



Heat effects of wet oxidation of glucose: A biomass model compound



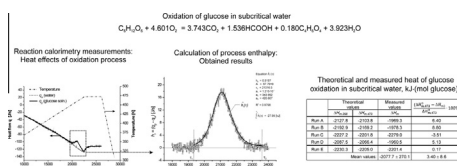
M. Imbierowicz*, M. Troszkiewicz, K. Piotrowska

Faculty of Process and Environmental Engineering, Lodz University of Technology, Poland

HIGHLIGHTS

- Glucose oxidation was studied under high pressures and temperatures.
- Heat effects of this process was measured using reaction calorimetry.
- The measured enthalpy of this process is in good agreement with theoretical value.

GRAPHICAL ABSTRACT



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ABSTRACT

Glucose, as a representative biomass model compound, was oxidized in an aqueous solution in a temperature range from 298 K to 473 K under pressure of 2.13–5.0 MPa. Results of measurements of heat effects generated during that process are presented and discussed in the paper. The measurements were taken using a heat-flow reaction calorimeter in non-isothermal conditions by heating the reaction mixture from 298 K to a final temperature of 473 K at a rate $R_t = 4.0$ and 0.5 deg min^{-1} . The oxidation was carried out for 3.5 and 8.5 h using different initial concentrations of glucose, i.e. 2.66, 3.65 and 4.93 g dm^{-3} . As a result of these experiments a 56–64% reduction of TOC was obtained. The products of glucose oxidation in these conditions were also formic and succinic acids. The value of molar enthalpy of glucose oxidation with oxygen in subcritical water was $\Delta H_m = -2077.7 \pm 270.1 \text{ kJ mol}^{-1}$ substrate used. Differences observed in the heat effects of oxidation in the experiments resulted from different values of TOC removal and changing composition of final products in the solution after oxidation. The values of the heat of wet oxidation of glucose were consistent with the results of thermochemical calculations and the average error of ΔH_m determination was 3.40%.

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1. Introduction

The oxidation of organic compounds in sub-critical water conditions using oxygen or air is an effective, industrial oxidation process used to treat a variety of hazardous wastes. The process consists of the oxidation of substances present in water at elevated temperature (up to 593 K) and under increased pressure (to 20.0 MPa) using oxygen or air [2]. Pressures higher than partial water vapor pressure at given temperature are applied in the process. In these conditions the oxidation process takes place in the liquid phase and does not require evaporation of big amounts of

water. The process of wet oxidation is used primarily to remove noxious pollutants from wastewater and to destroy excess activated sludge formed in biological sewage treatment plants.

The wet air oxidation (WAO) of organic compounds in subcritical water conditions gives a beneficial energetic effect. The recovery of this energy in the form of steam production, heating of water or for other purposes is very efficient, even low-quality fuels are used in this process [17,1]. Various forms of energy recovery in a WAO plant have been reported in the literature, but there are very few articles which give the values of heat effects of the oxidation of organic compounds. Othmer [14] reported that with most organics, for each gram per liter of the COD value given by a standard analysis, there is a heating value of $12.54\text{--}13.94 \text{ kJ (g O}_2\text{)}^{-1}$ (45–50 BTU per gallon) of liquid fed to the WAO reactor. Debellefontaine and Foussard [8] estimated the enthalpy of complete oxidation (mineralization) of an organic compound

* Corresponding author at: Faculty of Process and Environmental Engineering, Lodz University of Technology, ul. Wolczanska 213, 90-924 Poland. Tel.: +48 42 631 3720; fax: +48 42 636 81 33.

E-mail address: imbier@wipos.p.lodz.pl (M. Imbierowicz).

Nomenclatures

A	heat transfer area, m^2	JP	quality index, described by Eq. (A-4)
C	concentration, mol m^{-3}	n	cardinality of the data series, [–]
C_p	heat capacity, $\text{J mol}^{-1} \text{deg}^{-1}$	N	number of measurement points
q_i	heat flux, J s^{-1}	μ	expected value, $\mu = 0, \text{J s}^{-1}$
h_r	instantaneous heat effect of a chemical process, J s^{-1}	ν_i	stoichiometric coefficients
$\hat{h}(\tau)$	peak function, described by Eq. (A-3)	p	pressure, MPa
\bar{h}_r	the average of analyzed data series, J s^{-1}	R_t	heating rate, deg min^{-1}
$\Delta H_{m,298}^0, \Delta H_{m,473}^0$	glucose heats of combustion in standard and experimental conditions, kJ mol^{-1} glucose	S_x	standard deviation of the sample, J s^{-1}
ΔH_m	molar enthalpy of wet oxidation of glucose in subcritical water, kJ mol^{-1}	T	temperature, K
ΔH_r	total heat effect of wet oxidation of glucose, J	τ_1, τ_2	limits of integration, s
$h_{0,A}, \tau_z, a_1, a_2, a_3$	the unknown parameters of Eq. (A-3)	U	heat transfer coefficient, $\text{W m}^{-2} \text{K}^{-1}$
i, j, k	indices	u_i	standardized random variable, calculated from formula (A-1)

containing common heteroatoms with the formula $C_mH_nO_kCl_wN_xS_yP_z$ as $13.59 \text{ kJ (g O}_2\text{)}^{-1}$ or 435 kJ per mole of O_2 reacted.

The aim of present studies was to determine the heat effects of oxidation of glucose as carbohydrate model compound in subcritical water, using reaction calorimetry. The reaction calorimetry is a method which can provide (in real-time) valuable information on the kinetics of chemical reactions and heat transfer processes in wet oxidation reactors [22]. However, a great advantage of the reaction calorimetry is that the measurement of heat effects generated during wet oxidation of a selected waste stream allows us to assess if the tested substrates can be effectively used in energy production. Glucose was chosen as a biomass model compound because the mechanism and kinetics of wet oxidation of this substrate was studied earlier and is well described. Brett and Gurnham [4] studied wet oxidation of glucose using H_2O_2 as an oxidant and metal salts as catalysts. They found that, if H_2O_2 and potassium dichromate was used in the experiments, a mean decrease in COD was 74.2% at average temperature 443 K and pressure 5.2 MPa. In the absence of hydrogen peroxide and dichromate the mean decrease was only 1.9% of starting COD. Skaates et al. [20] studied the kinetics of wet oxidation of glucose at 450–533 K and oxygen partial pressure of 2.3 MPa. The activation energy for the rapid stage of this substrate oxidation was found to be $130 \pm 20 \text{ kJ mol}^{-1}$. The mechanism of noncatalytic oxidation of model carbohydrate compounds in aqueous solutions at 393–511 K and oxygen partial pressure 0.83–3.3 MPa was studied by McGinnis et al. [12]. They observed that the major product formed by wet oxidation of a series of model compounds (including D-xylose and D-glucose) was formic acid. Acetic acid was also formed; but its yield was much less dependent on the carbohydrate structure. A similar observation was made by Biermann et al. [3] – the oxidation of glucose in subcritical water resulted in a significant decrease of COD (60–80%) and formation of low molecular organic acids such as formic, acetic and succinic acid. All cited authors studied the mechanism and kinetics of glucose oxidation in subcritical water, but they did not discuss heat effects generated during that process. In the literature there is no data presenting the amount of energy released during glucose oxidation by oxygen in subcritical water.

2. Experimental

The measurements were taken using a heat-flow reaction calorimeter (Metler–Toledo). The measurement of heat effects of glucose oxidation consisted of measuring the heat-flow rate between a reaction mixture and cooling liquid. A detailed description of the operation and method for preparation of heat balance

used in a Metler–Toledo RC-1 reaction calorimeter can be found in the paper by [19]. Heat flux generated during the process of glucose oxidation was calculated from the following relation:

$$q_i = \pm U \cdot A \cdot (T_r - T_j) \quad (1)$$

where: q_i – heat flux removed from (or supplied to) the reaction system [W], U – heat transfer coefficient [$\text{W m}^{-2} \text{K}^{-1}$], A – heat transfer area [m^2], T_r – temperature of the reactor content [K], T_j – temperature of the heating/cooling liquid [K].

The measurement of heat effects of glucose oxidation in subcritical water was carried out in a stainless steel batch reaction calorimeter with a volume of 1.7 dm^3 . Glucose solutions used in the experiments had a volume of 0.70 dm^3 . In these conditions the volume of gas space of the calorimeter was 1.0 dm^3 . To prepare the solutions, crystalline glucose (Sigma–Aldrich) of purity above 99.5% was used, and for oxidation oxygen gas (Air Liquide) of 99.5% purity was applied. In the experiments a large stoichiometric excess of oxygen was used. The RC-1 reaction calorimeter was equipped with a gas impeller and systems for measuring and recording temperatures of the reaction content and cooling/heating liquid.

The heat effect of glucose oxidation in subcritical water was measured in three stages. First, the measuring system was calibrated which included determination of the value of product $U \cdot A$ in formula (1). A detailed description of these studies and their results were published earlier [18]. The values of $U \cdot A$ were determined for different temperatures and at different rotational speeds of the impeller. It was found that at a temperature of 298 K the value of $U \cdot A$ at a speed of 700 rpm^{-1} was 380 W K^{-1} , while at 473 K it increased to 795 W K^{-1} . The values of $U \cdot A$ determined during the calorimeter calibration were used in subsequent experiments with glucose oxidation in subcritical water.

In the next phase of the test a blank experiment was performed whose aim was to obtain an experiment baseline. For this aim the whole experiment was carried out using distilled water as a feed to the RC-1 calorimeter. During the blank experiment heat fluxes q_w in the calorimeter were recorded. The determination of an experiment baseline greatly facilitated the interpretation of results. An instantaneous heat effect of a chemical process h_r could be calculated by subtracting heat fluxes recorded during the blank experiment $h_r = q_g - q_w$ from the heat fluxes measured during glucose oxidation. Using this method one could eliminate from further calculations parts of balance equations which described heat losses to the environment (convection and radiation), heating power supplied during mixing and the heat accumulation in the reaction mixture. It also enables consideration of the heat of oxygen dissolution in water and to compensation of the heat required for rising

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