Thermodynamics of Enzymatic Resorcinol Carboxylation Utilizing CO_2 from Amine Scrubbing

TECHNISCHE BIOKATALYSE TUHH

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Introduction

- The carboxylation of resorcinol to 2,6-dihydroxybenzoic acid (2,6-DHBA) is performed by the 2,6-DHBA decarboxylase (2,6-DHBD)
- In the carboxylation dissolved CO_2 is utilizated
- 2,6-DHBA is used in a wide range of industrial, pharmaceutical and agricultural applications (Durairaj, 2005)

Aim

- Combination of CO_2 scrubbers and biocatalytic carboxylation
- Reaction optimization in aqueous triethanolamine (TEA) solution
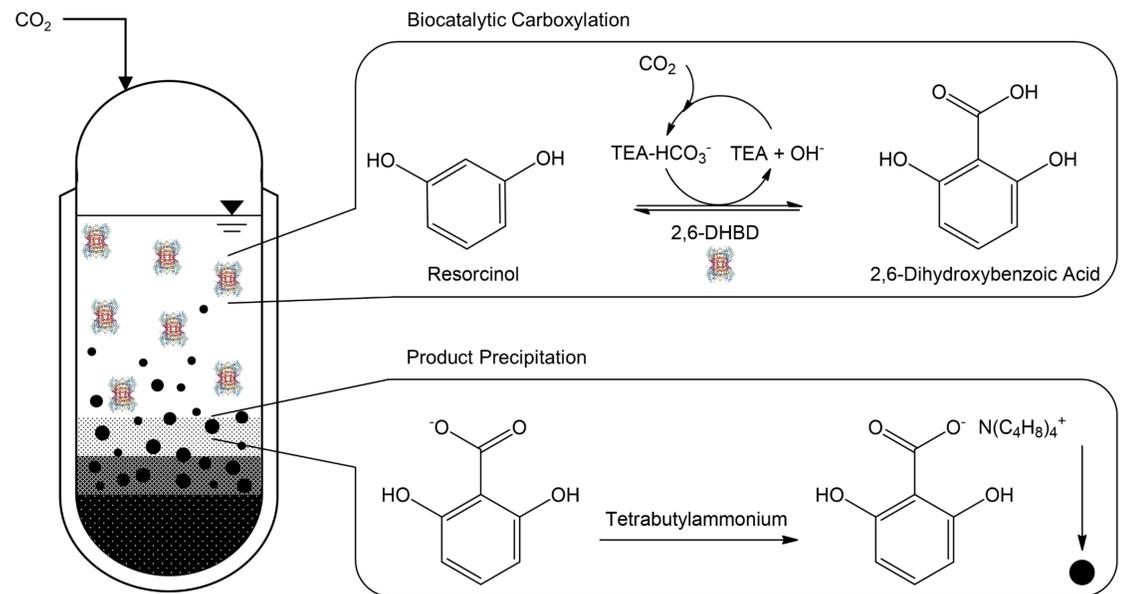- Assessing an *in situ* product removal approach

Fig. 1: Enzymatic carboxylation of resorcinol towards 2,6-dihydroxybenzoic acid in aqueous triethanolamine for efficient utilization of CO_2 with additional *in situ* product precipitation by tetrabutylammonium.

Biocatalytic Carboxylation

- Equilibrium yield experiments revealed the optimal TEA content
- Highest yield is reached at 50% (v/v) aqueous TEA
- The optimum correlates to the CO_2 loading capacity of TEA
- Varying the substrate ratio, the experimental data is fitted to the equilibrium constant K_{eq}
- Calculated K_{eq} of 5.83×10^{-4} mM^{-1}

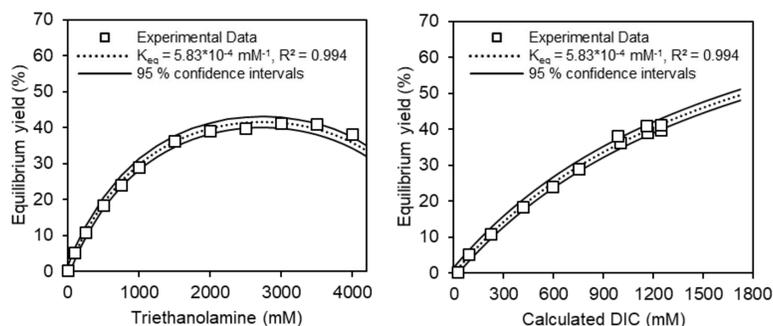$$K_{eq} = \frac{c_{DHBA,eq}}{c_{resorcinol,eq} \cdot c_{C1-substrate,eq}}$$

Fig. 2: Comparison between experimental and calculated equilibrium yields for the triethanolamine (TEA) and dissolved inorganic carbon (DIC) dependencies. Reaction conditions: CO_2 presaturation of TEA solution with subsequent addition of resorcinol and 2,6-DHBD to final concentrations of 80 mM and 0.38 mg/ml, respectively. Incubation at 30°C for 24 h and 48 h in a closed vessel.

CO_2 Loading of Triethanolamine

- Dissolved inorganic carbon concentration (DIC) is proportional to TEA concentration
- TEA-DIC correlations from literature reveal:
  - Highest (DIC) at 50% (v/v) TEA
  - Maximal CO_2 loading of 0.92 mol CO_2 per mol TEA at 30 °C
- TEA is a tertiary amine, which reacts with OH$^-$ and CO_2 to form bicarbonate
  - $DIC = CO_2 \; loading \cdot c_{TEA}$
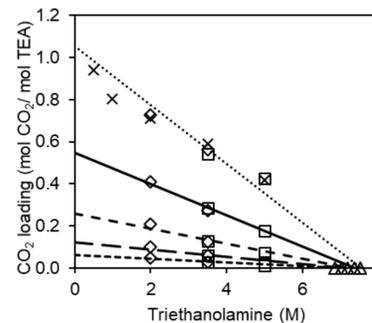

Fig. 4: Solubility of CO_2 in aqueous triethanolamine solutions at 100 kPa CO_2 partial pressure shown as CO_2 loading.
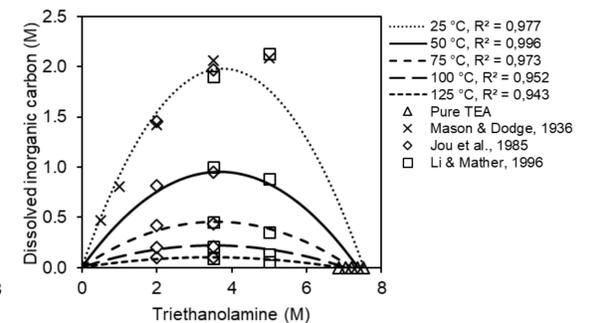
Fig. 5: Solubility of CO_2 in aqueous triethanolamine solutions at 100 kPa CO_2 partial pressure shown as dissolved inorganic carbon concentration (DIC).
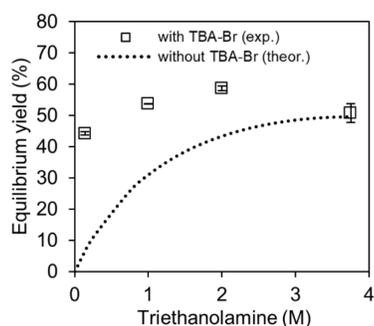
Product Precipitation

Fig. 3: Equilibrium yield for the carboxylation of 80 mM resorcinol in CO_2-sat. TEA by 0.378 mg/ml 2,6-DHBD at 30 °C after 24 h with and without 350 mM tetrabutylammonium bromide (TBA-Br). Experiments were performed as dublicates.

- Tetrabutylammonium bromide (TBA-Br) precipitates resorcinol and 2,6-DHBA
- Enhanced equilibrium yield below 50% (v/v) TEA
- Diminishing precipitation effect at increasing TEA concentration
- Possible method for product purification and recycling of TEA

Summary

- CO_2 loading capacity correlations of TEA fit to the thermodynamic data
- 50% maximum yield limitation when performing the reaction at 1 bar
- Utilization of TBA-Br achieved a partial *in situ* product precipitation improving achievable yields significantly
- Precipitation effect is diminished at high TEA concentrations

Outlook

- Determination of enzyme kinetics and stability
- High pressure experiments to further improve CO_2 loadings and yields
- Improving *in situ* product removal approach
- Demonstration of product purification and amine recycling

References:
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- J.W. Mason, B.F. Dodge, Equilibrium absorption of carbon dioxide by solutions of the ethanolamines. Doctoral dissertation, New York, 1936.
- F.-Y. Jou, F.D. Otto, A.E. Mather, Equilibria of H_2S and CO_2 in triethanolamine solutions, Can. J. Chem. Eng. 63 (1985) 122–125.
- Y.-g. Li, A.E. Mather, Correlation and Prediction of the Solubility of CO_2 and H_2S in Aqueous Solutions of Triethanolamine, Ind. Eng. Chem. Res. 35 (1996) 4804–4809.

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