SUPERCRITICAL WATER AS REACTION MEDIA

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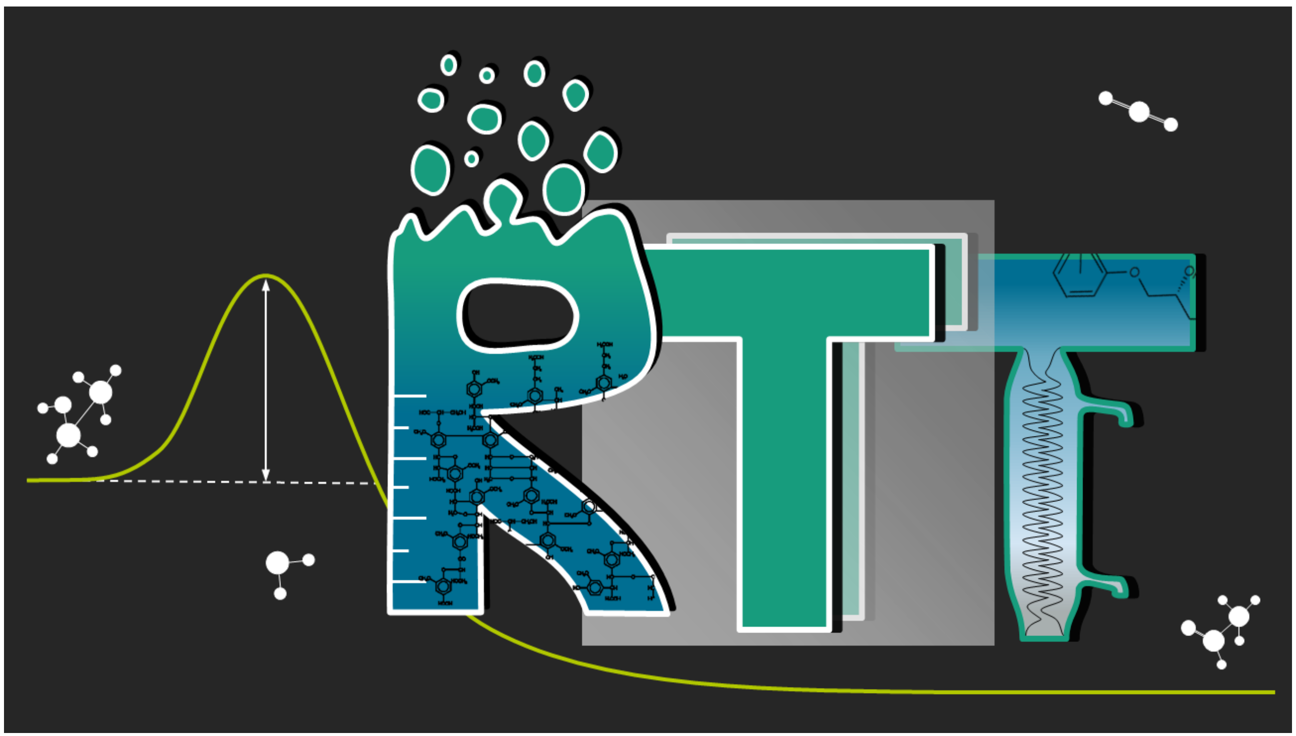
Fh ICT; Group: „Reaction and separation techniques“ (RTT)



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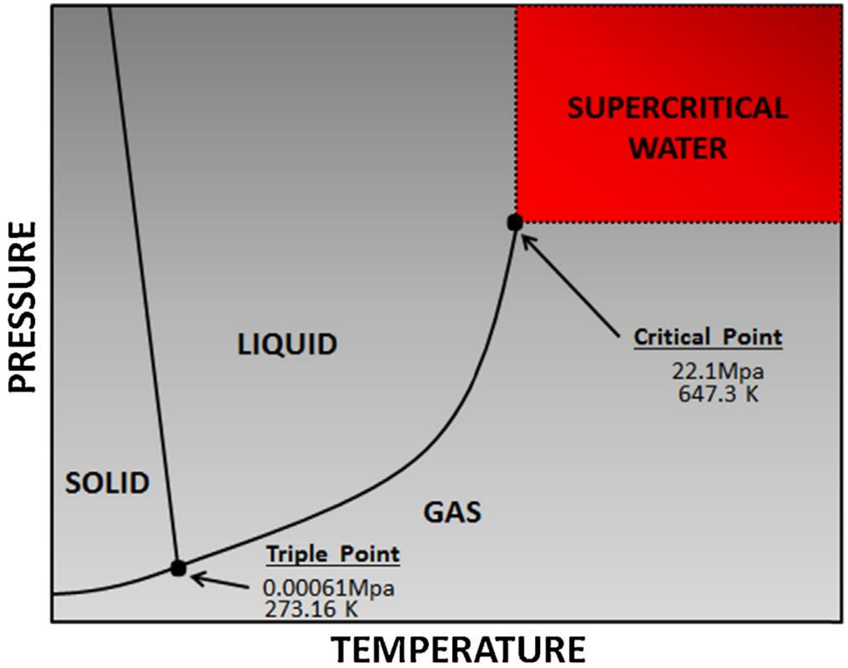
CONTENT

- Supercritical H_2O (scH_2O) and its advantages
- Reactions in scH_2O
  - Alcohol to olefins in scH_2O
  - Catalytic oxidation of HTC-waste water via supercritical water oxidation (SCWO)
- Conclusion

SUPERCRITICAL H_2O (scH_2O) AND ITS ADVANTAGES



Source: Caniaz, R. O.; Erkey, C.: Chemical Engineering Research and Design (2014), 92, p. 1845-1863.

Positive Effects

- High sensitivity of the density against p,T-change
  - with > T: < ρ ; with > p: > ρ
- high pKw-value => non polar solvent
- low dielectric constant (ε_R) => Solvation of aprotic organic solvents
  - with > T: < ε

⇒ high pKw and low ε_R leads to change to aprotic, nonpolar solvent

  - Organic solvents (e. g. cyclohexane, coke precursor)
  - Gases (e. g. O_2)

  can be solved completely

Caniaz, R. O.; Erkey, C.: Chemical Engineering Research and Design (2014), 92, p. 1845-1863. ; L. Haar, J.S. Gallagher: NBS/NRC Wasserdampftafeln, 1. Aufl., Springer Verlag, Berlin, 1988, 19-214. ; Kruse, A.; Dinjus, E.: Journal of Supercritical Fluids (2007), 39(3), p. 362-380.

SUPERCRITICAL H_2O (scH_2O) AND ITS ADVANTAGES

- Excellent mass transport properties
  - High diffusion coefficient (D_i)
    - With > T: < D_i ; with > p: > D_i
- Low dynamic viscosity (μ)
  - < 1/10 $\mu_{H2O;standard\ conditions}$

⇒ Reactions in scH_2O can deliver good space-time yields

⇒ Through out film-/pore diffusion

Negative Effects

- High temperature and pressures
- Corrosive impact

Source: Caniaz, R. O.; Erkey, C.: Chemical Engineering Research and Design (2014), 92, p. 1845-1863.

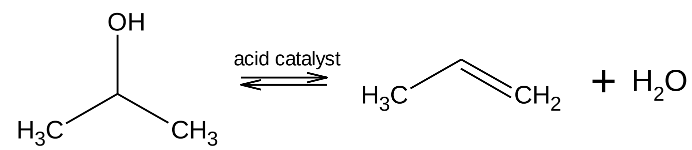
Fluid	Ordinary water	Subcritical water	Supercritical water		Superheated steam
Temperature, T (°C)	25	250	400	400	400
Pressure, p (MPa)	0.1	5	25	50	0.1
Density, ρ (g/cm^3)	0.997	0.80	0.17	0.58	0.0003
Dielectric constant, ϵ	78.5	27.1	5.9	10.5	≈1
pK_w	14.0	11.2	19.4	11.9	–
Heat capacity, c_p (kJ/kg K)	4.22	4.86	13.0	6.8	2.1
Dynamic viscosity, μ (mPa s)	0.89	0.11	0.03	0.07	0.02
Heat conductivity, λ (mW/m K)	608	620	160	438	55

Lamb, W. J.; Hoffman, G. A.; Jonas, J.: Journal of Chemical Physics (1981), 74(12), p. 6875-6880. ; Yoshida, K. et al.: Journal of Chemical and Engineering Data (2010), 55(8), p. 2815-2823. ; VDA e. V.: VDI-Wärmeatlas 2013, Springer Verlag, Berlin, Heidelberg., p.175-356. ; Marrone, P. A.; Hong, G. T.: J. of Supercritical Fluids (2009), Volume 51, p. 83-103.

REACTIONS IN scH_2O
ALCOHOL TO OLEFINS IN scH_2O

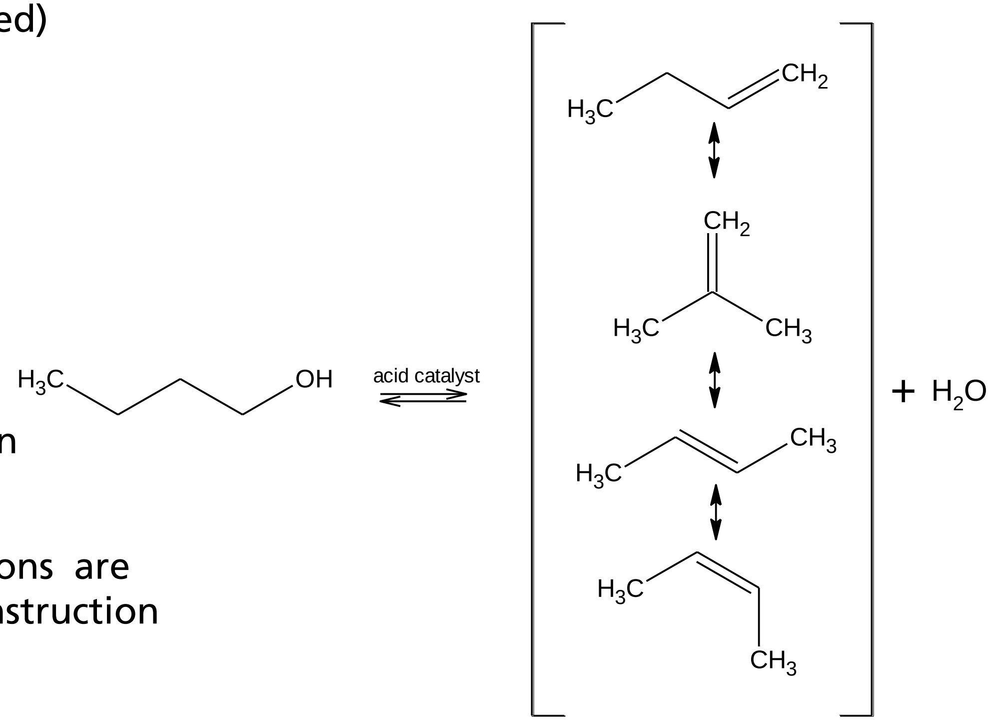
Funded by:
Federal Ministry of Education and Research

Dehydration of 2-propanol and butanol



State of the art:

- Continuous gas phase dehydration
- Catalyst: e. g. (modified) Al_2O_3; (modified) Zeolite, Hetropoly acids
- T = 247 - 470 °C
- p = 1 - 10 bar
- $S_{Olefins}$ = > 94 %
- $X_{Alcohol}$ = >79 %
- Feed:
  - high concentrated alcohol solution
  - inert gas diluted clean alcohols
  - if low alcohol concentrated solutions are used special adjusted complex construction are needed



Mekhemer, G.A.H. et al.: Monatshefte für Chemie (2005), 136(12), p. 2007-2016. ; Patent, US, 2012/0238788 A1, Wright M. E. ; Zhang, D.; Barri, S. A. I.; Chadwick, D.: Applied Catalysis A: General (2011), 403(1-2), p.1-11. ; Kamiguchi, S. et al.: Journal of Cluster Science (2007), 18(2), p. 414-430. ; Patent, EP, 0379803 B1, Wright M. E. ; Patent, US, 2009/0259086 A1, Bailey C. et al. ; Patent, US, 9144780 B2, Taheri, H., Sarin Y., Ozero B.

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REACTIONS IN scH_2O
ALCOHOL TO OLEFINS IN scH_2O

Aim:

- Production of light olefins from fermentation broth (low alcohol concentrations) with simple processing
  - ⇒ New Approach necessary

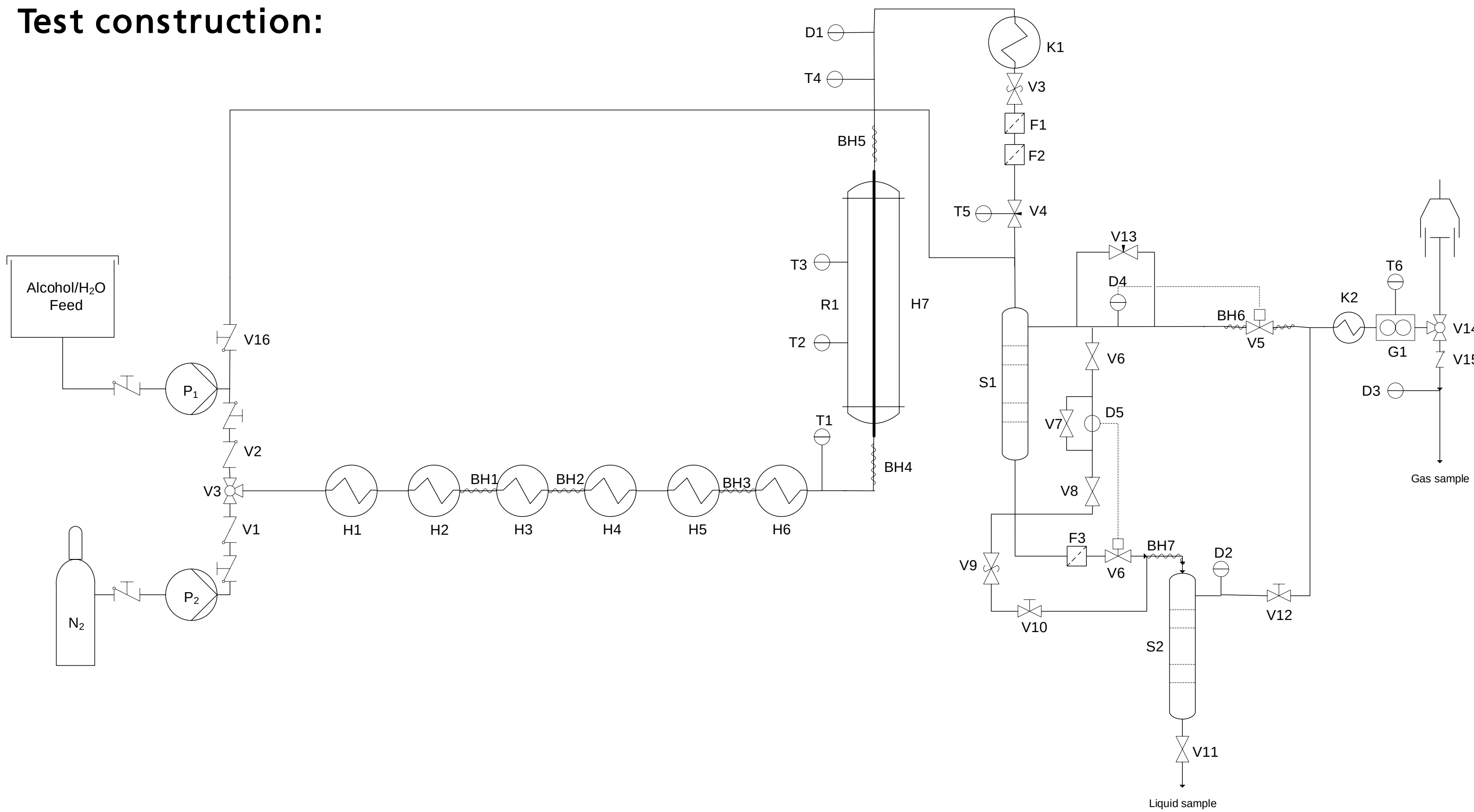
New approach:

- Heterogeneous catalyzed dehydration of the alcohols in supercritical water (scH_2O)
  - Positive effects are:
    - Excellent mass transport
    - Low viscosity
    - No surface tension
    - Good solubility of all compounds (reactants and products)
    - ⇒ High expected space time yield through good film and pore diffusion
    - Easy separation of the product and catalyst
  - Homogenous supercritical dehydration showed promising but developable results
    - ($X_{Propanol}$ = 70 %; $X_{Butanol}$ = 75 %; $S_{Propylene/Butenes}$ = 90 %)

Moreira, A.; Linden, C.: Butanol toxicity in the butylic fermentation. Conference Paper: Biotechnology and bioengineering symposium (1982). ; Caniaz, R. O.; Erkey, C.: Chemical Engineering Research and Design (2014), 92, p. 1845-1863. ; Barr-David, F.; Dodge, B.F.: Journal of Chemical and Engineering Data (1959), 4(2), p.107-121. ; Maczynski, A. et al.: Journal of Physical and Chemical Reference Data (2007), 36(1), p. 59-132. ; Goral, M. Wisniewska-Goclowska, B. Maczynski, A.: Journal of Physical and Chemical Reference Data (2006), 35(3), p. 1391-1414. ; Vogel, G.H.: Chemie Ingenieur Technik (2011), 83(9), p.1390-1398. ; Henk, W.: Untersuchungen zur Dehydratisierung von Alkoholen und zur Esterverseifung sowie zum Verhalten von anorganischen Materialien in überkritischem Wasser. Dissertation, 2004. TU Darmstadt.

REACTIONS IN scH_2O
ALCOHOL TO OLEFINS IN scH_2O

Test construction:



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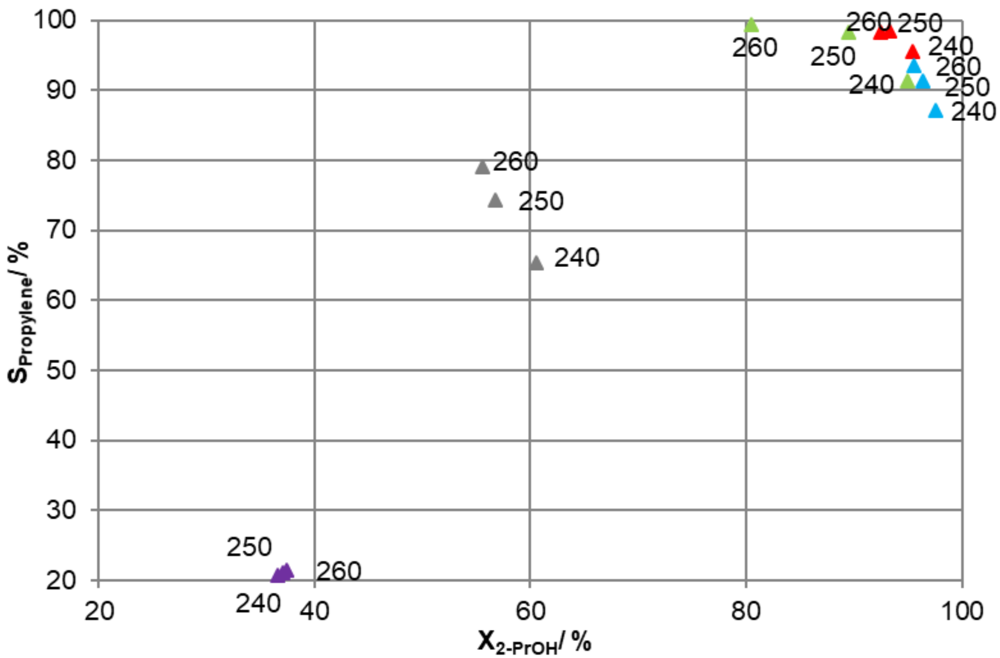
REACTIONS IN scH_2O
ALCOHOL TO OLEFINS IN scH_2O

2-Propanol to propylene:

Catalyst screening



Screened catalysts:

	Composition
▲ (green)	γ-Al_2O_3
▲ (red)	θ-Al_2O_3
▲ (blue)	Al_2O_3/SiO_2 (90/10)
▲ (grey)	ZrO_2
▲ (purple)	Y_2O_3/ZrO_2 (5/95)

Reaction conditions:

- T_R = 390 °C
- p_R = 240, 250 or 260 bar (figures in diagram)
- Feed: 40 wt% 2-Propanol/water-solution
- Flowrate: 30 ml/min

- Best Catalyst: θ-Al_2O_3 ($X_{2\text{-PrOH}}$ and $S_{Propylene}$ ≈ 95 %, at 240 bar, 390 °C)

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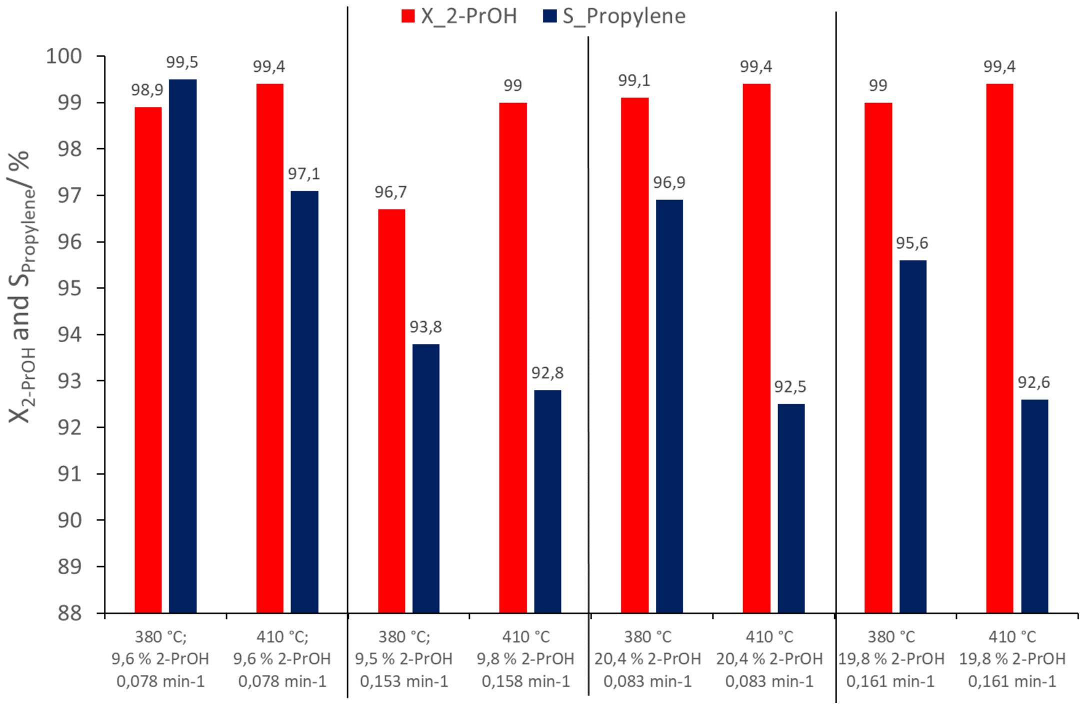
REACTIONS IN scH_2O
ALCOHOL TO OLEFINS IN scH_2O

<u>Parameter screening (Catalyst: θ-Al_2O_3; p_R = 250 bar)</u>

Temperature influence:



⇒ Main product: Propene

⇒ Byproducts:
- Hydrogen
- Acetone
- Alkanes

⇒ increasing T_R
- slightly increase of $X_{2\text{-}PrOH}$
- decrease of $S_{Propylene}$

Reason :
- Increasing side reactions

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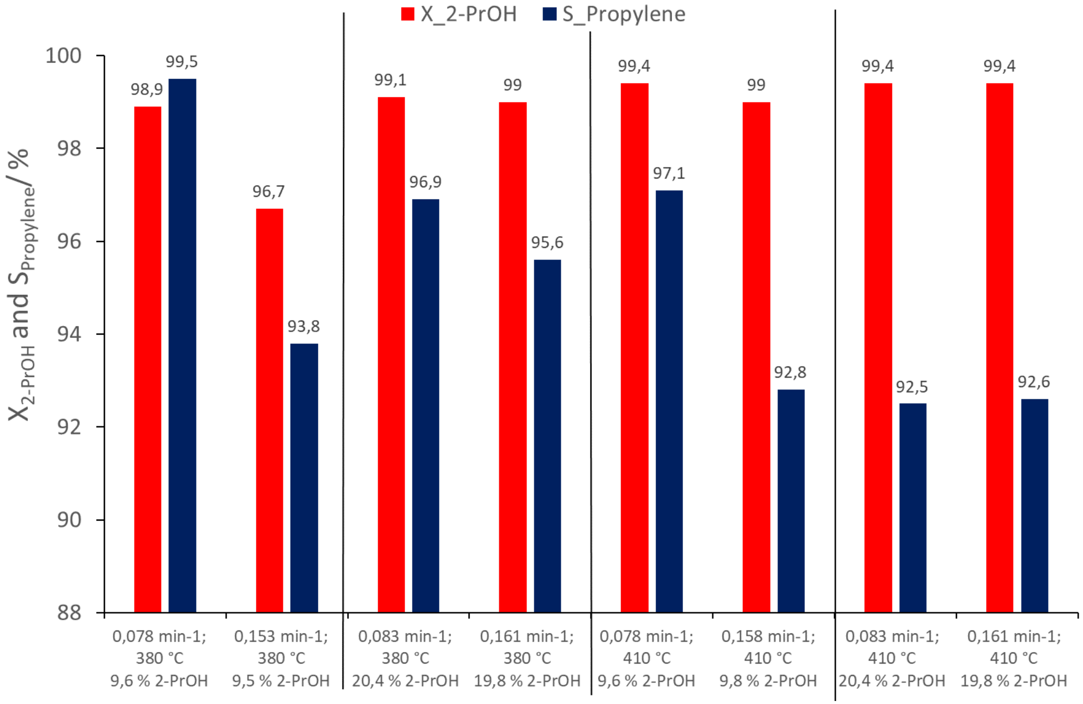
REACTIONS IN scH_2O
ALCOHOL TO OLEFINS IN scH_2O

WHSV influence:



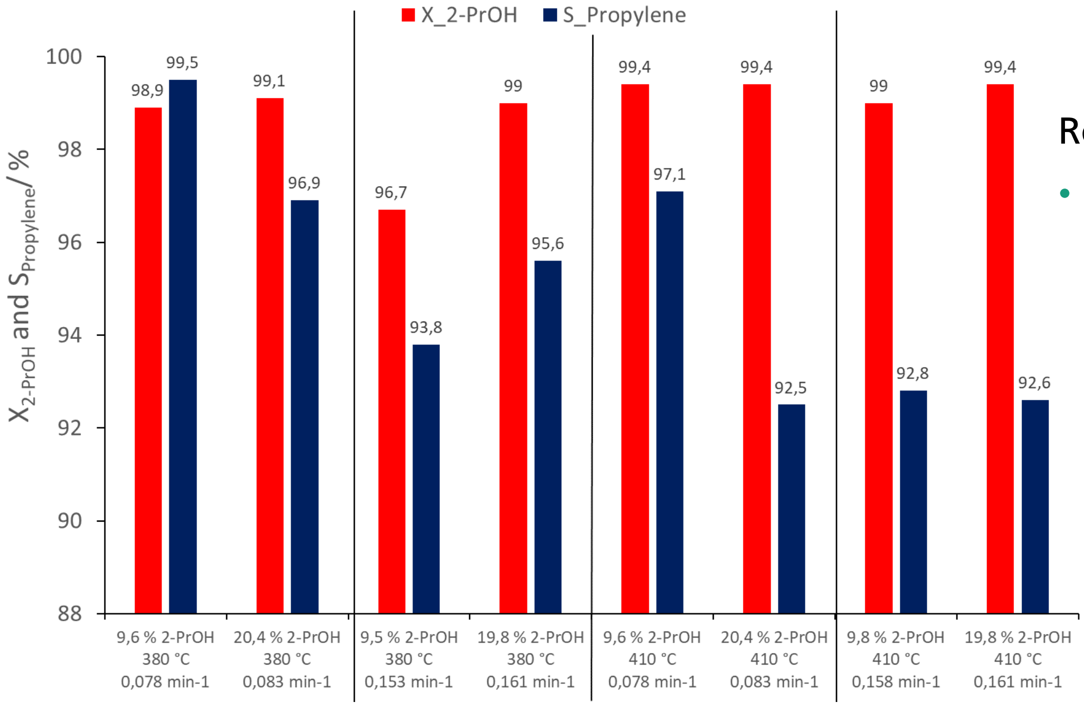
⇒ Increasing WHSV
- slightly decrease of $X_{2\text{-PrOH}}$
- decrease $S_{propylene}$

Reason:

- X decreases due to lower τ
- S decreases because of faster side reactions are running competitively combined with lower τ

REACTIONS IN scH_2O
ALCOHOL TO OLEFINS IN scH_2O

Feed-Concentration:



⇒ Increasing Feed-concentration

- slightly increase of $X_{2\text{-PrOH}}$
- decrease $S_{propylene}$

Reason:

- Increasing side reactions due to higher 2-PrOH content in the reactor

Conclusion:

⇒ Optimal 2-PrOH dehydration at low WHSV, low T and low feed concentration

⇒ 380 °C; 0,078 min^{-1} WHSV:

- $X_{2\text{-PrOH}}$ = 98,9 %
- $S_{Propylene}$ = 99,5%
- < 10 % $c_{2\text{-PrOH}}$
- Easy processing

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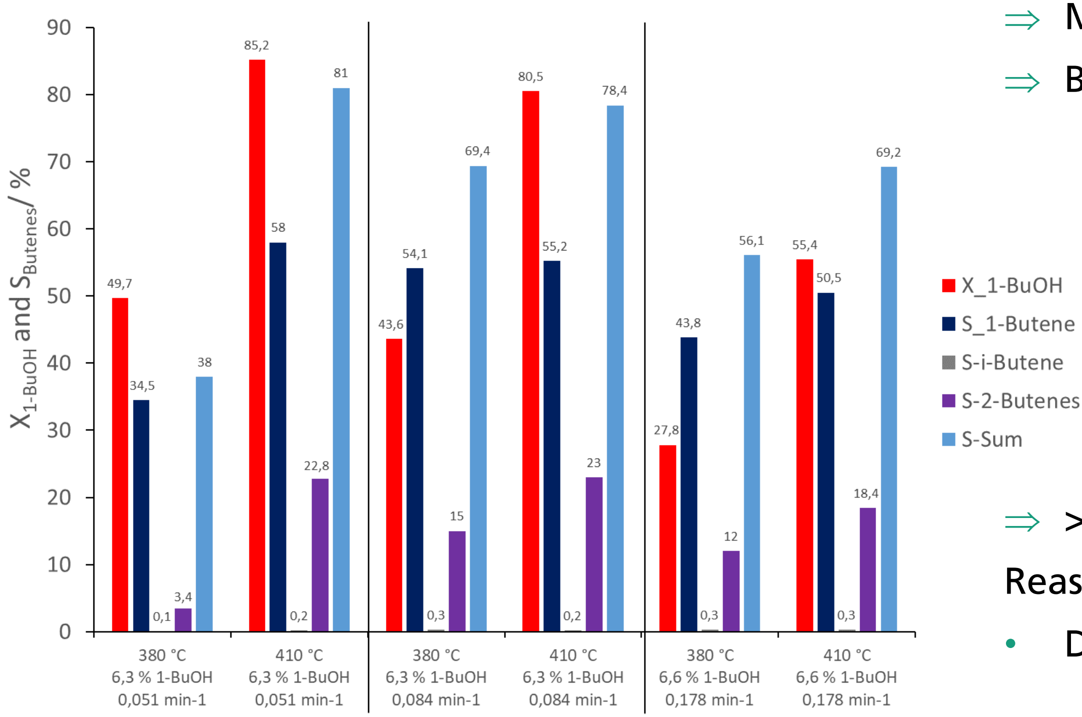
REACTIONS IN scH$_2$O
ALCOHOL TO OLEFINS IN scH$_2$O

1-Butanol to butenes:

Parameter screening (Catalyst: θ-Al$_2$O$_3$; p$_R$ = 250 bar)

Temperature:



⇒ Main product: 1-Butene

⇒ Nearly no i-Butene

⇒ Medium selectivity to 2-Butenes

⇒ Byproducts:

- Hydrogen
- Butanal
- 2-Butanol
- Alkanes
- Ethylene
- Propylene

⇒ > T_R : increase $X_{1\text{-}BuOH}$; increase $S_{Butenes}$

Reason:

- Dehydration faster as dehydrogenation

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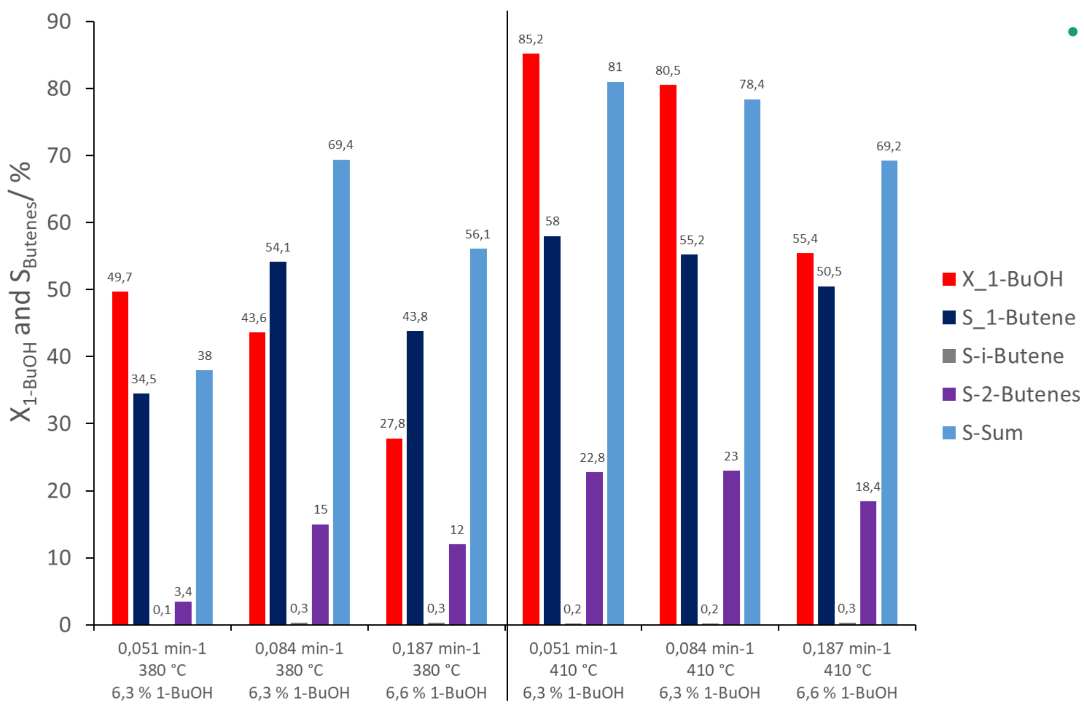
REACTIONS IN scH_2O
ALCOHOL TO OLEFINS IN scH_2O

WHSV:



⇒ > WHSV

- decrease of $X_{1\text{-BuOH}}$
- decrease $S_{Butenes}$

Reason:

- X decreases due to lower τ
- S decreases due to a complex reaction network

Conclusion:

⇒ Optimal 1-BuOH dehydration at low WHSV and high T

⇒ With 410 °C and 0,051 min^{-1} WHSV:

- $X_{1\text{-BuOH}}$ = 85,2 %
- $S_{Butenes}$ = 81 %
- Ca. 6,5 % $c_{1\text{-BuOH}}$
- Easy processing

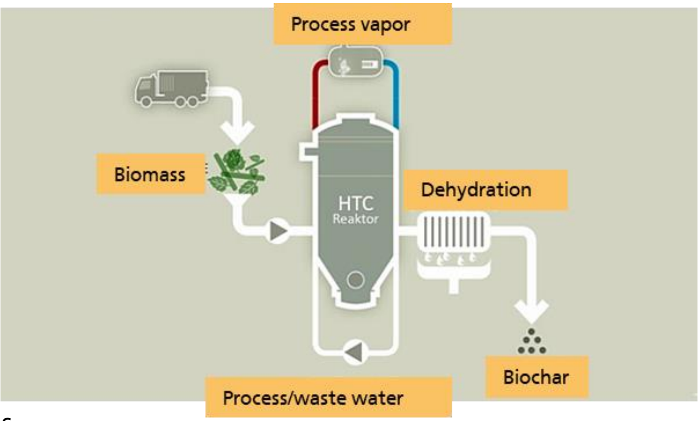
Reactions in scH_2O

Catalytic oxidation of HTC-Waste Water via supercritical water oxidation (SCWO)

Aim:

- Reduction of chemical oxygen demand (COD) of HTC-waste water to zero in short times

The HTC-Process:



Source:
http://www.karlsruhe-macht-klima.de/klimaschutzvorort/forschungentwicklung/demonstrationsanlage.de

- Imitation of natural carbonization of biomass in a few hours
- But high amount of organic loaded process/waste water is produced (COD = 30.000 – 50.000 mg/l)
  - Purification before disposal is necessary

Büchler, B.: HTC-Verfahren - die Vor- und Nachteile, Umwelt Perspektiven, 1-2012 ; Funke A., Ziegler F. Biofuels, Bioprod. Bioref (4/2010), p. 160-177. ; Berge, N. et al.: Environ. Sci. Technol. (2011), 45, p. 5696–5703 ; Patent, DE, 102012024463 A1, Wilhelm H.-J. ; Ramke,H.-G.;Blöhse,D.; Lehmann,H.-J.; Fettig,J., 2009: Hydrothermal Carbonization of Organic Waste. In: COSSU, R.; DIAZ, L.F.;STEGMANN, R. (EDTS.), 2009: Sardinia 2009: Twelfth International Waste Management and Landfill Symposium, Sardinia, Italy, 05-09 October 2009, Proceedings, CISA Publisher.

CATALYTIC OXIDATION OF HTC-WASTE WATER VIA SUPERCRITICAL WATER OXIDATION (SCWO)

State of the art purifications

- Ultra filtration (UF) (batch, conti)
  - Decrease of COD about 66 %
- Anaerobic biological conversion of water soluble pyrolysis condensates in laboratory scale

  => fermentation to bio gas (CH_4) (batch, conti)
    - Runtime days to weeks to reduce COD
    - Reduction of COD not completely (ca. 80 %)
- Wet oxidation (WO) (conti)
  - Oxidation of organic compounds with O_2 (120 – 220 °C, 3 - 28 bar, 15-120 min, Fe^{2+}-catalyst) (e. g. Loprox-process) to easier bio-decomposable organic compounds and gases
  - COD reduction about 20 – 90 % (COD_{Start}: 30,8 g/l)
- Conclusion:
  - Only incomplete COD reduction and/or reductions in long residence times and with complex process designs are possible => Fast and complete reduction technologies needed

Krebs, R.: DBFZ HTP-Fachforum, 11-12.11.14; URL: https://www.dbfz.de/fileadmin/htp/docs/HTP_FACHTAGUNG_2014.pdf - p. 120-129, Download from 01.03.2019. ; Hübner, T., Mumme, J.: Bioresource Technology (2015), 183, p. 86-92 ; Wirth, B.; Mumme, J.: Applied Bioenergy (2013), p. 1-10. ; Nilsson, E.: Examina work Uppsala Universitet; URL: http://sjostad.ivl.se/download/18.449b1e1115c7dca013acf52/1498141600595/Erik_Nilsson.pdf, Download from 01.03.2019. ; Villamil, J. A. et al.: Front. Sustain. (2018), https://doi.org/10.3389/fsufs.2018.00017. ; Patent, EP, 2206688 A1, Kleinert M., Wittmann T. ; Riedel G. et al.: Chem. Eng. J (2015), 279, p. 715-724 ; Ohlert, J.: Hydrothermale Carbonisierung (HTC) von Klär- und Faulschlämmen, veröffentlichte Diss., Carl von Ossietzky Universität Oldenburg 2015.

CATALYTIC OXIDATION OF HTC-WASTE WATER VIA SUPERCRITICAL WATER OXIDATION (SCWO)

New approach:

- Heterogeneous catalyzed oxidation of the organic compounds in supercritical water
  - Optimizations are expected due to
    - very good solubility of O_2 and organic compounds in scH_2O
    - higher reaction temperatures that should lead to higher degradation yields under kinetic control
  - Drawbacks
    - High temperature and pressure should shift thermodynamic equilibrium to the reactants under thermodynamic control (exothermic reaction)
    - High energy demand
  - Reaction agents: O_2 (!Air!); H_2O_2

Reaction:

$$\text{a Organic Compound} + \text{b } O_2/H_2O_2 \xrightarrow[scH_2O]{\text{catalyst}} \text{c } CO_2 + \text{d } H_2O$$

CATALYTIC OXIDATION OF HTC-WASTE WATER VIA SUPERCRITICAL WATER OXIDATION (SCWO)

Experimental Setup:

Reaction Parameters:

- Supercritical conditions
  - T_R = 400 °C
  - p_R = 250 bar
- Subcritical conditions
  - T_R = 300 °C
  - p_R = 100 bar
- Catalyst particle size: 2 - 4 mm
- 2 waste waters:
  - Tailored waste water (TWW)
  - HTC-waste water

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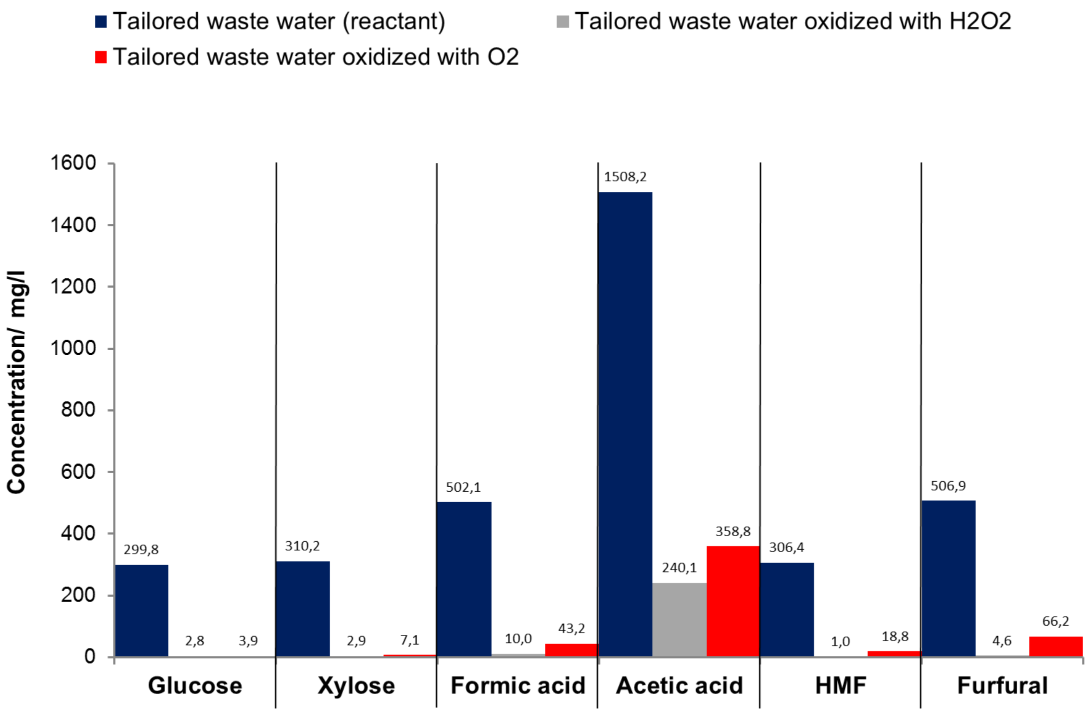
SCWO TESTS ON TAILORED WASTE WATER (TWW)

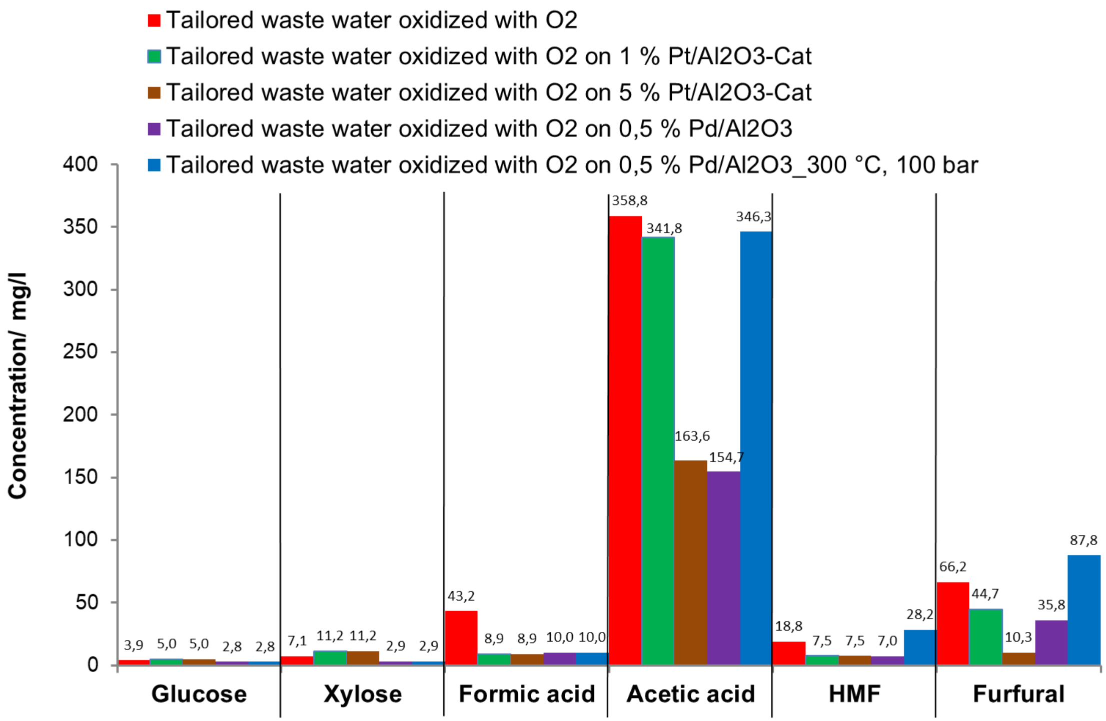


Process parameter TWW-Oxidation:

- $Feed_{H2O2}$ = 38,40 ml/min
  - 9,54 ml/min waste water
  - 0,23 ml/min H_2O_2 (30 %)
  - 28,63 ml/min H_2O (dilution)
  - **τ_{H2O2} = 180 s (3 min)**
- $Feed_{O2}$ = 62,91 ml/min
  - 9,54 ml/min waste water
  - 24,74 ml/min O_2
  - 28,63 ml/min H_2O (dilution)
  - **τ_{O2} = 12 s (0.2 min)**

- Concentrations of organic compounds are drastically reduced with H_2O_2 and O_2
- Oxidation with H_2O_2 showed better results (reduction: 98 % formic acid, 84 % acetic acid; 100 % HMF, 99 % furfural) than with O_2 (85 % formic acid, 76 % acetic acid, 93 % HMF, 87 % furfural)

SCWO TESTS ON TAILORED WASTE WATER (TWW)



- SCWO with O_2 as oxidant can be improved by using oxidation catalysts => equal or better as H_2O_2 (0,5 % Pd/Al_2O_3: 98 % formic acid, 90 % acetic acid , 98 % HMF, 93% Furfural)
- At subcritical conditions (blue balk) the oxidation runs in lower reduction of organic components (0,5 % Pd/Al_2O_3: 98 % formic acid, 77 % acetic acid, 91 % HMF, 83 % Furfural)

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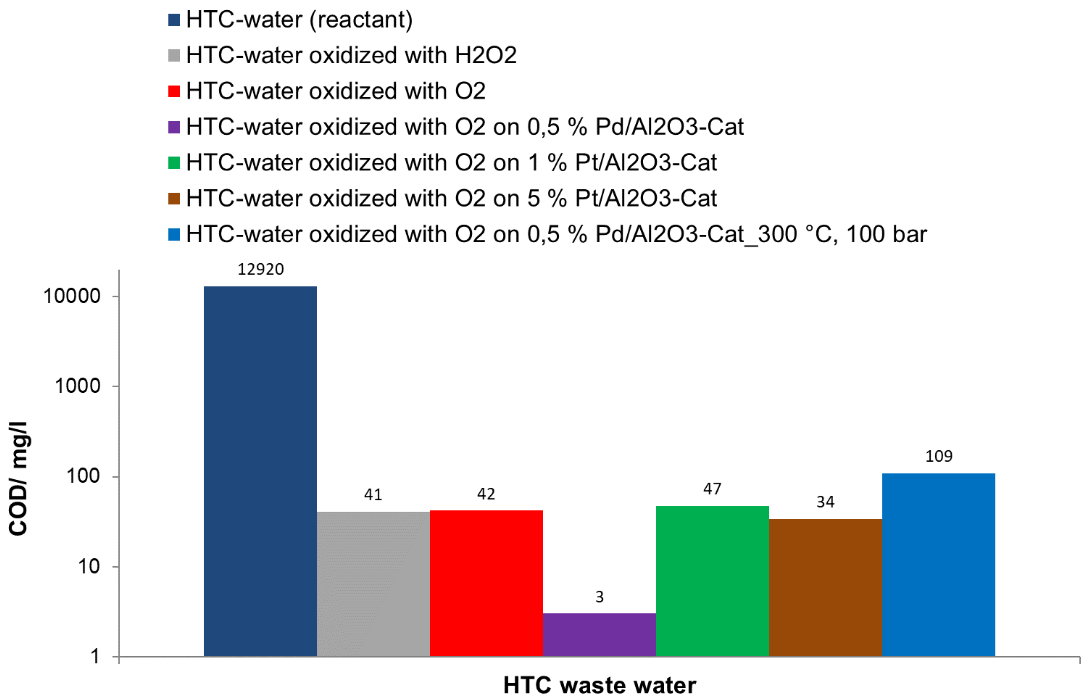
SCWO TESTS ON HTC-WASTE WATER



Oxidation HTC-waste water:

- $Feed_{H2O2}$ = 38,40 ml/min
  - 0,45 ml/min waste water
  - 0,23 ml/min H_2O_2 (30 %)
  - 37,73 ml/min H_2O (dilution)
  - **τ_{H2O2} = 20 s (0,33 min)**
- $Feed_{O2}$ = 63,11 ml/min
  - 0,45 ml/min waste water
  - 24,94 ml/min O_2
  - 37,73 ml/min H_2O (dilution)
  - **τ_{O2} = 12 s (0.2 min)**

- H_2O_2 and O_2 are both reducing the COD nearly completely, also for real HTC-waste waters (H_2O_2: 99,7 %; O_2: 99,7 %)
- Results of SCWO are better than those of subcritical water oxidation (subCWO) (blue balk) (SCWO: 100%; subCWO: 99,2 %)

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CONCLUSION

- scH_2O is a good media for chemical reactions because of
  - special solubility properties (aprotic, non polar)
  - high space time yields due to excellent mass transport properties and viscosity
- Dehydration of alcohols to olefins in super critical water
  - 2-Propanol can be converted to propylene in scH_2O in high yields over θ-Al_2O_3 from low concentrated feed solutions (< 10 wt%)
    - $X_{2\text{-PrOH}}$ = 98,9 %; $S_{Propylene}$= 99,6 %; $Y_{Propylene}$ = 98,5 %
  - 1-Butanol can also be dehydrated to butenes in high yields over θ-Al_2O_3
    - $X_{1\text{-BuOH}}$ = 85,2 %; S_{Butene}= 81 %; Y_{Butene} = 69 %
    - 1-Butene is the major product
    - 1-BuOH concentrations of only 6,5% can be used as feed
- Supercritical water oxidation (SCWO) of HTC-waste waters
  - COD value of organic loaded HTC-waste waters can be totally reduced in seconds by oxidation in scH_2O
    - if heterogeneous oxidation catalysts are used, even O_2 or Air can be used as oxidation media

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