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Development of a new reactor concept for oxidation reactions

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Master Thesis

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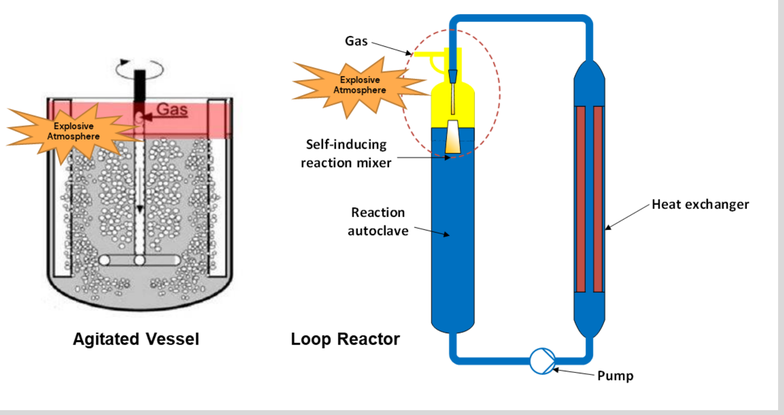
INTRODUCTION

Oxidation reactions comprises an important class of reactions. One key commercial product in DSM – Firmenich' s portfolio contains an oxidation step using 100% O_2. Oxidation reactions are highly exothermic, often operated in an organic solvent. With a possible ignition source, this will lead to a high-risk potential regarding explosion. To obtain a safe process, it is desirable to avoid an explosive atmosphere, but this will cause limitations regarding process temperature and pressure. In reactions with 100% O_2, very high explosion pressures must be expected. An inherently safe mode of operation is only possible if the apparatus were constructed to be pressure shock resistant and the process temperature is kept between a certain range.

CONCEPT

The goal of this master thesis is the development of a new reactor concept for gas-liquid phase reactions with focus on oxidation reactions. Based on the design of a loop-reactor, the gaseous oxidizing agent O_2 is transferred to the liquid reaction mass using membrane technology. The concept keeps the liquid phase saturated with O_2, while minimizing the creation of an explosive atmosphere inside the reactor. The approach of a head space free reactor is a significantly increase of process safety while minimizing the constraints with regards to the solvent selection and process conditions.

Reactor configurations for oxidation reactions



Approach

- Head space free loop reactor
- Integration of membrane technology
- Suitable for oxidation reactions

Benefits

- Separation of liquid & gas phase leading to significant safety improvements
- Good mass transfer properties that can be modulated: High A/V

Oxidation reactions

- Flammable solvent
- Oxygen as a reactant
- Possible ignition source

Safety Risks

- Explosion risks!!
  - Vapor formation
  - Aerosol formation

Limitations

- Reaction temperature Tr < flash point
- Solvent selection -> high flash point
- Pressure -> $p_{max} < p_{design}$

Workstream

1. Conceptual Phase
2. Construction of the loop reactor
3. Operation of the loop reactor
4. Comparison with existing reactor systems
5. Proof of concept

Fig. 1: Concept and goal of the thesis

Measurement of mass transport properties: k_La – values

The chemical sulfite method is used to determine the volumetric liquid sided mass transfer coefficient k_La under steady state conditions. An oxygen - saturated salt solution is continuously gassed with oxygen in the presence of a Co^{++} catalyst. A defined amount of sodium sulfite (Na_2SO_3) is added. Via an installed oxygen sensor, the oxygen content in the solution is monitored. The oxidation time of sodium sulfite, which determines the mass transport, is measured. This method [1], can be used to compare different type of reactor systems.

Reaction

$$\underset{\text{sodium sulfite}\\ \text{MW: 126.04}}{Na_2SO_3} + \underset{\text{oxygen}\\ \text{MW: 32.00}}{0.5\ O_2} \xrightarrow[\text{Water}]{Co^{2+}\text{- Catalyst}} \underset{\text{sodium sulfate}\\ \text{MW: 142.04}}{Na_2SO_4}$$

Evaluation

$$k_La = \frac{m_{Na2SO3} \cdot 0.5 \cdot M_{02}}{M_{Na2SO3} \cdot t_{oxi} \cdot V \cdot c^*}$$

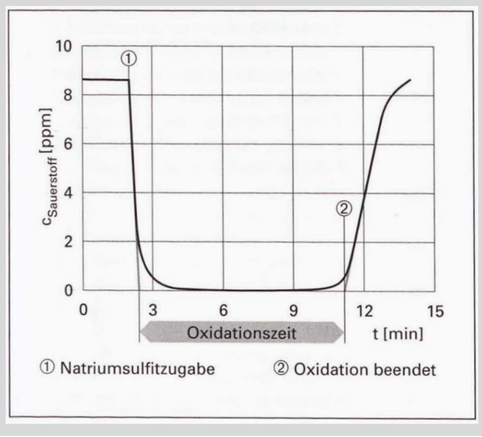


Fig. 2: Methodology of the chemical sulfite reaction

RESULTS

After construction of the loop reactor, the system was set into operation. The membrane module is the main part of the reactor and contains a hollow ceramic membrane which has the benefit to separate the gas from the liquid phase that reduces the risk of forming an explosive atmosphere.

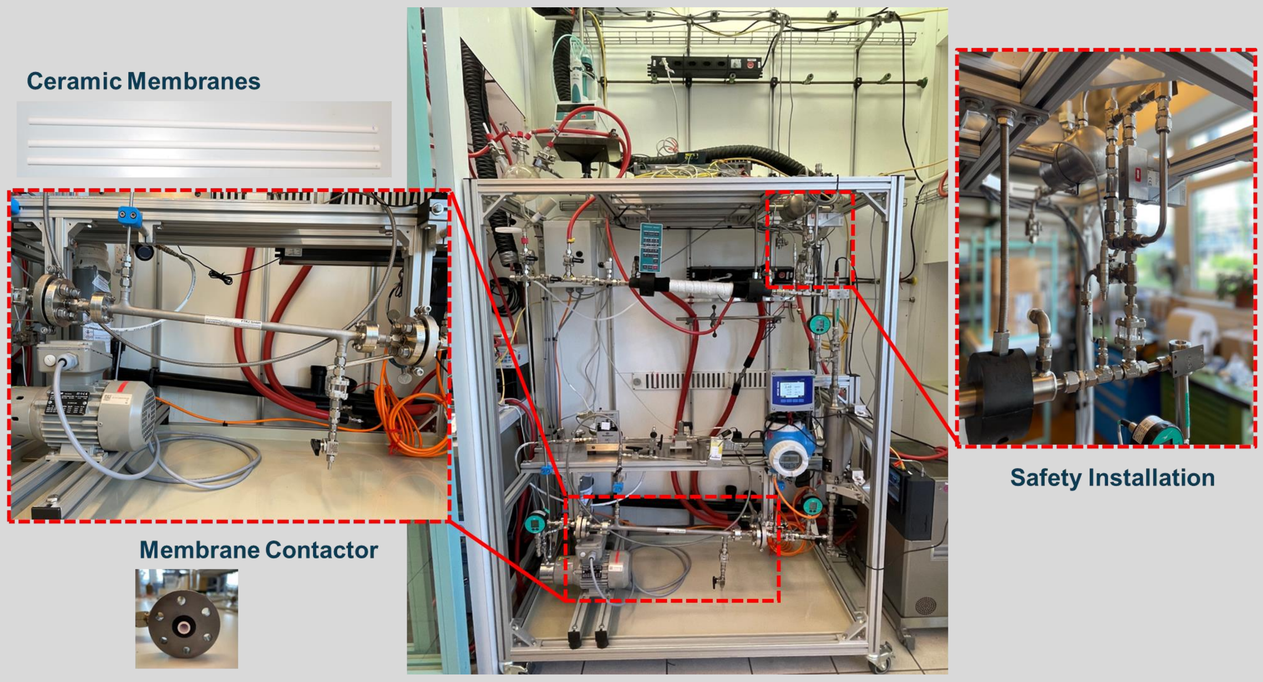
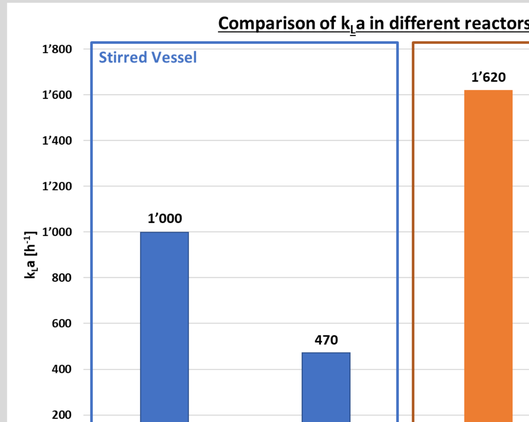


Fig. 3: Final construction of the loop reactor



The reactor was compared to an agitated vessel and a jet loop reactor regarding mass transport (k_La).
The loop reactor shows comparable mass transport properties to an agitated vessel and a jet loop reactor.
Comparison was also made using another oxidation in an organic solvent. Comparable yields were achieved in both reactor systems.

Fig. 4: Comparison of mass transport properties with other type of reactors

In the loop reactor fine disperse bubbles are visible (right) during reaction compared to pure solvent (left). Almost no creation of gas phase during reaction.

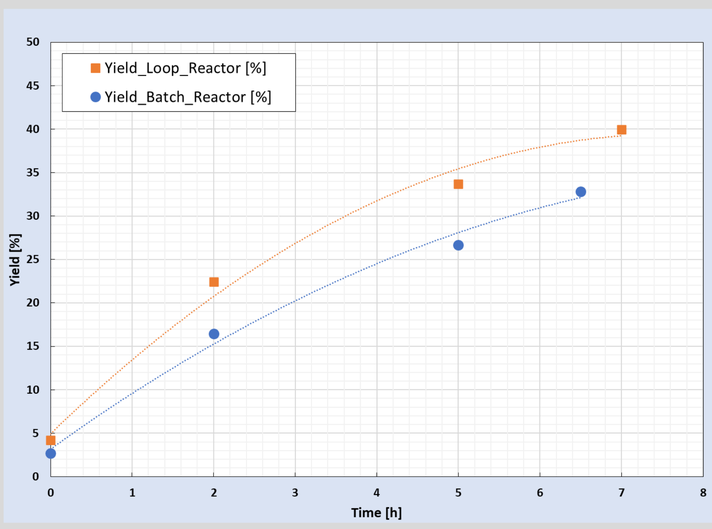


Fig. 5: Test of the concept with an oxidation in an organic solvent

CONCLUSION

The reactor concept is feasible for aqueous as well as organic solvents to perform oxidation reactions. The formed bubbles were small, and a significant decrease was visible, indicating a sufficient oxygen consumption and a good mass transport. Only a disperse phase of small bubbles in liquid is present in the reactor. The probability to form an explosive atmosphere is thus reduced. A safer process may be feasible but that need to be proven.

REFERENCES

[1] Strütt, H., Rünzi, D., (1991) Handbuch der Rührtechnik. EKATO Rühr und Mischtechnik GmbH, Schopfheim 1990.161 S., Weinheim: WILEY-VCH Verlag.
[2] Keller, A. and Leuthe, B. (2001) Memo_Resultate k_La im 60 L Tantal Reaktor
[3] Gaddis, E.S. (1999) 'Mass transfer in gas–liquid contactors', Chemical Engineering and Processing, 38(1), pp. 503-510

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