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DETERMINATION OF HEAT EFFECTS DURING THE OXIDATION OF BIOMASS IN SUBCRITICAL WATER

WYZNACZANIE EFEKTÓW CIEPLNYCH REAKCJI UTLENIANIA BIOMASY W ŚRODOWISKU WODY PODKRYTYCZNEJ

Abstract: The search of alternative energy sources is one of the most important elements of sustainable development policy. The biomass is a valuable source of renewable energy but its transformation into biofuel needs a big amount of energy because many kinds of biomass have high hydrations level. The wet oxidation (in subcritical water conditions) of substances containing biopolymers gives a beneficial energetic effect of the process. We do not lose energy for the dehydration of biomass, which is directed towards the burning process. The waste containing cellulose (or another similar biopolymers) is a potential, valuable source of renewable energy. The wet oxidation process in subcritical water conditions can become an attractive alternative for the conventional burning processes.

Keywords: biomass, wet oxidation, subcritical water, renewable energy, cellulose, glucose, reaction calorimetry

We should treat our environment as borrowed from future generation and we should do everything to keep it in the same or better condition [1]. Nowadays the lack of energy sources is the growing problem. Trying to solve this difficult situation we should focus our attention on biomass as an alternative to fossil resources. It has always been a major source of energy for mankind and is presently estimated to contribute to 10÷14% of the world's energy supply. This form of renewable energy is widely used in the third world. It is necessary to increase the use of biomass in the Western world using the adequate methods. Biomass production can generate employment because of its availability in many countries [2].

Much attention should be focused on identifying suitable biomass species, which can provide highenergy outputs, to replace conventional fossil fuel energy sources. Due to global warming caused by excessive use of fossil fuel resource, renewable biomass resources should become more important in the future as alternatives to fossil resources. Together with the depletion of fossil resources and deterioration of our global environment, it will become more and more important to utilize biomass resources [3].

One of the most important and urgent problems in environmental management is waste treatment. A zero emission process for the efficient treatment of biomass waste should be developed. The conversion of biomass into energy, for example, fuels and chemicals, can be achieved in a number of ways. The most important problem is that resources should be environment-friendly utilized. The development of a process that could recover chemical resources from biomass wastes to control the circulation of carbon in biosphere is desirable [4]. The conversion of biomass into energy can be achieved by the application of a number of technologies. Each characterizes specific requirements, advantages and disadvantages.

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The technologies, which can convert biomass to sources of energy, should help to solve energy and environmental problems.

Biomass as a resource of energy

Biomass is a term for all organic material that stems from plants (including algae, trees and crops). One simple method is to define four main types of biomass: woody plants, herbaceous plants/grasses, aquatic plants, manures. Biomass is produced by green plants converting sunlight into plant material through photosynthesis and includes all land- and water-based vegetation, as well as all organic wastes [2]. Typically photosynthesis converts less than 1% of the available sunlight to store in chemical energy. The plant material is derived from the reaction between CO₂ in the air, H₂O and sunlight. The result is carbohydrates that form the building blocks of biomass. The biomass resources are also considered to be organic matter, in which the energy of sunlight is stored in chemical bonds. Chemical energy is released when the bonds between adjacent carbon, hydrogen and oxygen molecules are broken. It can be caused by digestion, combustion or decomposition. Biomass is also useful feed material for energy and chemical resources. It can be converted into three main types of product: electrical/heat energy, transport fuel and chemical feedstock.

Plant biomass is renewable, its combustion is neutral with regard to the carbon - dioxide cycle, as long as the usage and plantation are repeated under good control [5], and not only produces energy, but also chemicals [6]. For the reasons, we envision plant biomass as a future substitute for fossil fuels; it is necessary to find maximum utilization technology of biomass (especially cellulose biomass).

Cellulose - main component of biomass structure

Cellulose is one of the main components of biomass. It is the most abundant organic resource on the Earth [7]. Cellulose plant material represents an as-of-yet untapped source of fermentable sugars for significant industrial use [8]. Lignocelluloses or woody biomass are composed of carbohydrate of polymers - cellulose, lignin and smaller parts as extractives (acids, salts and minerals). The cellulose comprises typically two-thirds of the dry mass of plants. It is polysaccharid, which can be hydrolyzed to sugars and eventually be fermented to ethanol [9].

Cellulose (C₆H₁₀O₅)_n (40÷60% of the dry biomass) is a linear polymer of cellobiose (glucose-glucose dimer). It consists of linear chains (1,4)-D-glucofuranose units, in which the units are linked 1-4 in β-configuration, with an average molecular weight around 100,000 [2]. The orientation of the linkages and additional hydrogen bonding make the polymer rigid and difficult to break. Unless very large excess of enzyme is used, the enzymatic digestibility of cellulose in native biomass is low (<20% yield) because of its structural characteristics [8].

In hydrolysis the polysaccharide is broken down to free sugar molecules by the addition of water. This is also called saccharification. The product, glucose - C₆H₁₂O₆, is a six-carbon sugar (hexose) [9]. Cellulose is a valuable renewable energy resource, and also glucose and its oligomers, which are obtained by its hydrolysis process, are expected to be valuable chemicals, food and feedstock [10].

Wet air oxidation (WAO)

The conversion of biomass into energy can be achieved by the application of a number of technologies. The really important feature in the convert reactions is water. Sub- and supercritical waters have unique features with respect to density, dielectric constant, ion product, viscosity, diffusivity, electric conductance and solvent ability. Two major reactions in sub- or supercritical water are: oxidation and hydrolysis [4].

Wet air oxidation (WAO) is an effective and extensively used industrial oxidation process to treat a variety of hazardous wastes and heavily polluted effluents [11]. The basic idea of the wet air oxidation process (Zimmeman and Diddams, 1960) is to enhance contact between molecular oxygen and the organic matter to be oxidised [12]. WAO is the oxidation of soluble or suspended oxidizable materials by using oxygen in aqueous phase, at high temperature (150÷350°C) and high pressure (50÷150 bar) [13]. In the ideal case, oxidation of organics compounds would only produce CO₂, H₂O, N₂ and metal oxide. However, in WAO processes, the oxidation is rarely complete and often leads to the production of refractory materials like acetic acid, which is the main compound [13]. The general pattern of oxidation compounds containing C, H, O atoms is described as follows:

organic materials → alcohols → aldehydes → carboxylic acids → carbon dioxide

and it is generally admitted that degradation mechanisms of organic materials is non-catalytic. The biggest advantage of WAO technology is that it is waste-free.

Calorimetric methods in kinetic reaction studies

The aim of our studies is determination heat effects during the oxidation of some kind of biomass using oxygen, increasing temperature and pressure. The study will present the results of non-catalytic WAO of glucose. We want to calibrate the method for our studies by using this simple substance, which heat of oxidation is known. Municipal wastes often contain cellulosic materials that originated from biomass. When cellulose could be converted to various saccharides by scission of glucoside bond in the consecutive reactions:

cellulose → oligosaccharides (cellotriase, cellobiose) → hexose (glucose)

Among these components, glucose is often considered as useful chemical resource that could be used as a starting material in chemical or biochemical reactions [4]. In our studies the really important reaction is oxidation of glucose:



Calorimetry - one of the oldest methods known to science - is based on the fact that all chemical reactions and physical transformations generate or consume heat. The basis for calculation of accurate calorimetric data is the balancing of heat and mass flow.

The calorimetric measurements, which are researching in calorimetric reactor RC1, will be used for these studies. A Mettler-Toledo reaction calorimeter with 2 dm³ jacketed batch reactor equipped with a gas type stirrer was used in this study as a pressure reactor (Fig. 1).

The calorimetric principle applied in RC1 apparatus is based on a continuous measurement of the temperature difference between the reactor content (T_r) and the heat transferred to fluid in the outer jacket (T_j). At any given time, the heat transferred between the fluid in the jacket and the reactor content, q_{flow}, is given by:

$$q_{\text{flow}} = UA(T_r - T_j)$$

Where U is the heat transfer coefficient and A is the heat exchange area. These parameters are determined by the calibration process.

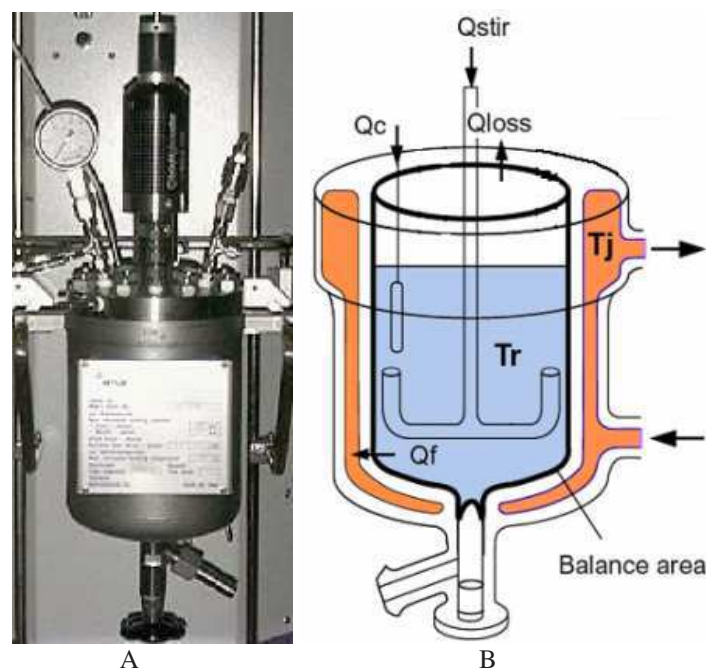


Fig. 1. Calorimetric reactor RC1 made by Mettler Toledo Company: A) photo, B) diagram

We applied 700 g samples of glucose solutions to the reactor, in different conditions of temperature (from 20 to 200°C) and pressure. Applied solutions concentrations of glucose ranged from 1000 to 2000 ppm. The same experiments were carried out for water (in the same conditions) for creating baseline.

Results

Our first calculations rest on calorimetric rules. The reaction of enthalpy is determined by integrating the peak of the heat generation rate Q_r . In the evolution we define the start and end point of possible reaction and its baseline (we use a pure water as baseline). Between the start and end pairs for the reaction limits, the integral is calculated as the area between Q_r curve and the baseline Q_b (Fig. 2).

Overall heat generated during the process ΔH_r was estimated from the following equation:

$$\Delta H_r = \int_S^E (Q_r - Q_b) dt$$

where:

ΔH_r - reaction enthalpy [J/mol],

Q_r - heat generation rate, calculated from the sum of the selected heat flow terms [W],

Q_b - baseline for Q_r [W].

As an area between recorded thermal curves Q_r and base line Q_b .

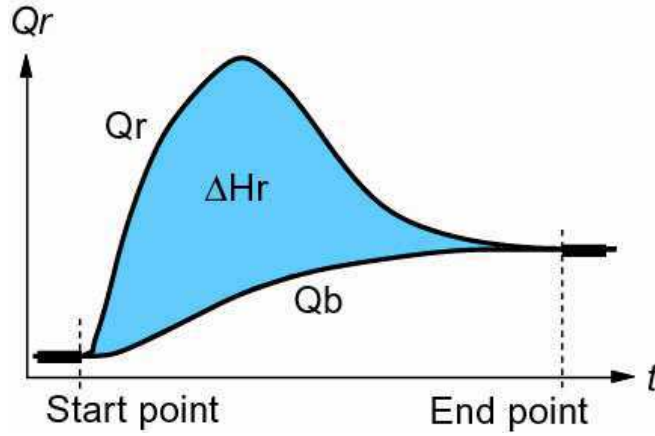


Fig. 2. Heat flow curves of possible reaction and its baseline

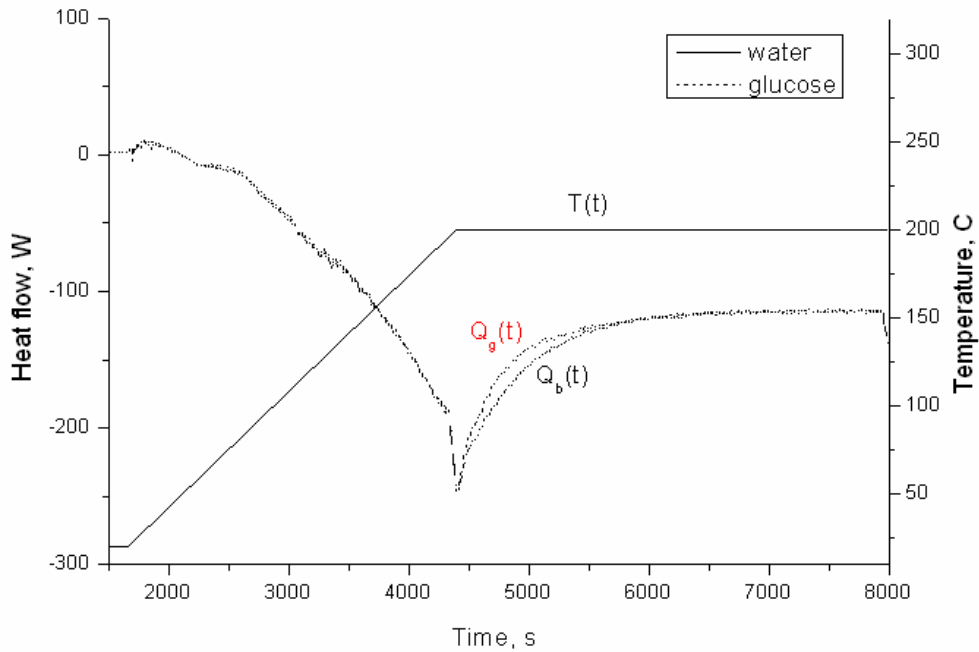


Fig. 3. Changes of water and glucose solution heat flow in RC-1 reactor ($C_0 = 1198$ ppm of glucose)

Our first results, which rest on these rules, show curves of water (baseline- Q_b) and glucose solution (Q_g) heat flow in time and temperature (Fig. 3). We do not observe any reaction during the first 4500 s of the reaction. When the temperature reaches 200°C, we can see the area between q_g curve and the baseline curve (Q_b). It is result of heat effects. The area between these curves is heat of glucose decomposition in wet oxidation reaction. We can calculate decreasing of total organic carbon (TOC) in glucose solution, too. The area converted into decreasing TOC unit gives us minor heat of reaction.

Basing on the diagram (Fig. 1B) we can create heat flow balance for our studies:

$$Q_r = Q_{\text{flow}} + Q_m + Q_{\text{loss}}$$

where:

Q_r - heat generation rate of chemical or physical reaction [W],

Q_{flow} - heat flow through the reactor wall - calibration power [W],

Q_m - heat accumulation by the reaction mass and insert,

Q_{loss} - heat flows through the reactor head assembly (radiation, conduction).

This method is suitable for the studies of heat processes. It can be used for the wet air oxidation studies. Due to technique described above we can calculate both heat effect of process and deduce the kinetics and mechanism of oxidation reaction.

The kinetic model, suggested in these studies, will be used for the simulation of installations' work producing using energy in the process of biopolymers' oxidation in subcritical water. We do not lose energy for the dehydration of biomass, which is directed towards the burning process. The waste containing cellulose (or another similar biopolymers) is a potential, valuable source of renewable energy.

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Abstrakt: Poszukiwanie alternatywnych źródeł energii jest jednym z ważniejszych elementów polityki zrównoważonego rozwoju. Biomasa jest w tym kontekście cennym źródłem energii odnawialnej, jednak ze względu na fakt, iż wiele rodzajów biomasy ma wysoki stopień uwodnienia, przekształcenie jej w biopaliwo wymaga dużych nakładów energetycznych. Stosując utlenianie substancji zawierających biopolimery w warunkach wody podkrytycznej (tzw. mokre utlenianie), uzyskujemy korzystny efekt energetyczny procesu, gdyż nie tracimy energii na odwadnianie strumieni kierowanych do spalania. W tym ujęciu odpady zawierające celulozę (lub inne podobne biopolimery) są potencjalnym, cennym źródłem energii odnawialnej, a proces utleniania w warunkach wody podkrytycznej może stać się atrakcyjną alternatywą dla konwencjonalnych procesów spalania.

Słowa kluczowe: biomasa, mokre utlenianie, woda podkrytyczna, energia odnawialna, celuloza, glukoza, reakcja kalorymetryczna