

# SUPERCRITICAL WATER OXIDATION OF LACTOSE

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New data on total organic carbon (TOC) reduction and H<sub>2</sub> production were obtained by using supercritical water oxidation of lactose with and without oxidant agents (H<sub>2</sub>O<sub>2</sub> and t-BHP) in a continuous Inconel 625 flow reactor. The oxidation reactions were carried out at 550 and 700 °C, 22.5 MPa, 0.025 g/g (2.5 wt%) lactose concentration, feed flow rate of 5 g · min<sup>-1</sup>, and a total reaction time of 90 min. The average production of H<sub>2</sub> yielded 4.5 mol/mol lactose with TOC reduction of ~99 %. The results obtained in this study with supercritical water oxidation (SCWO) may be used to generate energy via production of H<sub>2</sub> from dairy industry effluents.

**Keywords:** SCWO, continuous flux reactor, lactose, TOC reduction, hydrogen production

## INTRODUCTION

Industry wastes from various types of dairy product processing (e.g. milk, milk beverage, cheese, candy, ice cream, cream, etc.) are obtained worldwide in huge amounts and are considered environmental and economic challenges due to their organic matter content in carbohydrates (major lactose), fats, salts, and proteins. Thus, researchers have been developing new technologies that aim to reduce the pollution effects by creating value-added products from these dairy industry wastes.

Among the different dairy industry effluents, cheese whey is produced in large quantities: approximately 90 million tons per year.<sup>[1]</sup> The European Union and the USA generate approximately 70 % of the whey produced in the world. Whey is a saline effluent with a high organic load. It is composed of water (93–94 %), lactose (4.5–5.0 %), proteins (0.7–0.9 %), minerals (0.6–1.0 %), and other minor components, such as some fats and enzymes.<sup>[2–3]</sup> It should be noted that effluents released in water streams reduce the concentration of dissolved oxygen (COD)<sup>[4]</sup> and consequently disturb the local environment. Values of biochemical oxygen demand (BOD) between 27 and 60 g/L and chemical oxygen demand (COD) between 50 and 102 g/L have been reported for whey.<sup>[5–7]</sup> Furthermore, compounds from the sanitization processes, such as acids, phosphates, alkaline agents (NaOH and KOH), and oxidizing agents can also be found in the effluent.

Whey can be treated in a sequence of unit operations. However, such treatment is complex and expensive, and it hampers the scale-up process. Because of the high water content (near 90 %), the employment of the supercritical water technology can be a more suitable choice for the treatment of cheese whey (supercritical water oxidation, SCWO), resulting in the production of hydrogen (supercritical water gasification, SCWG).<sup>[8–9]</sup>

Water has unique properties as a reaction medium<sup>[10]</sup> when supercritical conditions are reached, i.e. T<sub>c</sub> ≥ 374 °C, P<sub>c</sub> ≥ 22.1 MPa. SCWG of biomass is an efficient and established method for the production of hydrogen, which is an attractive

product because of its energy efficiency and low generation of pollutants.<sup>[11]</sup> In SCWG, biomass with high water content can be easily converted to hydrogen.<sup>[12]</sup> The water in the gasification process is not only a solvent but also a reagent that provides hydrogen atoms to form H<sub>2</sub>.<sup>[12–13]</sup>

There are few publications in the literature on SCWG of effluents from the dairy industry. Muangrat et al.<sup>[14]</sup> investigated gasification of whey using a closed batch autoclave reactor, subcritical water in the range of 300–390 °C, 9.5–24.5 MPa, 5 g · min<sup>-1</sup>, reaction time up to 120 min, and concentration of whey of 0.05 g/g (5 wt%) in the presence of NaOH and H<sub>2</sub>O<sub>2</sub>. They were able to extract 40 % of the possible theoretical hydrogen from this biomass. Söğüt et al.<sup>[15]</sup> conducted a study focused on the partial oxidation of whey (obtained through the production of cottage cheese from milk, and used in their experiments after coarse filtration and dilution with deionized water at a ratio of 1:10). They achieved TOC removal of about 99 % using H<sub>2</sub>O<sub>2</sub> at 400–650 °C, residence times of 6–21 s, TOC of 56 g · L<sup>-1</sup>, and 25.0 MPa.

In the present work, to investigate the oxidation (SCWO) and gasification (SCWG) processes of dairy industry effluents, gasification experiments using lactose (used as a model compound for whey), supercritical water, alkali salts (NaOH, KOH, and Na<sub>2</sub>CO<sub>3</sub>) as catalyst, and oxidants (hydrogen peroxide and *tert*-butyl hydroperoxide) were carried out for production of H<sub>2</sub>. The reactions were conducted at 550–700 °C, using concentrations of lactose between 0.005 and 0.025 g/g (0.5 and 2.5 wt%), feed flow rates between 5 and 7 g · min<sup>-1</sup>, and pressure of 22.5 MPa. The

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gases produced in the gasification of lactose were analyzed in a gas chromatograph and the liquid was analyzed using a TOC analyzer.

## EXPERIMENTAL

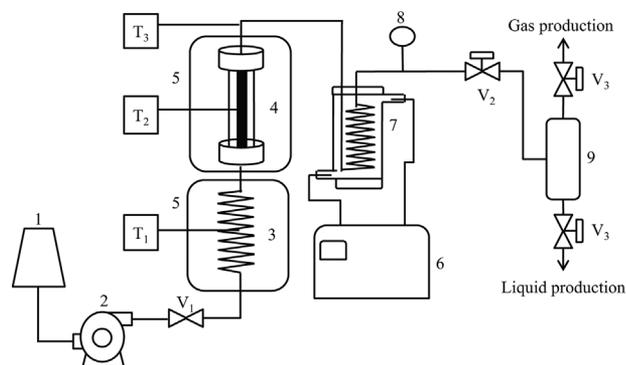
### Materials

Hydrogen peroxide ( $H_2O_2$ , 30 wt%) and *tert*-butyl hydroperoxide (t-BHP, 0.7 g/g (70 wt%)) were purchased from Synth (Diadema-SP, Brazil). Lactose monohydrate (> 0.98 g/g (98 wt%)) was obtained from Anidrol (Diadema-SP, Brazil). All chemicals and solvents used were of analytical grade.

### Experimental Procedure

The experimental apparatus scheme used for measurements of TOC reduction and hydrogen production is shown in Figure 1, according to Ferreira-Pinto et al.<sup>[16]</sup> The experimental apparatus consists of a continuous flow reactor built in Inconel 625, a condenser, a preheater, and 316 stainless steel tubings.

Lactose aqueous solution were prepared by weighting lactose with a high precision balance (Ohaus Analytical Standard, USA, uncertainty of 0.0001 g). Mixed lactose aqueous solution contained in a glass reservoir (1) was suctioned by a high pressure pump, HPLC type (2). The mixture was transferred to the valve  $V_1$  and then distributed to the preheater (3) at 50 °C and moved to the reactor (4). Both the heating of the reactor and the preheating device were carried out through two bipartite ovens (5), each equipped with two infrared ceramic resistors with a power of 1000 W. Inside the reactor, the lactose mixture was heated to temperatures varying from 550 to 700 °C, as described in Production of Gases. After that, the mixture flowed through the reactor to the heat exchange (6). Next, the mixture entered the condenser (7) for cooling at 10 °C. After that, the mixture reached the back-pressure valve ( $V_2$ ) for pressure adjustment observed on the gauge (8). Gas and liquid were separated in the separator vessel (9), where water, unreacted lactose, and other products were present in liquid phase, and gaseous reaction products such as  $H_2$ ,  $CO_2$ , CO, and  $CH_4$  were in vapour phase. Chemical analysis of the composites of liquid effluent and solid residue obtained from each experiment were not analyzed. However, liquid effluent was characterized by TOC.



**Figure 1.** Scheme of the SCWO apparatus. (1) Reservoir for the feed. (2) High pressure pump. (3) Preheater (50 °C). (4) Reactor (550–700 °C). (5) Oven. (6) Thermostatic bath. (7) Condenser. (8) Manometer. (9) Phase separator. (T1) Temperature controller of electrical resistance. (T2) Universal temperature indicator. (V1) One-way valve. (V2) Back-pressure regulator valve. (V3) Needle valve.

### Analysis Methodology

A carbon analyzer (Shimadzu L CPH/CPN, Kyoto, Japan) was used to measure the TOC of the liquid effluents. The difference between the concentrations of total carbon and inorganic carbon was used to determine the TOC of each run. The composition of the gas produced during the lactose degradation was determined by gas chromatography (CG Agilent 7890A, USA) using a column of 30 m × 0.535 mm × 20 μm (HP-PLOT Molesieve/5A columns, USA), helium as a carrier gas, and two detectors in series, one of them being a thermal conductivity detector (TCD) and the other a flame ionization detector (FID). The column temperature was held for 5 min at 40 °C, then it was increased to 180 °C using a 10 °C · min<sup>-1</sup> rate and maintained at 180 °C for 10 min. After that, the temperature was increased to 250 °C using a 5 °C · min<sup>-1</sup> rate, and finally, temperature was maintained at 250 °C for 10 min, following the methodology described by Ferreira-Pinto et al.<sup>[16]</sup> All samples were filtered by a membrane filter (0.45 μm) and posteriorly acidified to pH 2.

### Calculation Procedure

The reduction of the TOC, yield of  $H_2$  ( $Y_{H_2}$ ), yield of carbon species  $j$  ( $Y_j$ ), and molar fraction gaseous products ( $X_i$ ) were calculated using Equations (1–4):

$$Y_{H_2} (\%) = \frac{\text{mol of } H_2 \text{ in } F_{out}^i}{\text{mol of } H_2 \text{ in } F_{lactose,in}} \times 100 \quad (1)$$

$$Y_j (\%) = \frac{\text{mol of carbon species } j \text{ in } F_{out}^i}{\text{mol of carbon atom in } F_{lactose,in}} \times 100 \quad (2)$$

$$X_i = \frac{F_{out}^i}{\sum_i F_{out}^i} \quad (3)$$

$$\text{Reduction TOC } (\%) = \frac{TOC_{in} - TOC_{out}}{TOC_{in}} \times 100 \quad (4)$$

where  $F_{lactose,in}$  and  $F_{out}^i$  are the molar flow rates of lactose for species  $i$  in the inlet and outlet of the reactor, respectively.  $TOC_{in}$  and  $TOC_{out}$  are the values of TOC in the inlet and outlet of the reactor, respectively. The residence time ( $\tau$ ) can be calculated using Equation (5):

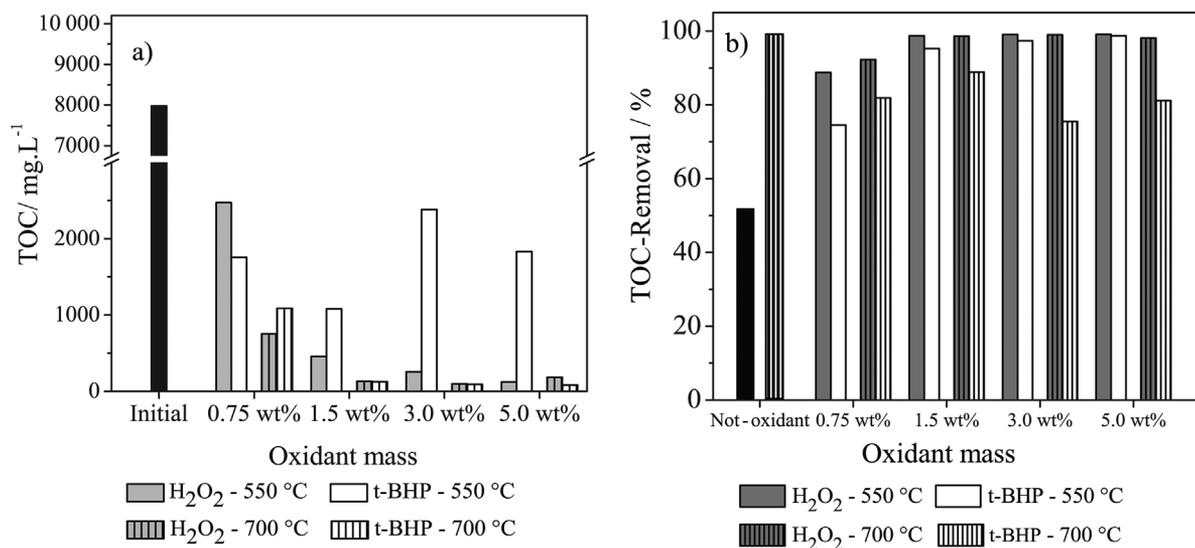
$$\tau = \frac{Vr \cdot \rho_{T,P}}{\phi_{m,STP}} \quad (5)$$

where  $Vr$  represents the geometric reactor volume,  $\rho_{T,P}$  represents the average water density at process temperature and pressure, and  $\phi_{m,STP}$  represents the mass flow rate at standard conditions (25 °C, 0.1 MPa). For residence time determination, the feed was assumed to consist only of pure water.

## RESULTS AND DISCUSSION

### Reduction of TOC

Lactose gasification reactions using hydrogen peroxide ( $H_2O_2$ ) and *tert*-butyl hydroperoxide (t-BHP) as oxidant agents were carried out.  $H_2O_2$ , an oxidant widely used in supercritical gasification oxidative reactions, shows considerable efficiency in the oxidation/destruction of biomass.<sup>[17–20]</sup> The second oxidant agent (t-BHP) is typically used in syntheses reactions, epoxidation,



**Figure 2.** Effect of amount of different oxidants on TOC removal for the SCWO of lactose at 22.5 MPa and  $5 \text{ g} \cdot \text{min}^{-1}$ : (a) values of input and output of TOC; (b) percentage removal of TOC (550 °C (symbol hatched) and 700 °C (symbol not hatched)).

and hydrodesulphurization oil, among others,<sup>[21–24]</sup> and has not yet been reported in the literature as an oxidant in gasification reactions.

The lactose TOC reduction was evaluated as a function of lactose concentration, temperature, and oxidant type. The feed flow ( $5 \text{ g} \cdot \text{min}^{-1}$ ) and system pressure (22.5 MPa) were kept constant. Figure 2 shows that the lactose TOC reduction is accelerated with increasing temperature, as usually observed in the literature. For samples without oxidant at low temperature (550 °C), the lactose

TOC reduction was approximately 50 %, while at high temperature (700 °C), the TOC reduction was close to 95 %. On the other hand, in the presence of the oxidant, the lactose TOC reduction was up to 99 %, regardless of the temperature used. The influences of the oxidant type and lactose concentration on TOC reduction were low at 550 °C and completely negligible at high temperature. For example, at a temperature of 550 °C, the lactose TOC reduction was lower for t-BHP than for  $\text{H}_2\text{O}_2$ ; however, at 700 °C, the oxidant presence did not affect lactose TOC reduction.

**Table 1.** Yield, gas mole fraction, and TOC reduction obtained for the SCWO of lactose using different types of oxidants ( $\text{H}_2\text{O}_2$  and t-BHP)<sup>a</sup>

T (°C) <sup>b</sup>	Oxidant	Amount (wt%; g/100 g)	TOC reduction (%)	Dry gas composition (mol/total mol)				Gas yield (mol gas/mol lactose fed)			
				$\text{H}_2$	$\text{CO}_2$	$\text{CH}_4$	CO	$\text{H}_2$	$\text{CO}_2$	$\text{CH}_4$	CO
550	No oxidant	–	51.3	$0.17 \pm 0.01$	$0.39 \pm 0.02$	$0.05 \pm 0.01$	$0.37 \pm 0.02$	$0.41 \pm 0.01$	$0.95 \pm 0.08$	$0.11 \pm 0.0$	$0.89 \pm 0.01$
	$\text{H}_2\text{O}_2$	0.75	$74.4 \pm 0.14$	$0.58 \pm 0.03$	$0.39 \pm 0.04$	$0.03 \pm 0.0$	$0.00 \pm 0.0$	$4.13 \pm 0.10$	$2.80 \pm 0.36$	$0.18 \pm 0.01$	$0.01 \pm 0.01$
		1.5	$95.0 \pm 0.24$	$0.57 \pm 0.02$	$0.40 \pm 0.02$	$0.02 \pm 0.0$	$0.01 \pm 0.0$	$3.68 \pm 0.26$	$2.54 \pm 0.07$	$0.14 \pm 0.01$	$0.03 \pm 0.01$
		3.0	$96.8 \pm 0.56$	$0.49 \pm 0.02$	$0.49 \pm 0.0$	$0.02 \pm 0.0$	$0.00 \pm 0.0$	$3.27 \pm 0.20$	$3.29 \pm 0.06$	$0.12 \pm 0.01$	$0.00 \pm 0.0$
		5.0	$98.7 \pm 0.01$	$0.34 \pm 0.03$	$0.66 \pm 0.02$	$0.01 \pm 0.0$	$0.00 \pm 0.0$	$2.30 \pm 0.19$	$4.51 \pm 0.14$	$0.05 \pm 0.01$	$0.00 \pm 0.0$
	t-BHP	0.75	$81.6 \pm 0.26$	$0.45 \pm 0.10$	$0.51 \pm 0.12$	$0.04 \pm 0.01$	$0.00 \pm 0.0$	$3.38 \pm 0.70$	$3.81 \pm 0.81$	$0.29 \pm 0.07$	$0.00 \pm 0.0$
		1.5	$88.5 \pm 0.33$	$0.44 \pm 0.10$	$0.51 \pm 0.12$	$0.05 \pm 0.01$	$0.00 \pm 0.0$	$3.17 \pm 0.67$	$3.62 \pm 0.43$	$0.33 \pm 0.12$	$0.00 \pm 0.0$
		3.0	$73.6 \pm 1.84$	$0.50 \pm 0.04$	$0.43 \pm 0.05$	$0.07 \pm 0.01$	$0.00 \pm 0.0$	$3.95 \pm 0.47$	$3.35 \pm 0.22$	$0.54 \pm 0.08$	$0.02 \pm 0.01$
		5.0	$81.1 \pm 0.01$	$0.59 \pm 0.09$	$0.30 \pm 0.09$	$0.10 \pm 0.0$	$0.01 \pm 0.0$	$4.77 \pm 0.41$	$2.44 \pm 0.81$	$0.77 \pm 0.02$	$0.05 \pm 0.0$
	700	No oxidant	–	96.6	0.29	0.36	0.20	0.09	1.20	1.49	0.82
$\text{H}_2\text{O}_2$		0.75	$92.1 \pm 0.16$	$0.64 \pm 0.06$	$0.34 \pm 0.06$	$0.02 \pm 0.0$	$0.01 \pm 0.0$	$4.23 \pm 0.55$	$2.25 \pm 0.34$	$0.10 \pm 0.02$	$0.05 \pm 0.01$
		1.5	$98.5 \pm 0.11$	$0.47 \pm 0.11$	$0.49 \pm 0.10$	$0.04 \pm 0.01$	$0.00 \pm 0.0$	$3.27 \pm 0.70$	$3.11 \pm 0.55$	$0.26 \pm 0.07$	$0.02 \pm 0.01$
		3.0	$99.0 \pm 0.06$	$0.38 \pm 0.04$	$0.60 \pm 0.04$	$0.02 \pm 0.0$	$0.00 \pm 0.0$	$2.55 \pm 0.31$	$4.02 \pm 0.18$	$0.11 \pm 0.02$	$0.01 \pm 0.02$
		5.0	$98.0 \pm 0.08$	$0.11 \pm 0.06$	$0.89 \pm 0.06$	$0.00 \pm 0.0$	$0.00 \pm 0.0$	$0.80 \pm 0.33$	$6.35 \pm 0.28$	$0.01 \pm 0.01$	$0.00 \pm 0.0$
t-BHP		0.75	$88.4 \pm 0.44$	$0.48 \pm 0.02$	$0.45 \pm 0.02$	$0.06 \pm 0.0$	$0.01 \pm 0.0$	$3.46 \pm 0.28$	$3.25 \pm 0.01$	$0.46 \pm 0.0$	$0.04 \pm 0.0$
		1.5	$98.6 \pm 0.07$	$0.53 \pm 0.09$	$0.34 \pm 0.13$	$0.11 \pm 0.04$	$0.01 \pm 0.0$	$3.98 \pm 0.46$	$2.56 \pm 0.65$	$0.84 \pm 0.31$	$0.07 \pm 0.03$
		3.0	$99.0 \pm 0.08$	$0.65 \pm 0.08$	$0.26 \pm 0.01$	$0.07 \pm 0.10$	$0.01 \pm 0.0$	$5.73 \pm 0.84$	$2.25 \pm 0.15$	$0.60 \pm 0.01$	$0.11 \pm 0.02$
		5.0	$99.0 \pm 0.08$	$0.48 \pm 0.01$	$0.36 \pm 0.01$	$0.14 \pm 0.0$	$0.01 \pm 0.0$	$4.02 \pm 0.13$	$3.05 \pm 0.01$	$1.20 \pm 0.02$	$0.10 \pm 0.0$

<sup>a</sup>Operating conditions (22.5 MPa, 550 °C,  $5 \text{ g} \cdot \text{min}^{-1}$ , feed of 0.025 g/g (2.5 wt%), and initial TOC of  $7983 \text{ mg} \cdot \text{L}^{-1}$ ); <sup>b</sup> $u(T) = 1.0 \text{ }^\circ\text{C}$ .

**Table 2.** Residence time ( $\tau$ ) calculated for reaction at a pressure of 22.5 MPa

Flow rate ( $\text{g} \cdot \text{min}^{-1}$ )	Residence time, $\tau$ (s)		
	25 °C	550 °C	700 °C
5	317	22	17

At lower temperature, these behaviours exploit the oxidant effect on lactose TOC reduction, since the level of lactose TOC reduction was the same without oxidant presence at the highest temperature.

#### Production of Gases

Lactose gasification reactions were conducted with and without the use of oxidant agent at 550 and 700 °C, with a lactose concentration of 0.025 g/g (2.5 wt%), feed flow rate of  $5 \text{ g} \cdot \text{min}^{-1}$ , initial TOC of  $7983 \text{ mg} \cdot \text{L}^{-1}$ , and pressure of 22.5 MPa. The oxidant concentrations used were 0.0075, 0.01, 0.03, and 0.05 g/g (0.75, 1.0, 3.0, and 5.0 wt%) for both  $\text{H}_2\text{O}_2$  (hydrogen peroxide) and t-BHP (*tert*-butyl hydroperoxide). The gases were collected and analyzed using gas chromatography equipment every 30 min over a total reaction time of 90 min. The weighted averages of yields and mass fractions of the gas obtained from the gasification reactions are presented in Table 1. The gas composition and yield were affected by temperature, oxidant concentration, and type of oxidant.

Generally, oxidants significantly increase the concentration of  $\text{H}_2$  and decrease concentration CO. In reactions with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) production of  $\text{H}_2$  has its maximum at the lowest concentration of the oxidant (0.0075 g/g (0.75 wt%)) and is significantly decreased at higher  $\text{H}_2\text{O}_2$  concentrations, especially at 700 °C. On the other hand, *tert*-butyl hydroperoxide (t-BHP) improved the  $\text{H}_2$  production, which reached its maximum at the highest concentration of the oxidant (0.05 g/g (5.0 wt%)). For both oxidants, changes in the production of  $\text{H}_2$  inversely affect the production of  $\text{CO}_2$ .

In addition, the coke formation was observed mainly in the reactions at 550 °C. The main gases that formed during the gasification reactions, regardless of the reaction conditions, were  $\text{H}_2$ ,  $\text{CO}_2$ , CO, and  $\text{CH}_4$ .

The residence time is directly related to feed flow rate, temperature, and pressure of the reactor operation. Table 2 shows the residency times for temperatures studied.

Each gasification reaction of lactose occurred during a period of 90 min whereas the sample collection and analysis of the gaseous and liquid phase were carried out every 30 min.

#### CONCLUSIONS

We propose the use of supercritical water for the removal of organic matter present in the dairy wastewater and simultaneous production of energy. To the best of our knowledge, such an approach has not been reported in the literature. The experimental results showed that the addition of oxidant agent increased the  $\text{H}_2$  yield and decreased lactose TOC reduction when compared with supercritical water oxidation of lactose without oxidant. Therefore, supercritical water oxidation of lactose in the presence of oxidant agents is a promising method to treat dairy wastewater and recover energy through production of gases, particularly  $\text{H}_2$ . The use of continuous flow processing through supercritical water

oxidation for waste treatment is fundamental to enable the scale-up of this process.

#### NOMENCLATURE

BOD	biochemical oxygen demand
$\text{CO}_2$	carbon dioxide
CO	carbon monoxide
COD	chemical oxygen demand
$\text{CH}_4$	methane
HPLC	high performance liquid chromatography
$\text{H}_2$	hydrogen
$\text{H}_2\text{O}_2$	hydrogen peroxide
KOH	potassium hydroxide
$\text{Na}_2\text{CO}_3$	sodium carbonate
NaOH	sodium hydroxide
SCWG	supercritical water gasification
SCWO	supercritical water oxidation
t-BHP	<i>tert</i> -butyl hydroperoxide
TOC	total organic carbon
( $\tau$ )	residence time

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#### REFERENCES

- [1] C. Mollea, L. Marmo, F. Bosco, "Valorisation of Cheese Whey, a By-Product from the Dairy Industry," in *Food Industry*, 1st edition, I. Muzzalupo, Ed., *InTech*, Rijeka 2013, accessed on 30 December 2016, <http://www.intechopen.com/books/food-industry/valorisation-of-cheese-whey-a-by-product-from-the-dairy-industry>.
- [2] A. R. Prazeres, F. Carvalho, J. Rivas, *J. Environ. Manage.* 2012, 110, 48.
- [3] P. Walstra, J. T. M. Wouters, T. J. Gwurts, *Dairy Science and Technology*, Taylor and Francis, Boca Raton 2006.
- [4] B. Demirel, O. Yenigun, T. T. Onay, *Process Biochem.* 2005, 40, 2583.
- [5] J. S. Yadav, S. Yan, S. Pilli, L. Kumar, R. D. Tyagi, R. Y. Surampalli, *Biotechnol. Adv.* 2015, 33, 756.
- [6] F. Carvalho, A. R. Prazeres, J. Rivas, *Sci. Total Environ.* 2013, 445, 385.
- [7] J. C. Frigon, J. Breton, T. Bruneau, R. Moletta, S. R. Guiot, *Bioresource Technol.* 2009, 100, 4156.
- [8] B. Balanec, G. Gésan-Guiziou, B. Chaufer, M. Rabiller-Baudry, G. Daufin, *Desalination* 2002, 147, 89.
- [9] V. B. Brião, C. R. G. Tavares, *Braz. J. Chem. Eng.* 2007, 24, 487.
- [10] Z. Fang, R. L. Smith Jr., H. Inomata, K. Arai, *J. Supercrit. Fluid.* 2000, 16, 207.
- [11] G. Brunner, *J. Supercrit. Fluid.* 2009, 47, 373.
- [12] M. J. Antal, S. G. Allen, D. Schulman, X. Xu, R. J. Divilio, *Ind. Eng. Chem. Res.* 2000, 39, 4040.
- [13] M. Watanabe, H. Inomata, K. Arai, *Biomass Bioenerg.* 2002, 22, 405.
- [14] R. Muangrat, J. A. Onwudili, P. T. Williams, *Bioresource Technol.* 2010, 101, 6812.

- [15] O. Ö. Söğüt, E. Kıpçak, M. Akgün, *Water Sci. Technol.* **2011**, *63*, 908.
- [16] L. Ferreira-Pinto, A. C. Feirhrmann, M. L. Corazza, N. R. C. Fernandes-Machado, J. S. dos Reis Coimbra, M. D. A. Saldaña, L. Cardozo-Filho, *Int. J. Hydrogen Energ.* **2015**, *40*, 12162.
- [17] T. Fujii, R. Hayashi, S. Kawasaki, A. Suzuki, Y. Oshima, *J. Supercrit. Fluid.* **2011**, *58*, 142.
- [18] M. B. García Jarana, J. Sánchez-Oneto, J. R. Portela, E. Nebot Sanz, E. J. Martínez de la Ossa, *J. Supercrit. Fluid.* **2008**, *46*, 329.
- [19] M. Goto, T. Nada, A. Ogata, A. Kodama, T. Hirose, *J. Supercrit. Fluid.* **1998**, *13*, 277.
- [20] R. Muangrat, J. A. Onwudili, P. T. Williams, *Bioresource Technol.* **2010**, *101*, 6812.
- [21] L. Gao, S. Xiong, C. Wan, Z. Wang, *Synlett* **2013**, *24*, 1322.
- [22] M. Kim, S. Sharma, J. Park, M. Kim, Y. Choi, Y. Jeon, J. H. Kwak, I. S. Kim, *Tetrahedron.* **2013**, *69*, 6552.
- [23] L. P. Stepovik, A. Y. Potkina, *Russ. J. Gen. Chem.* **2013**, *83*, 1047.
- [24] Q. Tang, S. Lin, Y. Cheng, S. Liu, J. R. Xiong, *Ultrason. Sonochem.* **2013**, *20*, 1168.

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