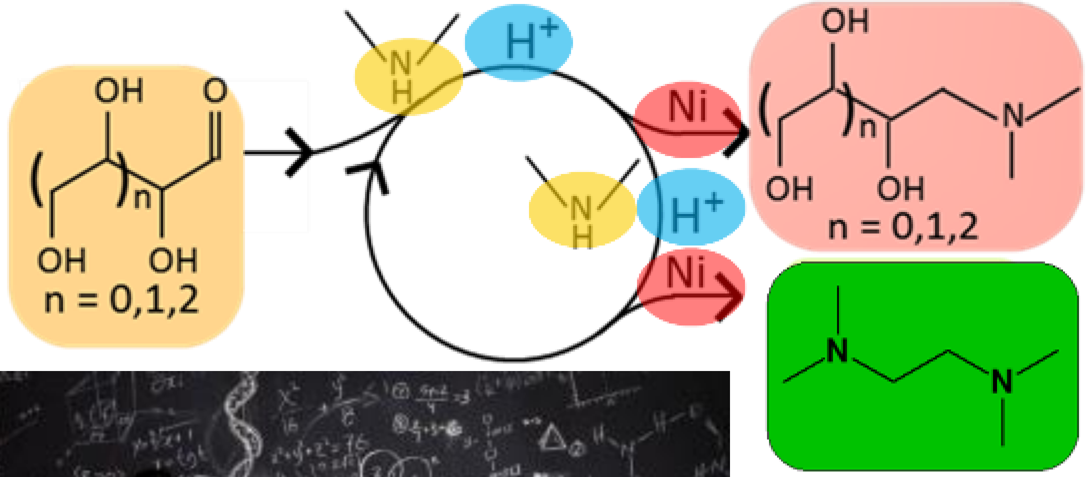
kinetic model construction

- reaction network – 3 types of catalysis
- model equations
- kinetic parameters and interpretation
- model performance

industrial reactor simulation

conclusions





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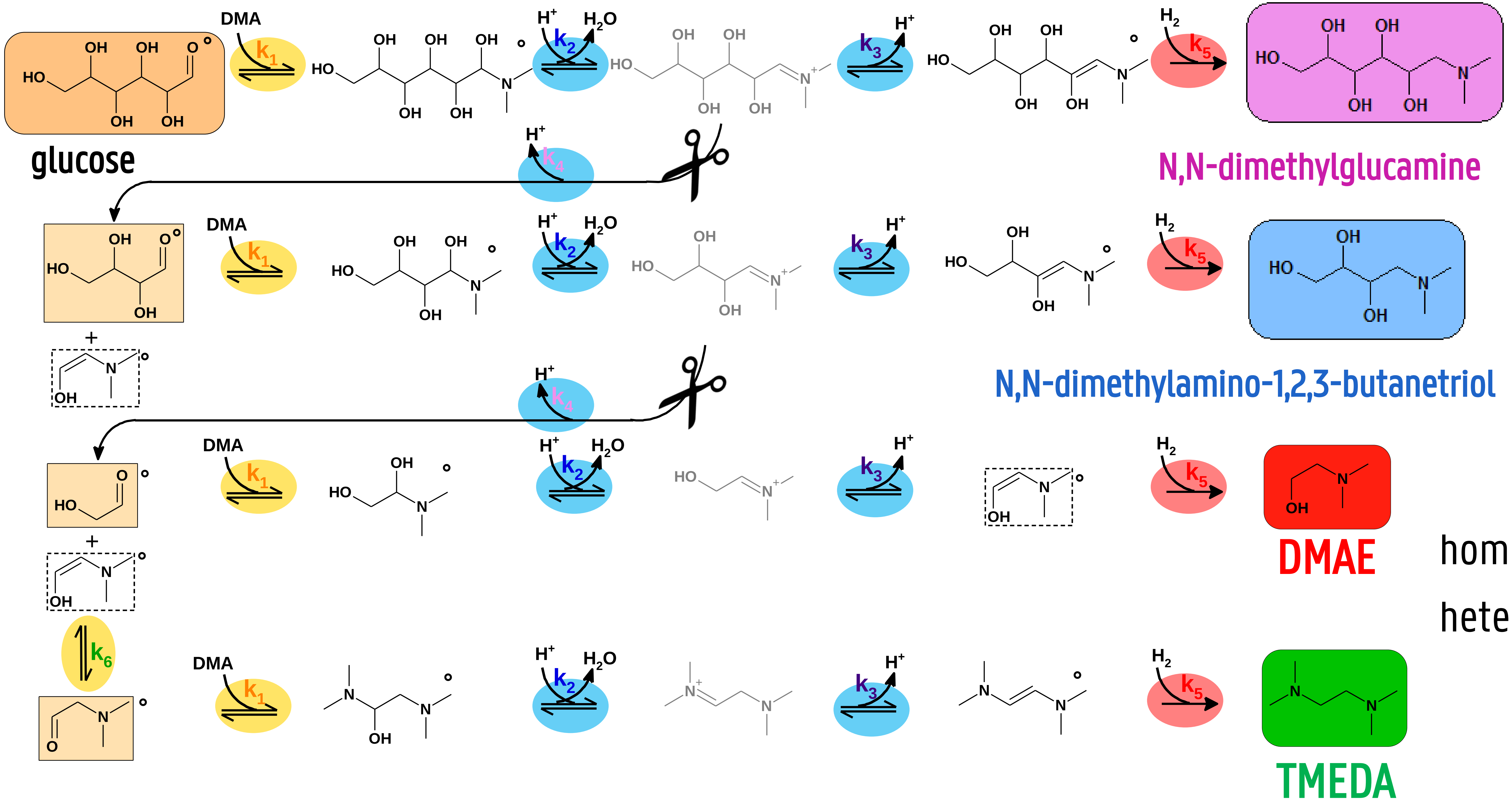
# reaction network



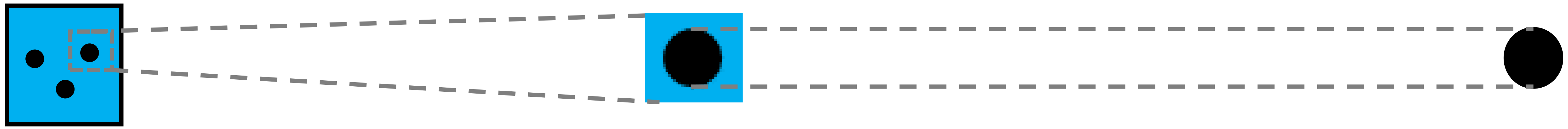
1. amination step
2. iminium ion formation
3. enamine rearrangement
4. retro-aldol
5. enamine hydrogenation
6. keto-enol tautomerism
7. degradation °

homogeneous catalysis: base

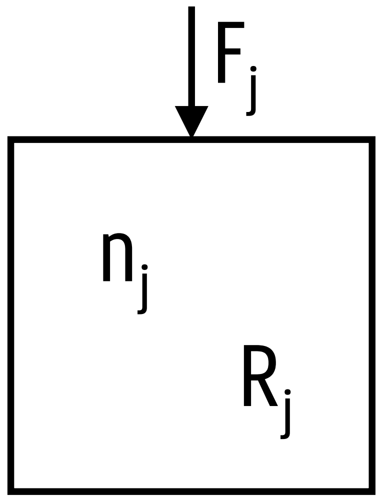
heterogeneous catalysis: metal

acid

# model equations



## fed batch reactor



## rate equations

$$r_1 = (k_1 a_{DMA}^2 a_{glucose} - k_{-1} a_{DMA} a_{hemi,C_6})\varepsilon$$

$$r_2 = (k_2 \theta_{\lozenge,hemiC_6} - k_{-2} \theta_{\lozenge,imC_6^+} a_{H_2O})\frac{W_{cat}}{V_r}$$

$$r_3 = (k_3 \theta_{\lozenge,imC_6^+} - k_{-3} \theta_{\lozenge,enamC_6})\frac{W_{cat}}{V_r}$$

$$r_4 = k_4 \theta_{\lozenge,imC_6^+} \frac{W_{cat}}{V_r}$$

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

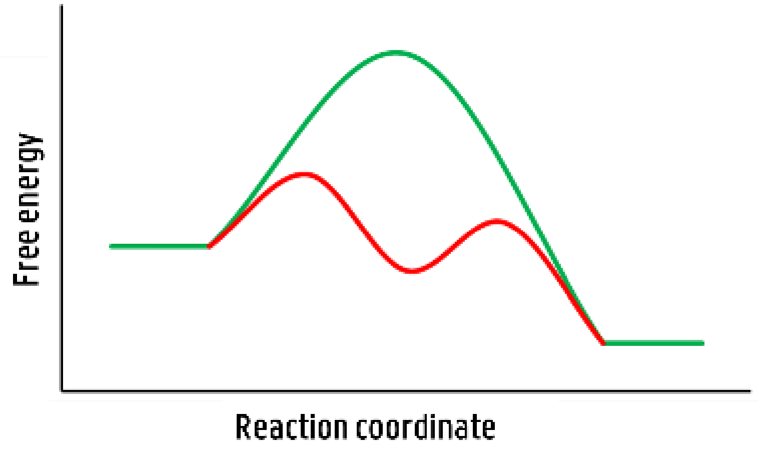
$$r_6 = (k_6 a_{enamC_2} a_{DMA} - k_{-6} a_{C_4H_9NO} a_{DMA})\varepsilon$$

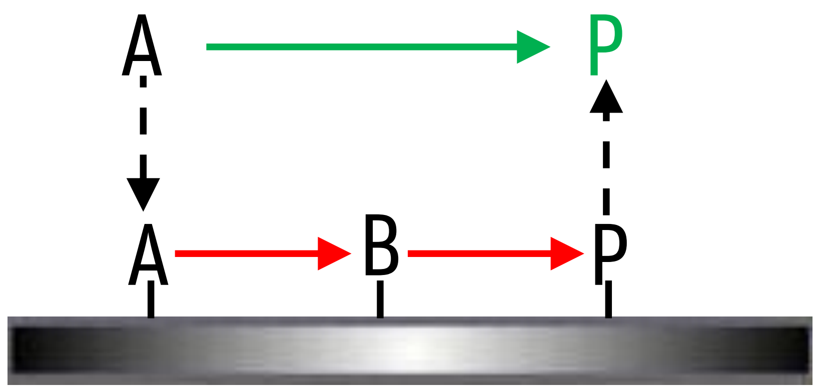
$$r_7 = k_7 a_{glucose}\varepsilon$$

$$k_i = k_{T_{ave},i} \exp\left(-\frac{E_{a,i}}{R}\left(\frac{1}{T} - \frac{1}{T_{ave}}\right)\right)$$

$$R_j = f(r_j)$$

## site balances





$$\theta_A = K_{ads,A} a_A \theta_\lozenge$$

$$\theta_\lozenge + \sum_{i=C_2,C_4,C_6} (\theta_{hemi,i} + \theta_{im,i} + \theta_{enam,i}) = 1$$

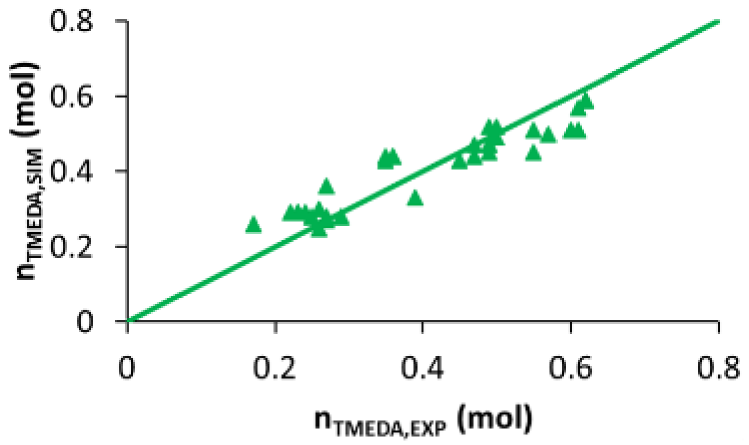
$$\theta_H = \sqrt{K_{ads,H_2} a_{H_2}}\,\theta_*$$

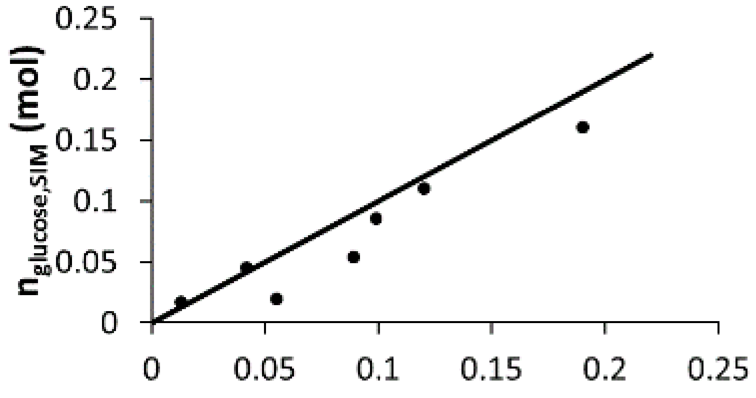
$$\theta_* + \theta_H = 1$$

# kinetic parameters

| Estimated average rate coefficient | | | | Estimated activation energy ( kJ mol$^{-1}$) | | |
|---|---|---|---|---|---|---|
| $k_{Tave,1}$ | $6.3\ 10^{-10}$ | $\pm 0.5\ 10^{-10}$ | $m^6_L\ mol^{-2}\ s^{-1}$ | $E_{a,1}$ | 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 |
| $k_{Tave,6}$ | $8.9\ 10^{-4}$ | $\pm 1.2\ 10^{-4}$ | $m^3_L\ mol^{-1}\ s^{-1}$ | $E_{a,6}$ | 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 ($m^3_L\ mol^{-1}$) | | | 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 |





all parameters significant ✓

→ 0 not included in any confidence interval

global regression significant ✓

→ $F = 160$, $F_{tab} = 2.79$

all parameters uncorrelated ✓

→ highest binary correlation coefficient 0.8

# interpretation of the kinetic model

| Estimated average rate coefficient | | | | Estimated activation energy ( kJ mol$^{-1}$) | | |
|---|---|---|---|---|---|---|
| $k_{Tave,1}$ | $6.3\ 10^{-10}$ | $\pm\ 0.5\ 10^{-10}$ | $m^6_L\ mol^{-2}\ s^{-1}$ | $E_{a,1}$ | 78.1 | ± 7.2 |
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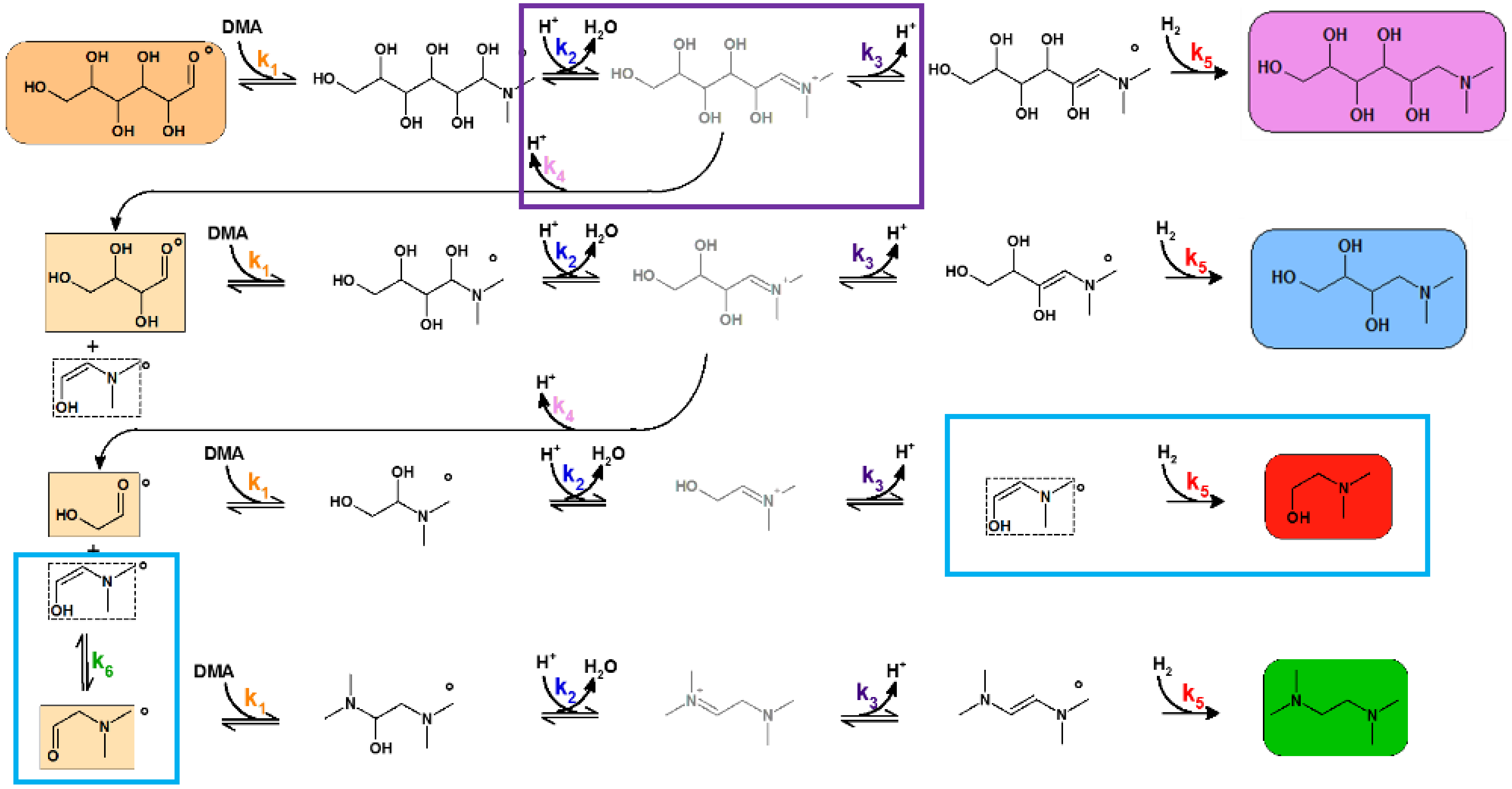
| $K_{Tave,H2}$ | 1.1 | ± 0.3 | $-\Delta H_{ads,H2}$ | -2.9 | ± 0.3 |



- higher temperatures required to favor retro-aldol cleavage
- $E_{a,4}$ lower than expected (± 110 kJ mol$^{-1}$), after prior amination
- no selectivity tuning between DMAE to TMEDA by adapting temperature
- very good temperature control required to avoid degradation

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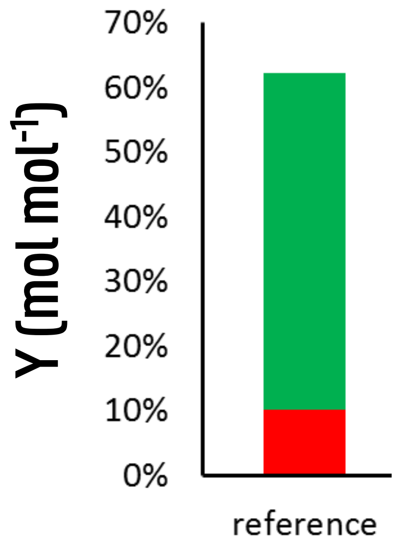
# model simulations

### reference

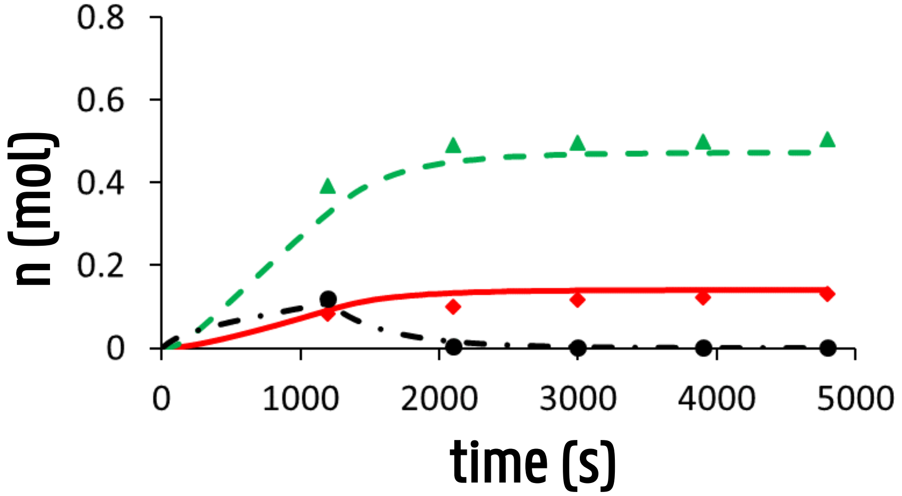
T = 398 K

p = 7.5 MPa

$n_{glucose}^{0}$ = 0.4 mol



### lower pressure (p = 6.0 Mpa)



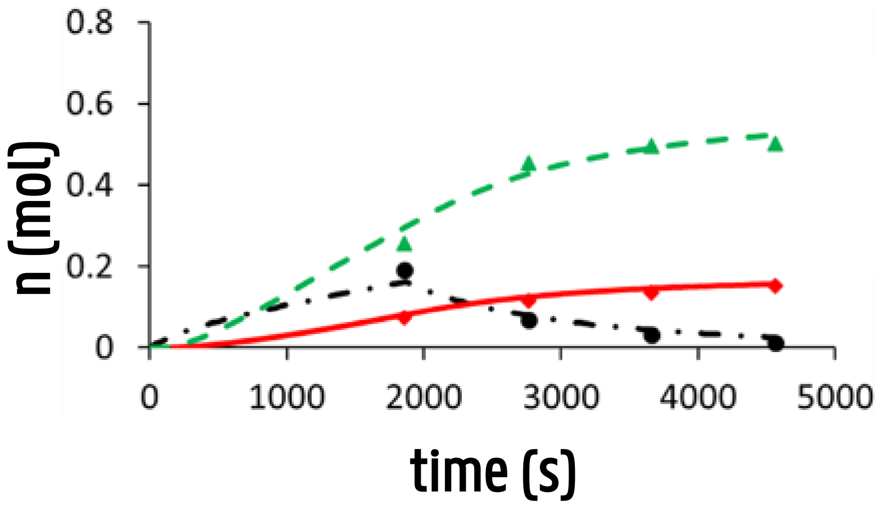
→ lower TMEDA yield

→ more pronounced degradation

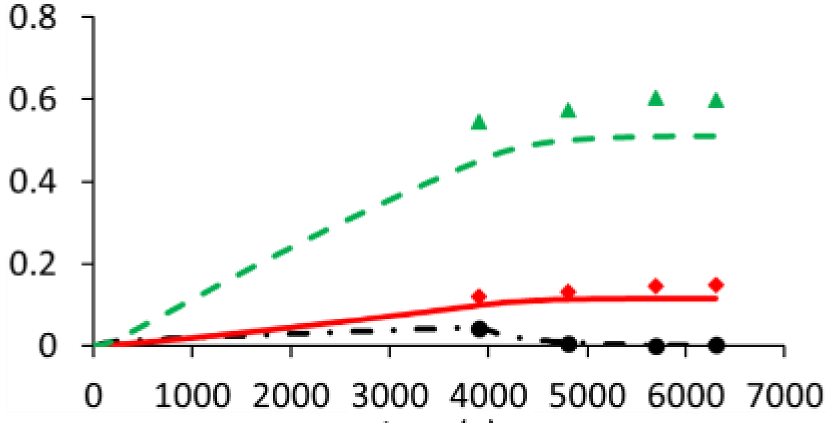
### lower temperature (T = 383 K)

→ lower TMEDA yield

→ glucose conversion slower: conversion kinetics properly captured



### lower feed rate ($t_0$ = 3900 s)



→ lower TMEDA to DMAE ratio

→ lower feed rate equivalent to higher $W_{cat}$

◆ DMAE (exp) ▲ TMEDA (exp) ● Glucose (exp)

— DMAE (mod) – – TMEDA (mod) –· Glucose (mod)

# kinetic model: conclusions

physically relevant, statistically and globally significant kinetic model

- accurate simulation of experimental data
- mathematical confirmation that retro-aldol occurs at lower temperatures than expected ✂
- too high temperatures lead to excessive degradation
- tuning the selectivity between DMAE and TMEDA is not possible by changing the temperature

# overview

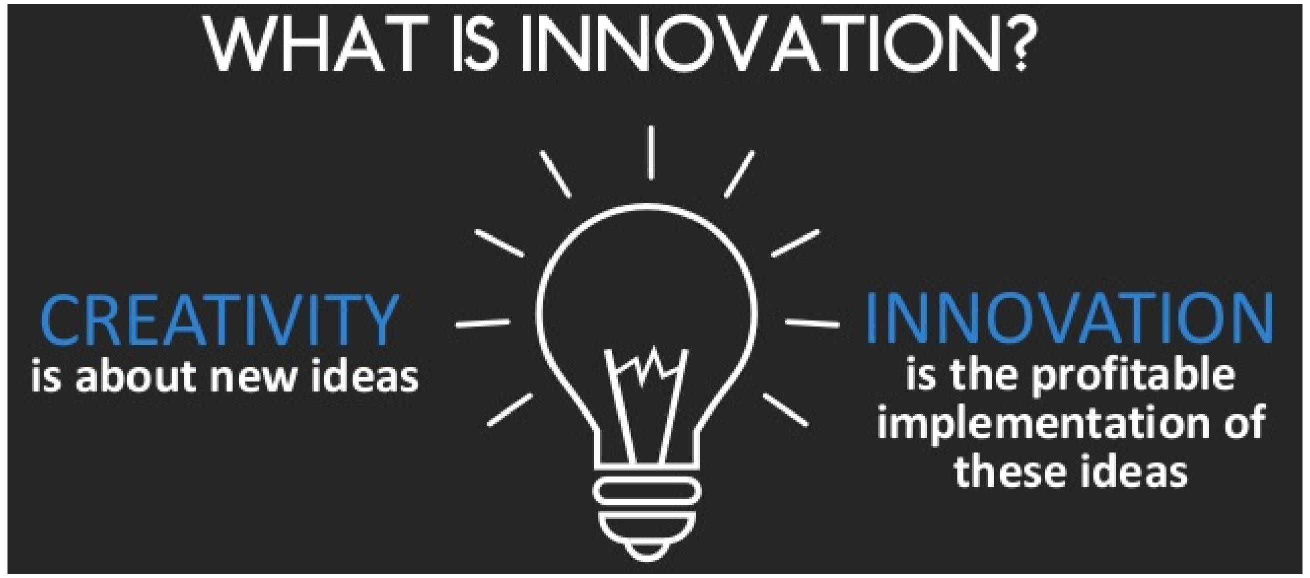
experimental assessment

kinetic model construction

industrial reactor simulation

- jet loop reactor
- trickle bed reactor

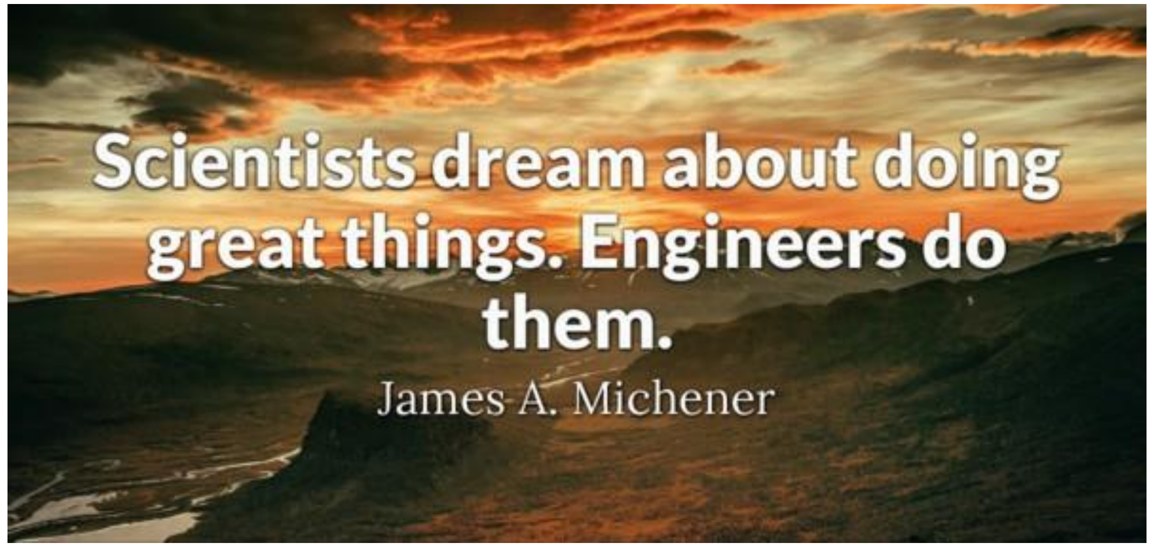
conclusions



WHAT IS INNOVATION?

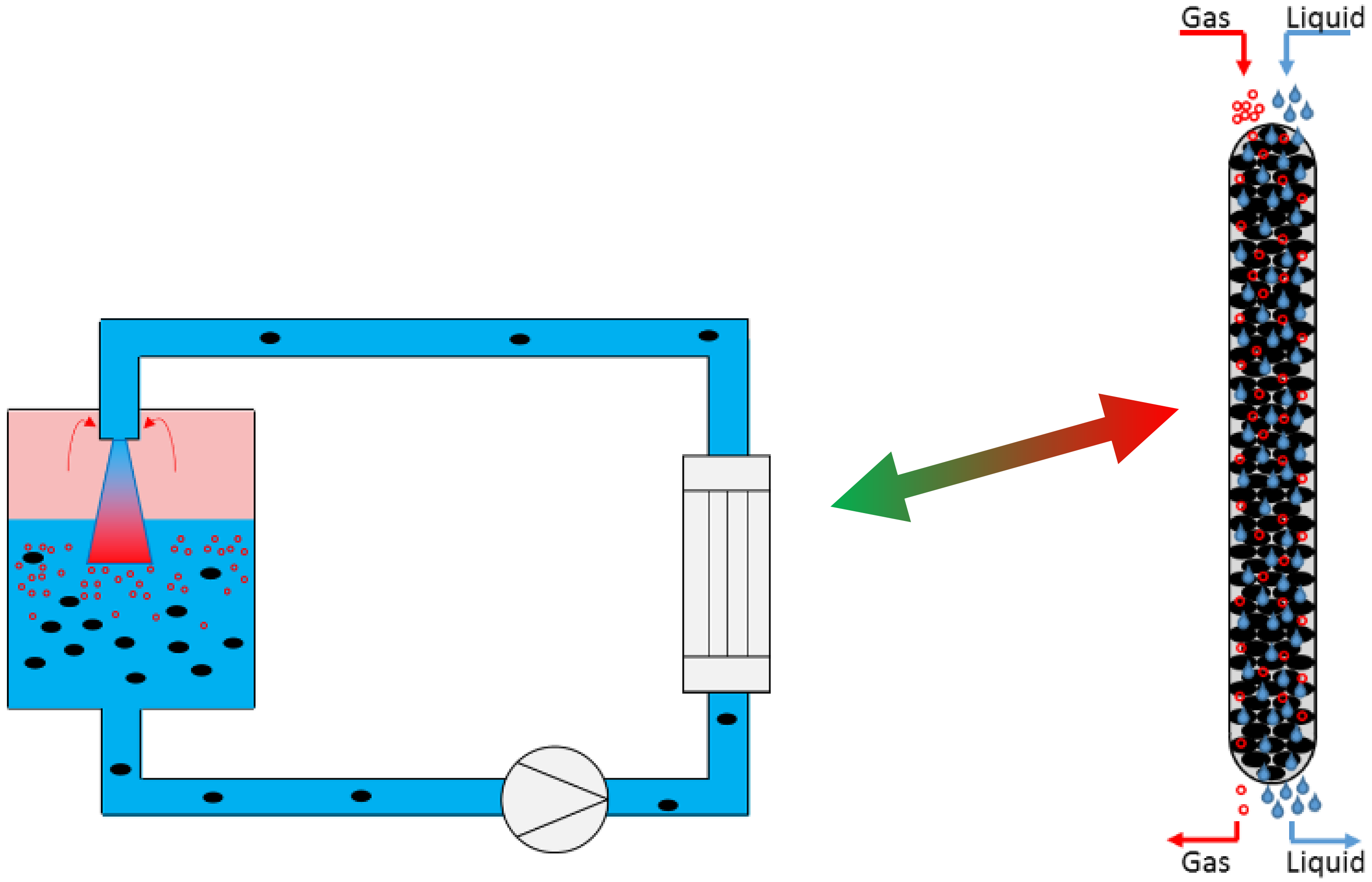
CREATIVITY is about new ideas

INNOVATION is the profitable implementation of these ideas



Scientists dream about doing great things. Engineers do them.

James A. Michener



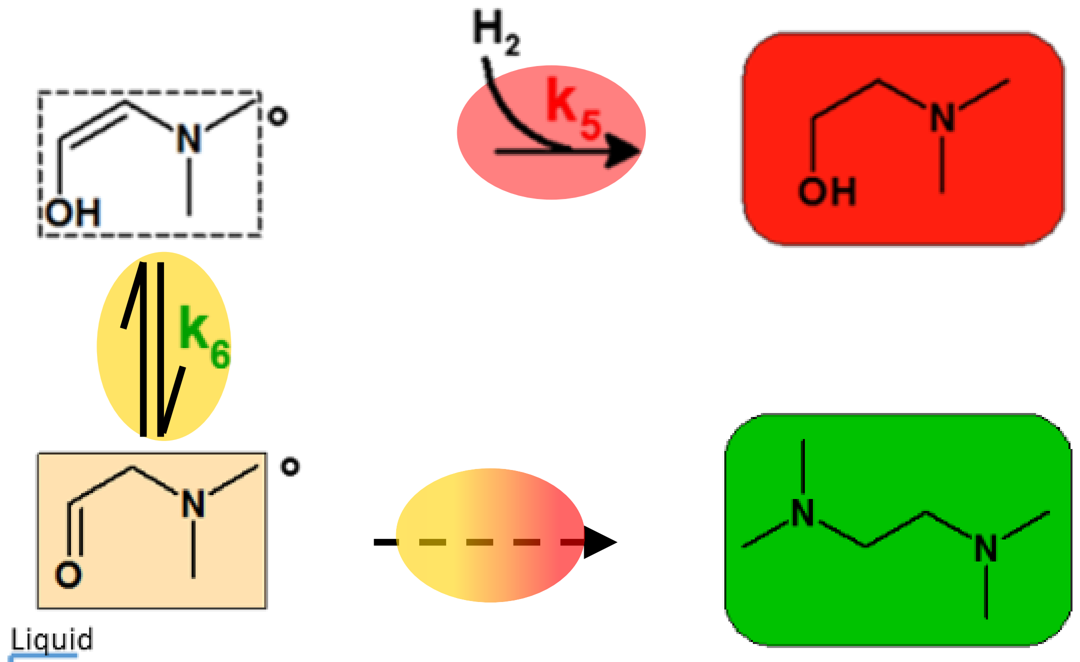
# two distinct reactor models

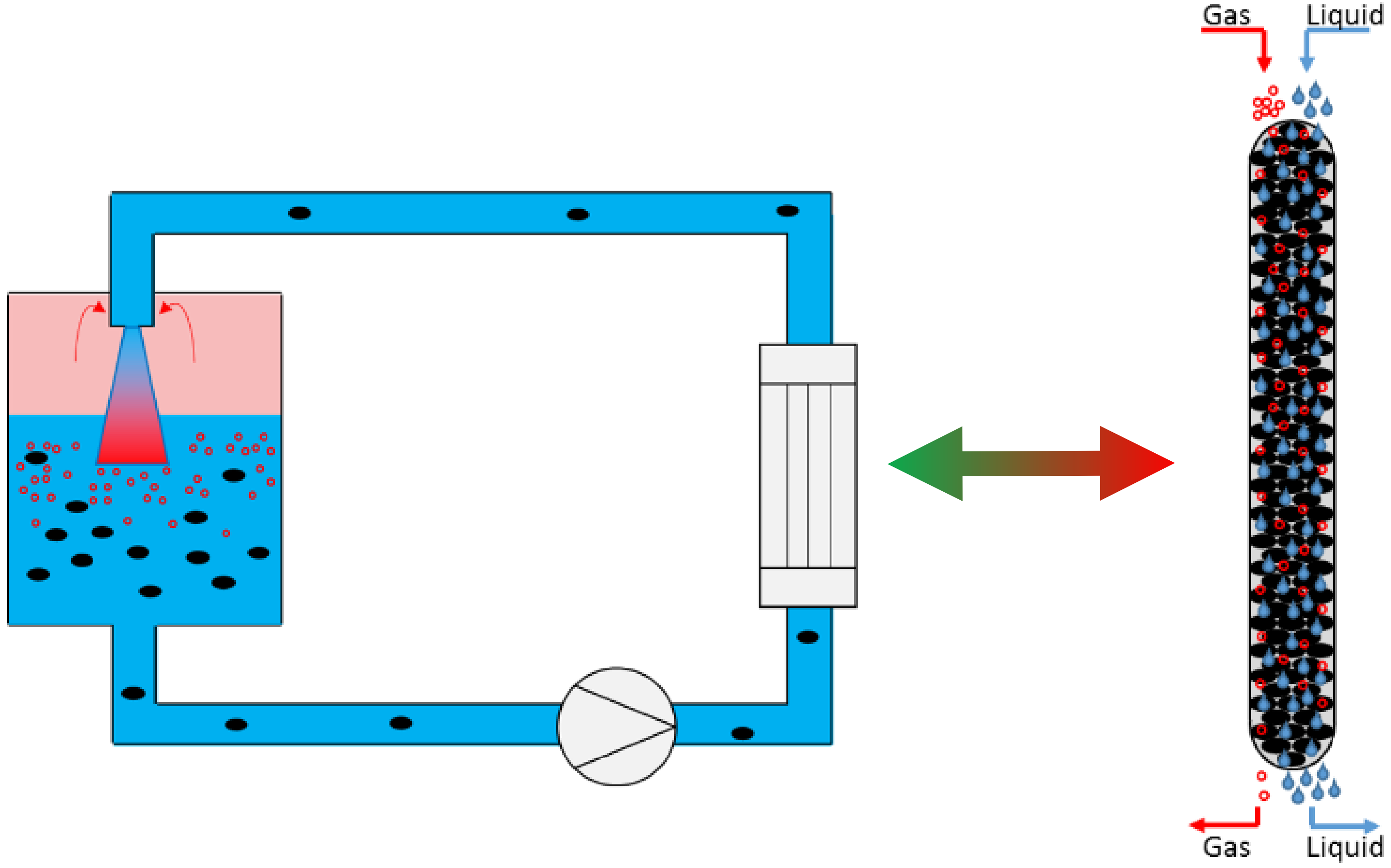
**why assess two completely different reactor models?**

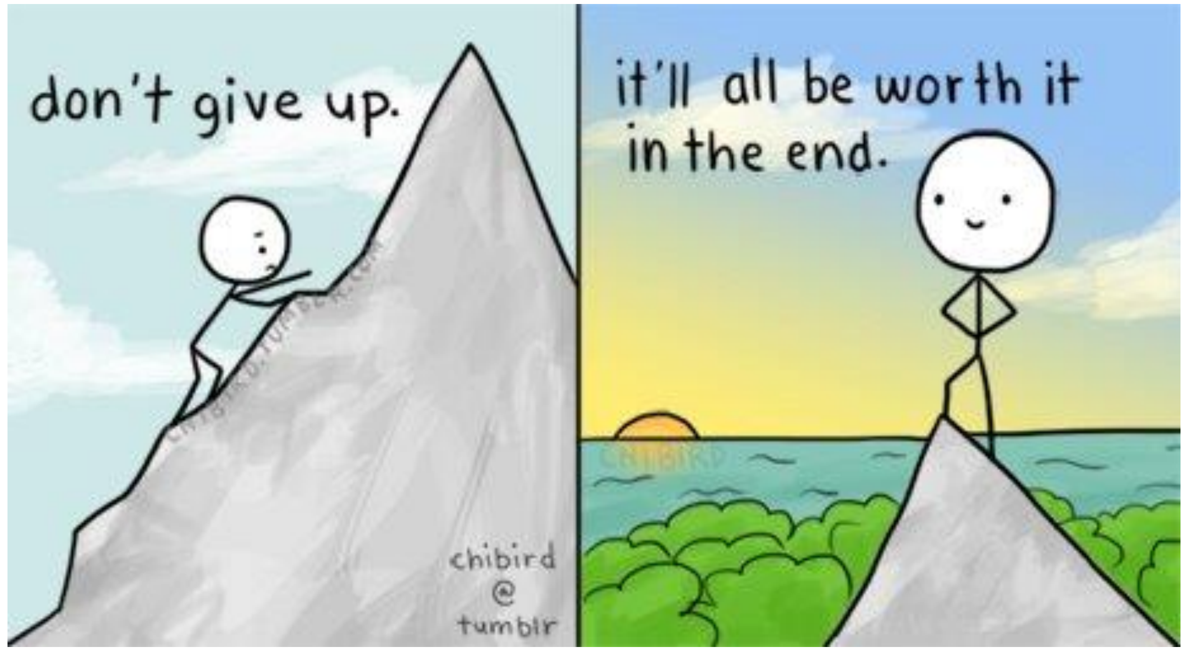
TMEDA always main product, but what if DMAE is desired?

kinetic model: no tuning possible by adapting the temperature

heterogeneously catalyzed vs homogeneous key reaction steps







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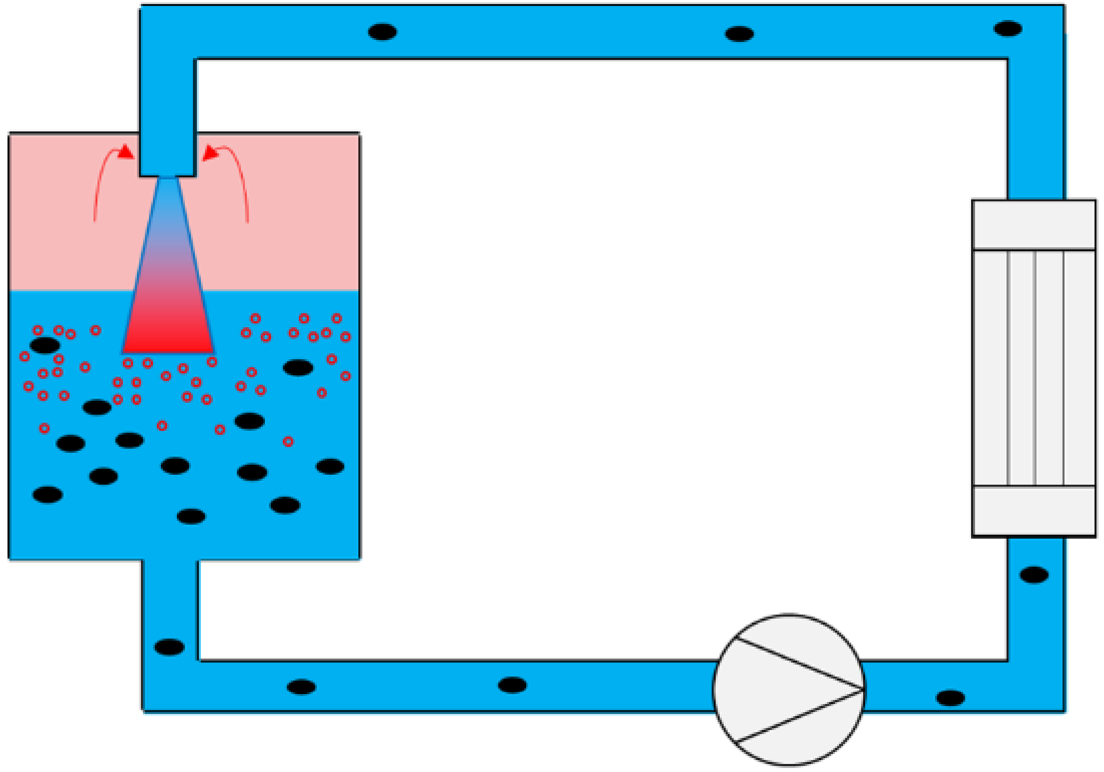
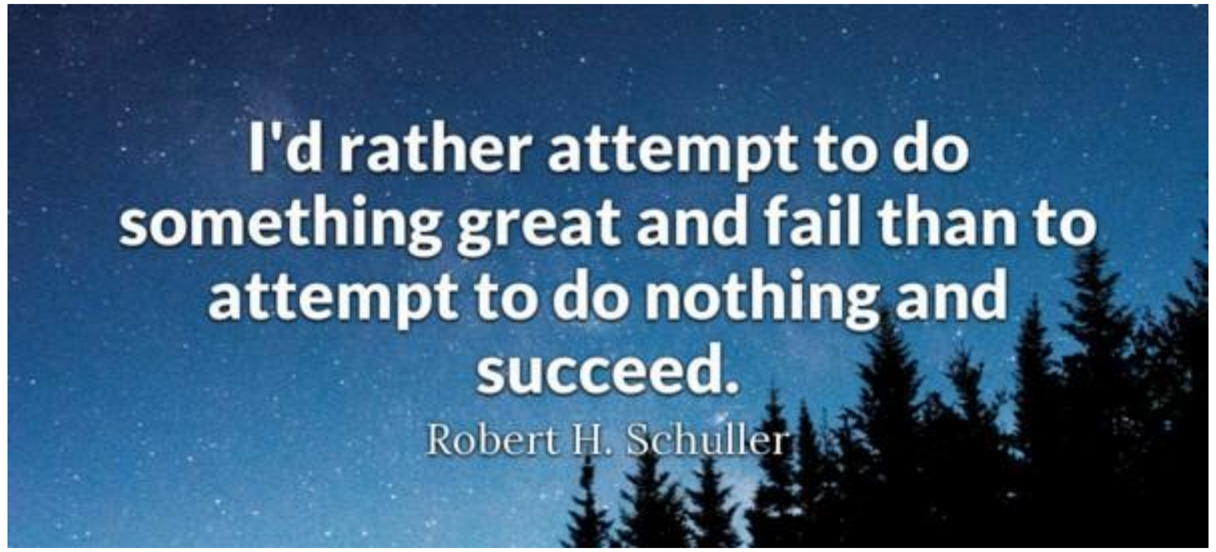
# jet loop reactor



## low catalyst-to-liquid ratio reactor

- reactor vessel + tubing continuous recycle of liquid phase
- heat exchanger built in the loop: ensure temperature control
- overall batch operation
- jet injector: efficient gas-liquid mixing
- catalyst flows along with liquid phase

→ goal: maximize TMEDA yield



I'd rather attempt to do something great and fail than to attempt to do nothing and succeed.

Robert H. Schuller

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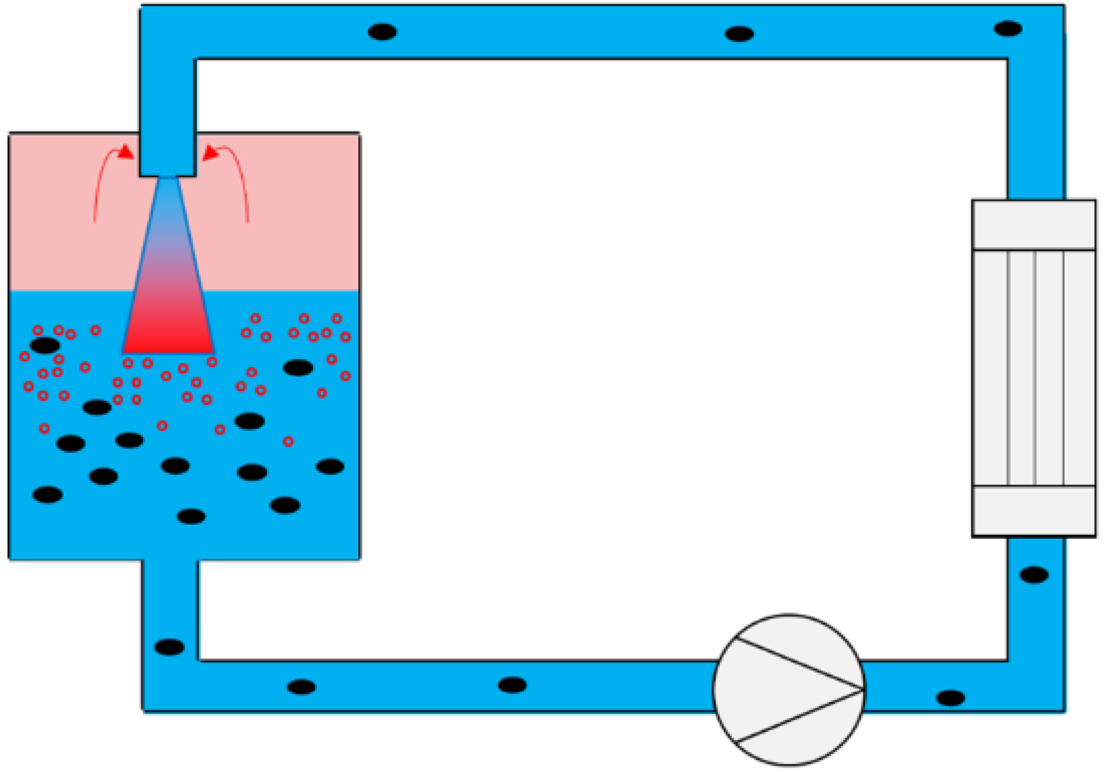
# glucose aminolysis product yields in the jet loop reactor



**operating conditions**

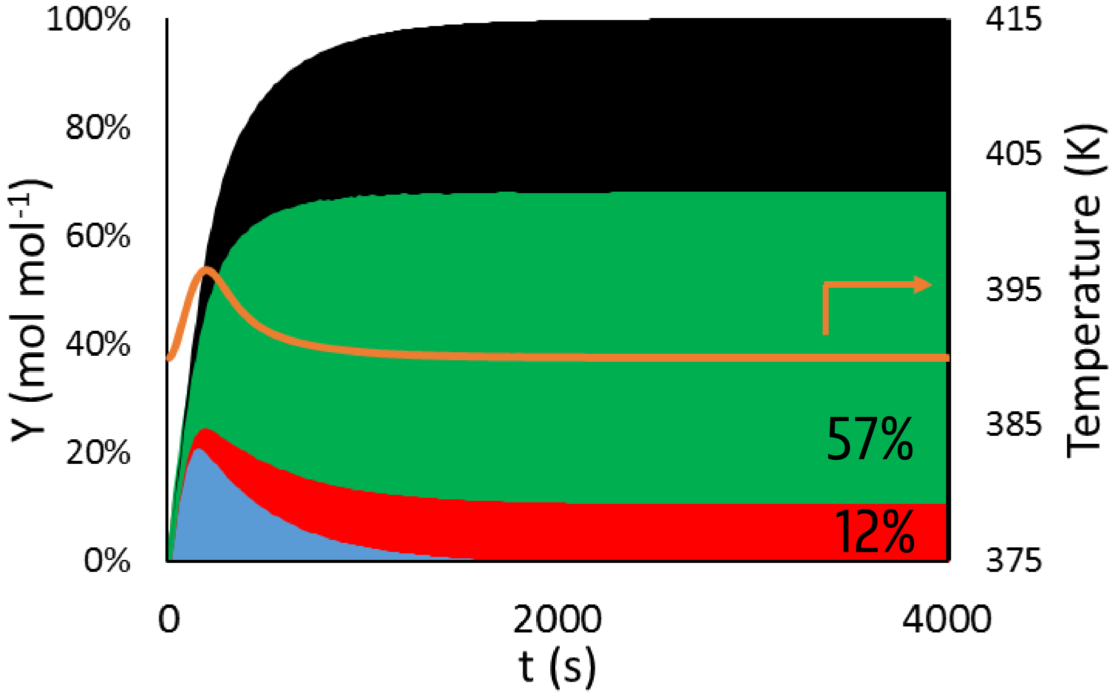
$W_{cat}$ = 35 $kg_{cat}$

$n_{DMA}/n_{glucose}$ = 40 $mol\ mol^{-1}$

$m_{glucose}$ = 153 kg

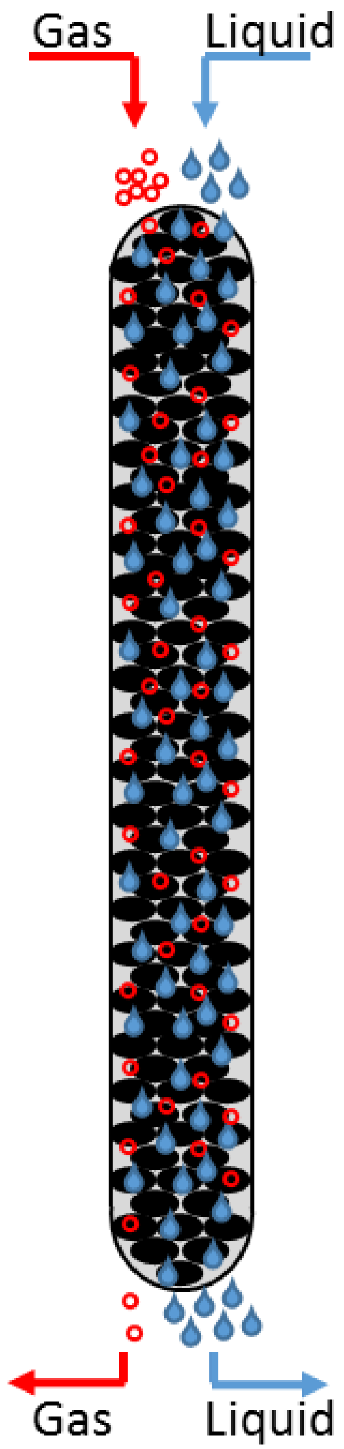
$T_0$ = 390 K

p = 7.5 MPa



- TMEDA main product with yields comparable to the lab scale batch
- good temperature control is ensured by the heat exchanger

# trickle bed reactor



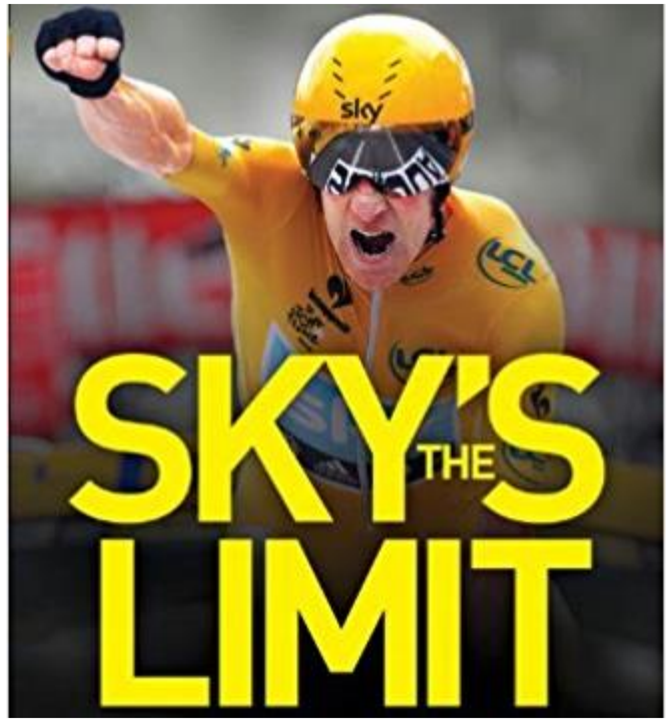
high catalyst-to-liquid ratio reactor

- catalyst located in a fixed bed in the reactor
- low flow rates of gas and liquid ‘trickle’ down the reactor
- interphase mass transfer main issue

→ goal: optimize DMAE yield

→ challenges:

  - control the temperature
  - optimize gas-liquid transfer to enhance DMAE yield might be very tricky



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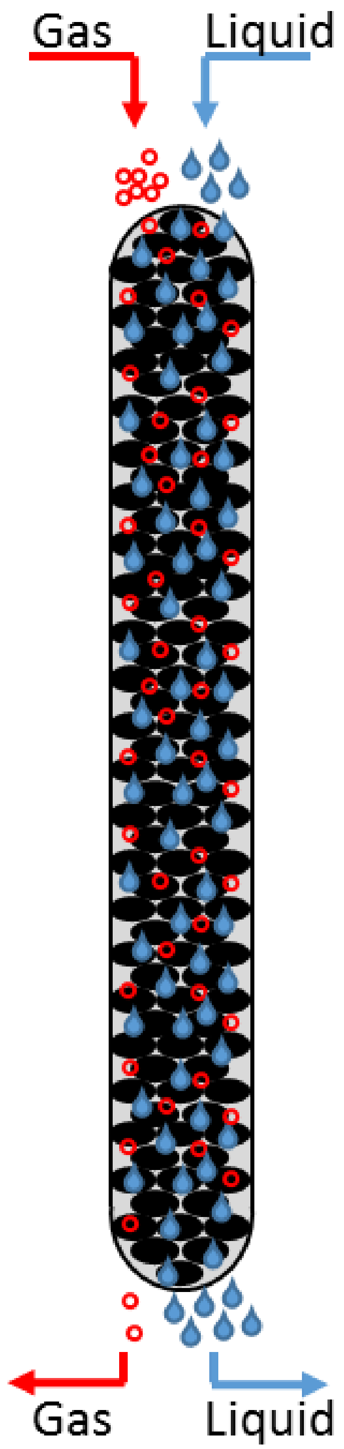
# glucose aminolysis product yields in the trickle bed reactor



**operating conditions**

$V_{TBR}$ = 235 x $10^{-4}$ $m^3$

$W_{cat}$ = 0.25 kg

$F_{DMA}$ = 3.0 x $10^{-4}$ mol $s^{-1}$

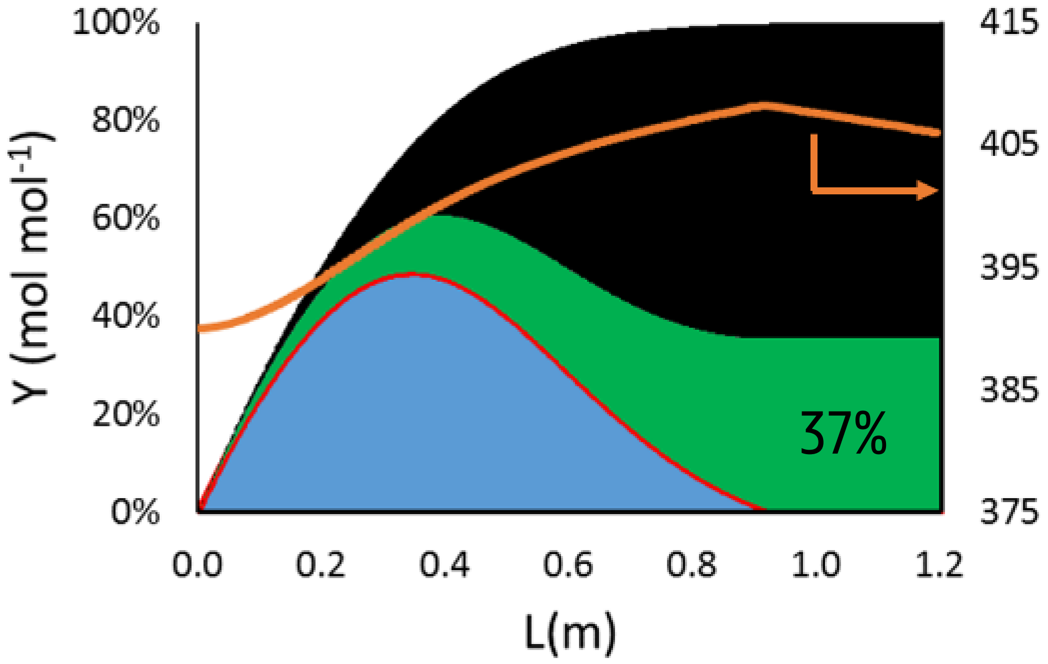
$F_{glucose}$ = 2.6 x $10^{-6}$ mol $s^{-1}$

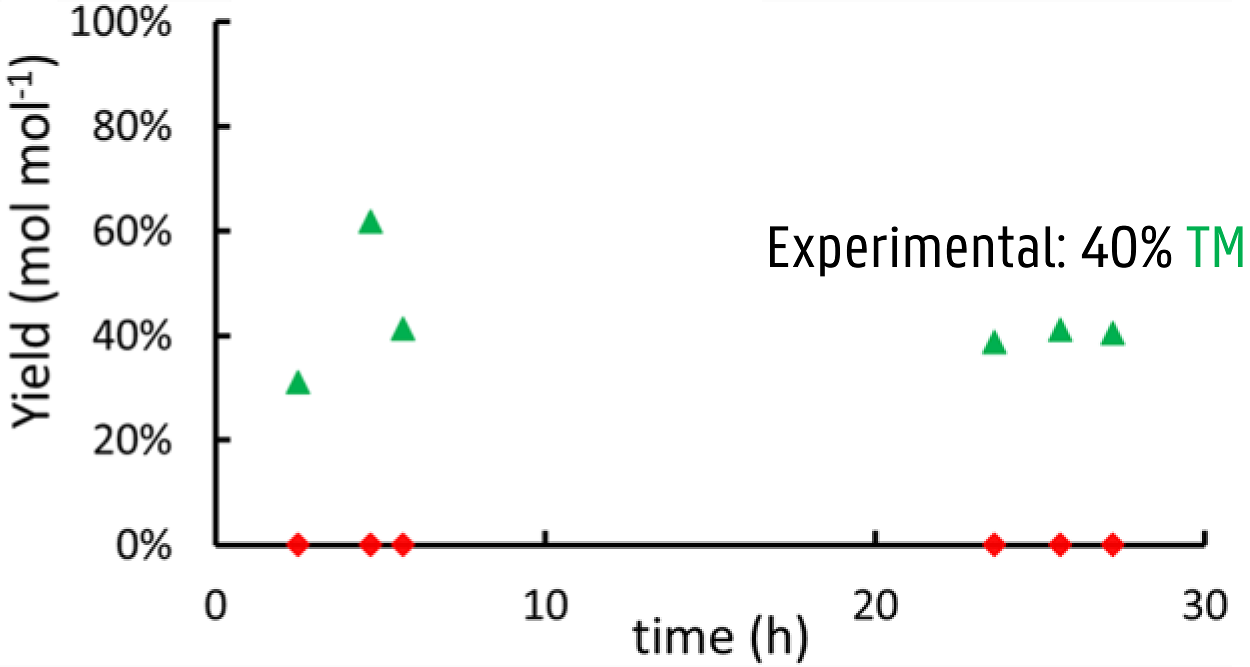
$F_{H2O}$ = 5.1 x $10^{-5}$ mol $s^{-1}$

$F_{H2}$ = 3.1 x $10^{-4}$ mol $s^{-1}$

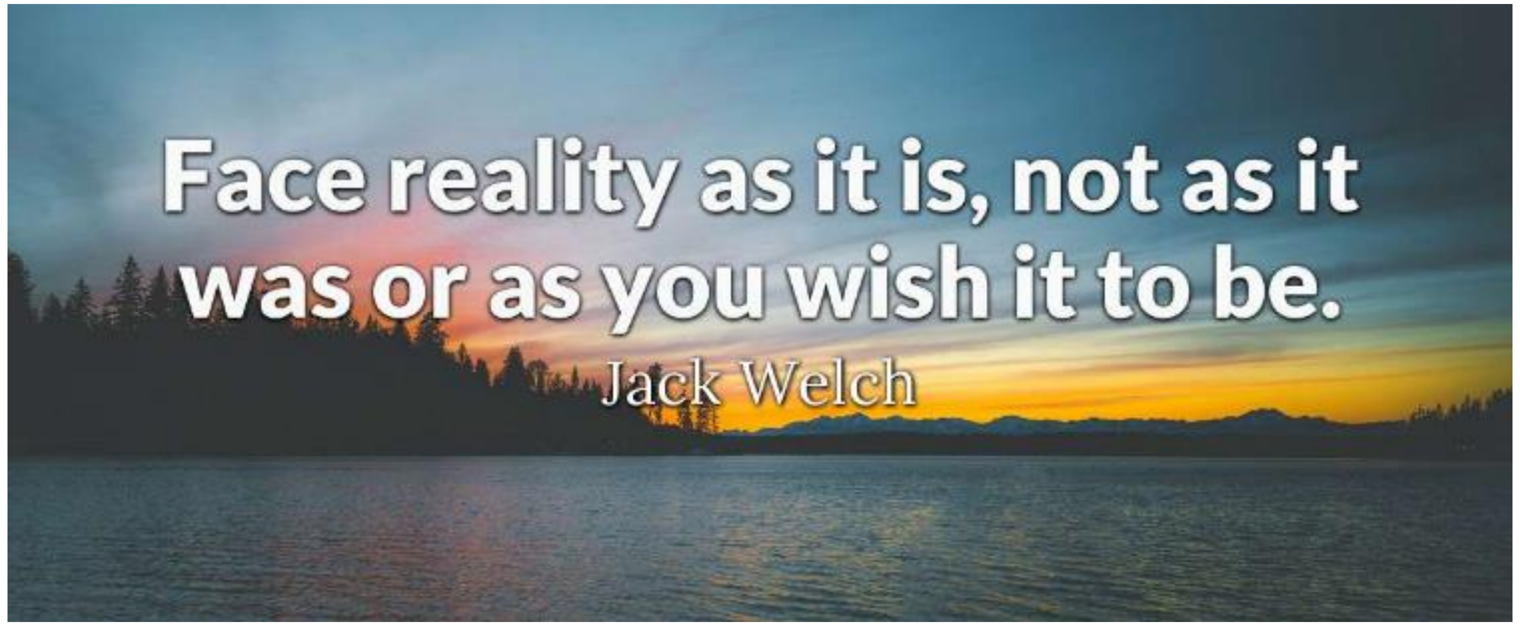
$T_0$ = 390 K

$p_{tot}$ = 7.5 MPa





Experimental: 40% TMEDA



Face reality as it is, not as it was or as you wish it to be.

Jack Welch

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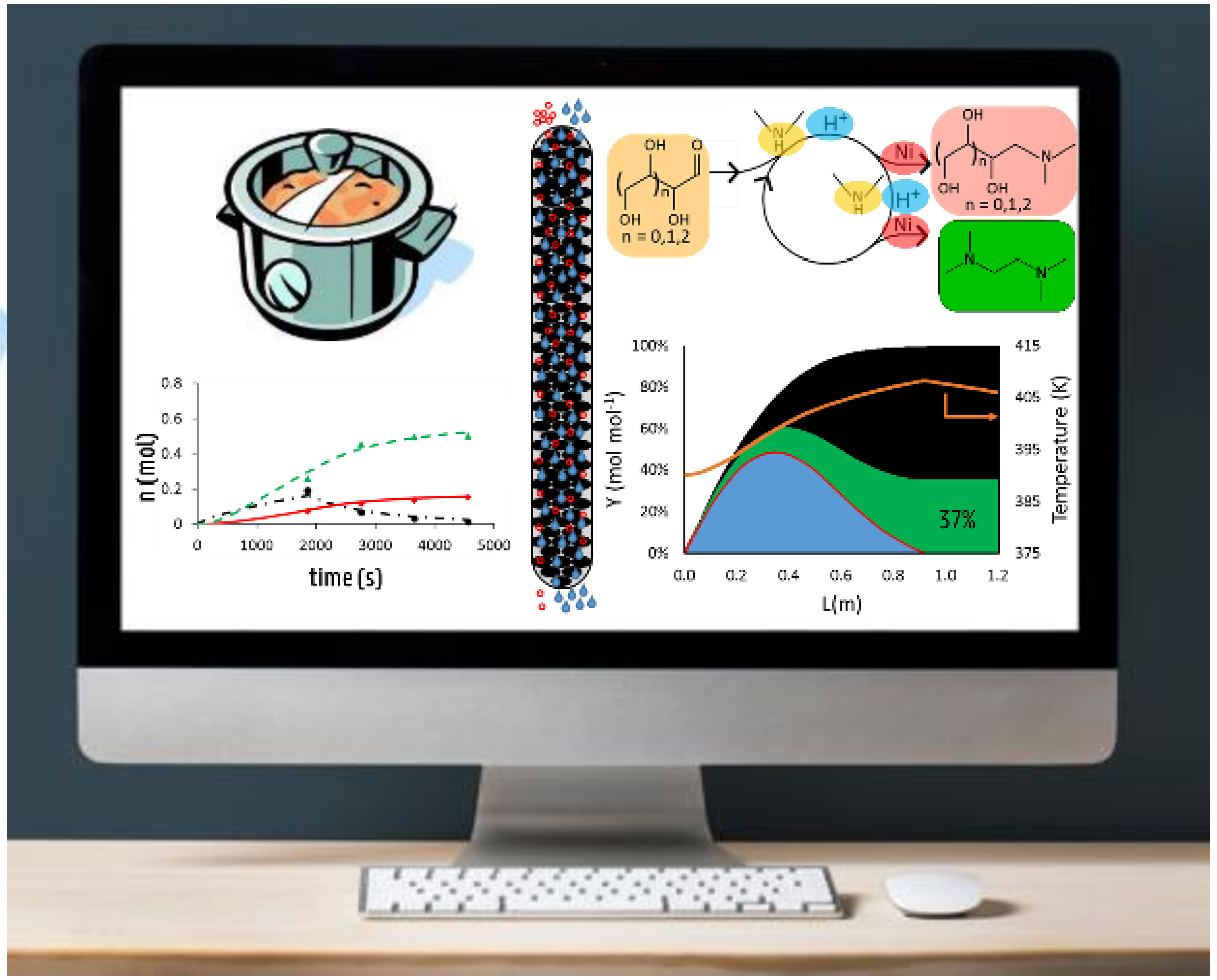
# overview

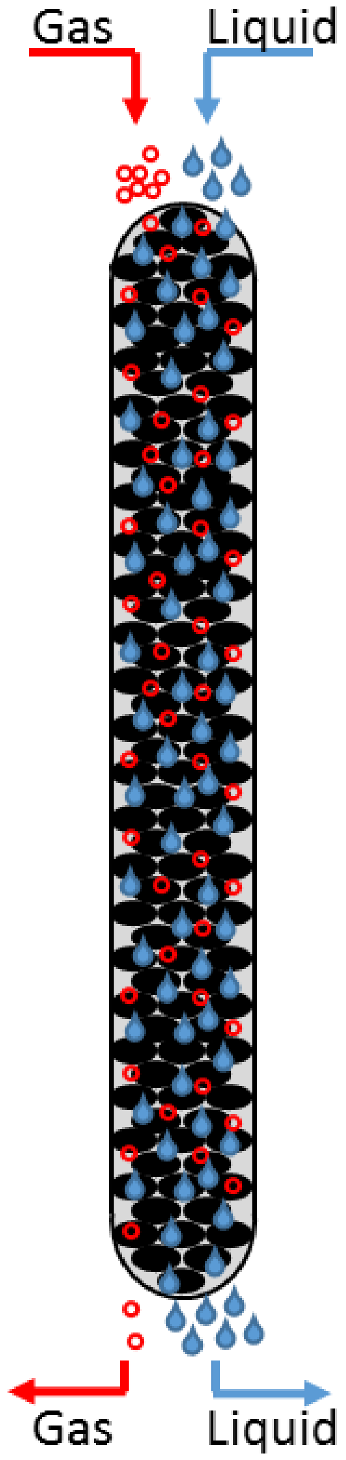
experimental assessment

kinetic model construction

industrial reactor simulation

conclusions





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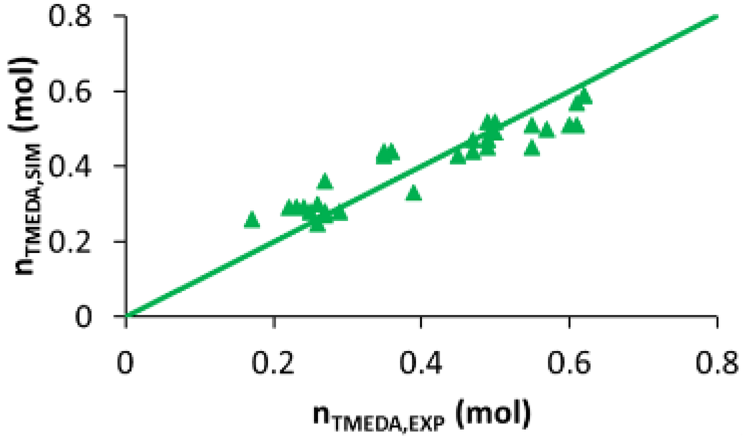
# conclusions

## experimental assessment glucose reductive aminolysis

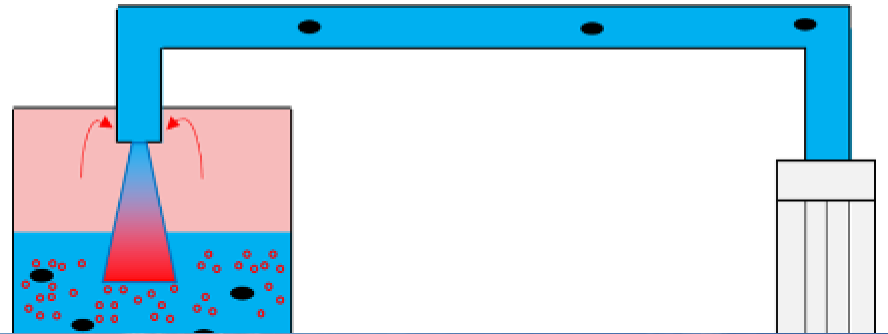
- 3 types of catalysis
- two main products: DMAE and TMEDA



## significant, statistically and physically relevant kinetic model

- a prior amination reduces the activation energy for retro-aldol cleavage

## industrial reactor simulation



- jet loop reactor (low catalyst-to-liquid): TMEDA main product

  → tuning between DMAE and TMEDA main challenge
- trickle bed reactor (high catalyst-to-liquid): TMEDA main product

  → temperature control and optimization of gas-liquid mass transfer main challenges

# Acknowledgments

this work was supported by:

- the 'Long Term Structural Methusalem Funding by the Flemish Government'.
- the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013) / ERC grant agreement n° 615456.
- Flanders Innovation & Entrepeneurship VLAIO(IWT), via the intermediary of FISCH/CATALISTI  contract 145020 – Carboleum

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