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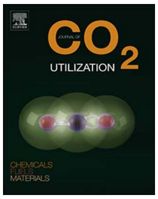

CO_2-intensified Hydrolysis of Rutin to Quercetin – A Comparison of Experimental Data and modelled Reaction Kinetics

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ABSTRACT

This work describes the possibility to hydrolyze rutin (quercetin-3-*O*-rutinoside) to quercetin using carbon dioxide (CO_2) and water without the addition of acids or enzymes. Eight hours of CO_2-intensified hydrolysis of aqueous rutin-solutions were carried out to investigate temperature (373.15 K–433.15 K) and pressure dependence (4–150 bar). Both temperature and CO_2-pressure dependence are studied. The parameter combination of 413.15 K and 150 bar gave a complete (100 %) conversion of rutin to quercetin. Temperature and pressure dependence were modelled. Models achieved correlation coefficients between $R^2 = 0.85$ and 0.99. Influence of H^+ ions was described by implementing the »H^+-factor« to explain the hydrolysis effect of CO_2-pressure in more detail. The results of this work demonstrate that CO_2-intensified hydrolysis is possible at moderate temperatures and pressures.

1. Introduction

Hydrolysis reactions are widely applied in industrial processes, e. g. for sugar substitutes: hydrolysis of sucrose, starch to glucose or glucose sirup and starch to maltit sirup [1,2]. The conventional way to cleave sugar moieties is carried out by acid catalyzed hydrolysis, for example in presence of hydrochloric acid [3], sulfuric acid [4] or nitric acid [5]. Neutralization of added acids after hydrolysis requires addition of alkaline solutions [6]. For specific cleavage of certain sugars, enzymes can be employed [7]. Over the last years several researchers focused on hydrolysis of natural substances in pressurized and tempered water. Research was conducted referring hydrolysis of lignin, cellulose, hemicellulose [8–11] or glycosides and is called hydrothermal degradation or hydrolysis/pretreatment in subcritical water (pressurized water at temperatures between 373.15 K and below critical temperature of water) [12–15]. N_2-pressure, CO_2-pressure and static pressure contribute to system pressure

Rogalinski et al. [16] published results referring to hydrolysis of glycosides in subcritical water and investigated the influence of the catalytic effect of CO_2 at CO_2- pressures of 250 bar and temperatures between 513.15 K and 583.15 K. da Silva et al. [17] studied CO_2-assisted autohydrolysis of wheat straw with an initial CO_2-pressure of 60 bar and temperatures between 453.15 K and 483.15 K. Morais et al. [18] demonstrated the conversion of wheat straw with high pressure water-CO_2 at temperatures between 403.15 K and 498.15 K and initial CO_2-pressures between 0 and 54 bar. Furthermore, Morais et al. [19] investigated the influence of CO_2 in: 1) dehydration reaction of xylose into furfural at initial CO_2-pressures between 0 (without CO_2) and 50 bar and temperatures between 433.15 K and 473.15 K with a holding time between 15 and 120 min. 2) dehydration of hemicellulose at temperatures between 433.15 K and 453.15 K at 50 bar (initial CO_2-pressure) for 30 to 90 min. Toscan et al. [20] investigated the pretreatment of sugarcane bagasse and elephant grass with high-pressure CO_2-water at temperatures between 453.15 K and 493.15 K and a constant initial CO_2-pressure of 50 bar. Fan et. al [21] investigated the mechanism of glycyrrhizic acid hydrolysis in subcritical water and described the reaction kinetic with an applied model. Glycyrrhizic acid was hydrolyzed at temperatures between 393.15 K and 453.15 K at 70 bar static pressure to glycyrrhetinic acid and glycyrrhetinic acid 3-*O*-mono-β-D-glucuronide. Ravber et al. [22] investigated subcritical water hydrolysis of rutin to quercetin at temperatures between 433.15 K and 493.15 K and pressures between 50 and 545 bar (CO_2 or N_2) for a duration of 30 min. The authors used 10 mL of rutin-water-suspensions at concentrations up to 5 mg/mL. Above temperatures of 448.15 K and chosen pressures quercetin, glucose and rhamnose start to decompose. Glucose and rhamnose can decompose to 5-hydroxymethylfurfural and

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5-methylfurfural. 5-hydroxymethylfurfural has shown potential toxicity and carcinogenicity in in-vitro tests [23]. The yields of quercetin were obtained at 215 bar CO_2- pressure. Experiments with N_2 showed lower yields of quercetin than experiments performed with CO_2. Following this, Ravber et al. [24] investigated the hydrothermal degradation of rutin between temperatures of 393.15 K and 493.15 K and at constant N_2 and CO_2-pressure of 215 bar. Increasing temperatures lead to increasing reaction rates. Reaction rates between 130 10^{-5} min^{-1} (CO_2, 393.15 K) and 380 10^{-4} min^{-1} ($CO_{2,}$ 433.15 K) were obtained for the reaction »rutin to quercetin«. Experiments performed with N_2 showed lower reaction rates than experiments performed with $CO_{2.}$ Isoquercetin was not quantified in the HPLC analysis and the introduced kinetic model was simplified to the direct reaction of rutin to quercetin. Ruen-ngnam et. al [25,26] investigated the reaction kinetics of hydrothermal hydrolysis of hersperidin under CO_2-pressure. Hesperidin (hesperitin-7-*O*-rutinoside) was hydrolyzed to hesperitin and hesperitin-ß-glucosid at constant CO_2-pressure of 250 bar and at temperatures between 383.15 K and 413.15 K up to 4 h. The authors obtained a conversion rate of hesperidin of 70 % and a formation rate of hesperitin of almost 95 %. Increasing temperatures lead to increasing reaction rates. Reaction rates between 0.05 s^{-1} (383.15 K) and 0.32 s^{-1} (413.15 K) were determined for the reaction »hesperidin to hesperitin-ß-glucosid«, reaction rates between 0.126 s^{-1} (383.15 K) and 0.140 s^{-1} (413.15 K) were determined for the reaction »hesperitin-ß-glucosid to hespertin« and reaction rates between 0.005 s^{-1} (383.15 K) and 0.100 s^{-1} (413.15 K) were determined for the reaction »hesperidin to hesperitin«. Relvas et al. [27] studied the conversion of xylan to xylooligossacharides, xylose and furfural and its degradation products. Constant temperature of 453.15 K, initial CO_2-pressures between 0 and 50 bar and residence times of up to 45 min were applied on the system. The author established reaction kinetic models and obtained for the hydrolysis reaction of xylan to xylooligossacharides reaction rates between 0.093 min^{-1} (autohydrolysis without CO_2) and a maximum of 0.127 min^{-1} at 20 bar (CO_2-pressure), with increasing CO_2-pressure reaction rates started to decrease to 0.073 min^{-1} at 50 bar CO_2-pressure. For the hydrolysis of xylooligossacharides to xylose the reaction rates increased with increasing pressure: 0.041 min^{-1} at 0 bar (autohydrolysis without CO_2) to 0.068 min^{-1} at 50 bar CO_2-pressure. The same behavior was observed for hydrolysis of xylose to furfural.

With these published results in mind the idea of this work was to investigate hydrolysis-kinetics of »rutin to quercetin« in the CO_2-water-system at lower pressures and temperatures than mentioned above. Lower conditions would reduce the risk of unwanted degradation products [28]. Temperature (between 373.15 K and 433.15 K) and CO_2-pressure (between 4 and 150 bar) were varied to investigate the kinetics of hydrolysis reaction of »rutin to quercetin«. From this experimental data two kinetic models (temperature-dependence and pressure-dependence) and the respective reaction rates were calculated.

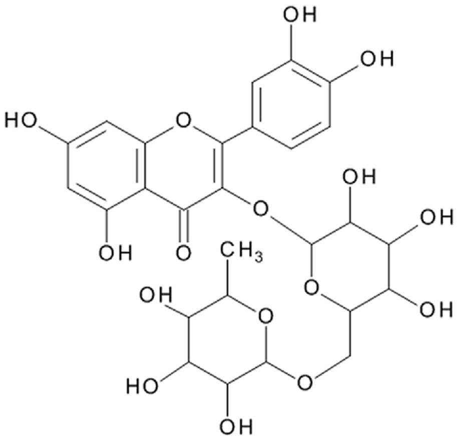

Fig. 1. Rutin (quercetin-3-*O*-rutinosid).

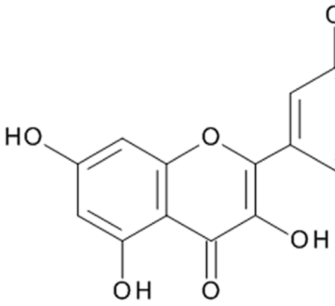

Fig. 2. Quercetin.

2. Experimental

2.1. Materials

Rutin (quercetin-3-*O*-rutinosid, Fig. 1) was selected as model compound. Rutin was purchased from Carl Roth as rutin trihydrat with a purity of ≥95%. Quercetin (Fig. 2) was purchased from Alfa Aesar as quercetin dihydrat with a purity of ≥97%. Methanol, ethanol, milli-Q ® water, acetic acid and acetonitrile were HPLC grade. Purified water was used for preparation of rutin solutions for hydrolysis. Carbon dioxide was purchased from Yara with a purity of 99.5 %.

2.2. Experimental set up and methods

In Fig. 3 the experimental set up for the CO_2-intensified hydrolysis is displayed. It consisted of a high pressure view cell (a) with a volume of 60 mL and three valves (valve b: CO_2-pressurization, valve c: CO_2-depressurization, valve d: sampling). The prepared rutin solution (50 mg/L) was injected at a t-junction (e). Rutin concentration was below maximum solubility (125 mg/L at 298.15 K [29]). The rutin solution was stirred inside the cell. CO_2-pressure was adjusted with a hand valve (b) and temperature was controlled with heating elements (h).

After injection of the rutin solution, the cell was rendered inert and heated up to the desired temperature within one hour. During heating, the rutin solution was pressurized with 4 bar CO_2-pressure. After reaching the desired temperature, the cell was pressurized with respective CO_2-pressure for eight hours. Six samples were taken for HPLC-analysis during each experiment (Table 1). Sampling of the hydrolyzed rutin solution was conducted by rejecting the first 0.5 mL and taking the additional 1 mL for HPLC-analysis. Pressure drop during sampling was compensated by adjusting the pressure with hand valve.

CO_2-intensified hydrolysis | temperature dependence: At first, temperature dependence of the CO_2-intensified hydrolysis was investigated. The pressure was set to 150 bar CO_2 pressure in each experiment. Experiments at each temperature (373.15 K, 393.15 K, 413.15 K, 433.15 K) were performed in triplicate.

CO_2-intensified hydrolysis | pressure dependence: As a result of »CO_2-intensified hydrolysis | temperature dependence« temperature was set to 413.15 K. Experiments at different CO_2-pressure (4 bar, 25 bar, 50 bar, 100 bar,150 bar) were performed in triplicate.

HPLC analysis: For quantitative analysis of quercetin and rutin, a high performance liquid chromatography device connected with a diode array detector (Agilent Technologies HPLC 1200 Quat Pump) was used. The injection volume was 10 µL and the separation was performed in an Agilent Zorbax Eclipse XDB-C18 150 × 4.6 mm 5 µm column at 308.15 K. The samples were diluted 1:1 with the eluent. Isocratic elution was performed and consisted of methanol/acetonitrile/water (40/15/45) (v/v/v%) containing 1% acetic acid at a flow