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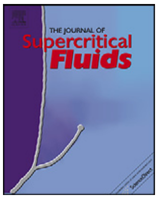

Hydrolysis of lignocellulosic biomass in water under elevated temperatures and pressures

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ABSTRACT

The hydrolysis of rye straw and rye silage in liquid hot water (LHW) as a pretreatment process for the utilization of lignocellulosic material (LCM) was investigated. Two different types of reactors, a batch autoclave (BA) and a continuous-flow (CF) apparatus, were used in this work. For both setups a certain time was needed to heat the reactor up to the desired temperature. The temperature profiles for both reactors were calculated and accurately predicted in order to assure comparable and defined operating conditions. For this purpose, a modified severity factor was used that accounted for the different temperatures during the heat-up phase in the reactors. The experimental results show that high degrees of biomass solubilization are possible using LHW, however, the yield of undesired degradation products increases with treatment severity as well. The particle size of the biomass and the substrate concentration seem to have no influence on the solubilization. The solubilization of rye silage seems to be easier compared to rye straw as parts of the protecting hemicellulose–lignin matrix have already been degraded by lactobacilli. The glucose formation and decomposition from rye straw were investigated using a simplified model according to the pattern of a single consecutive reaction following first-order kinetics and the results were compared to literature data dealing with the LHW treatment of starch as well as pure cellulose. Taking into consideration the advantages and disadvantages of the reactor types used, an optimal reactor concept is proposed for future investigations.

1. Introduction

The annual growth of plant-derived biomass is estimated to be 118×10^9 tonnes per year on a dry matter basis [1]. Against the background of this enormous growth of renewable material, plant biomass offers the potential of serving as a source of energy and feedstock for chemical products. Especially lignocellulosic waste (e.g. straw, stalks, bagasse) seems to be particularly suitable since it does not compete with animal feed and food industry. The composition of lignocellulosic material (LCM) is as follows: 34–50% cellulose, 19–34% hemicellulose, and 11–30% lignin [1]. The plant cells are composed of different layers, which differ from each other with respect to their structure and chemical composition. Basically, cellulose forms a skeleton, which is surrounded by the other substances functioning as matrix (hemicellulose) and encrusting (lignin) materials. Cellulose, hemicellulose, and lignin are closely associated and covalent cross-linkages have been suggested to occur between lignin and polysaccharides (lignin–carbohydrate complexes). Hence, biomass can be regarded as a composite material, in which the lignin serves as a protective layer. Due to the lignin content and the associated cross-linked structure, plant biomass exhibits a remarkable stability against biological attack and can only hardly be converted. Therefore, a pretreatment is necessary in order to improve the digestibility of the biomass for a subsequent enzymatic treatment. Although different process steps are necessary in order to convert the biomass to useful products, the intermediate is virtually always glucose. Glucose is the monomeric building block of the cellulose, and once this fraction is saccharified, the glucose can, e.g. be converted to ethanol [2–7] or hydroxymethylfurfural (HMF) [8]. Fig. 1 shows the degradation of the sugar monomers glucose and xylose to their main degradation products, HMF and furfural, respectively. If ethanol is going to be produced, the sugar degradation is undesired and has to be avoided in order to optimize the final ethanol yield. Hence, it is necessary to find pretreatment conditions, under which the plant polymers are converted to oligomeric and monomeric sugars but are not subject to further degradation reactions. Numerous pretreatment methods have been proposed and investigated, e.g. alkaline treatment, steam treatment with or without SO_2, ammonia fiber explosion, ammonia-recycled percolation, lime pretreatment or dilute acid pretreatment [2]. The economic and environmental constraints,

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Nomenclature

A_{av}	averaged heat exchange area (m^2)
c_{Cell}	concentration of the cellulose fraction in the LCM ($mg\,L^{-1}$)
c_{Glu}	glucose concentration ($mg\,L^{-1}$)
$c_{Glu,0}$	initial glucan concentration in the LCM ($mg\,L^{-1}$)
c_p	isobaric specific heat capacity of the fluid ($J\,kg^{-1}\,K^{-1}$)
d_{log}	logarithmical piping diameter (m)
DOC	dissolved organic carbon ($mg\,L^{-1}$)
E_A	activation energy ($kJ\,mol^{-1}$)
f	degree of solubilization on a carbon basis (%)
$\dot{H}_{in}$	fluid enthalpy at the inlet (W)
$\dot{H}_{out}$	fluid enthalpy at the outlet (W)
k_0	frequency factor (s^{-1})
k_1	rate constant (glucose production) (s^{-1})
k_2	rate constant (glucose decomposition) (s^{-1})
k_{app}	apparent heat transfer coefficient ($W\,m^{-2}\,K^{-1}$)
l	reactor length (m)
$\dot{m}$	mass flow ($mL\,min^{-1}$, $kg\,s^{-1}$)
$\dot{Q}_r$	reaction enthalpy released during substrate hydrolysis (W)
$\dot{Q}_W$	heat flow volume between the outer wall of the piping and the fluid (W)
R	universal gas constant, 8.3143 $J\,mol^{-1}\,K^{-1}$
R_0	severity factor
t	residence time (s, min)
T	temperature (K, °C)
T_{app}	apparent temperature (K, °C)
T_W	outer wall temperature (K, °C)
TOC	total organic carbon ($mg\,L^{-1}$)
u	fluid velocity ($m\,s^{-1}$)
Greek symbol	
ρ	fluid density ($kg\,m^{-3}$)

however, limit the applicability of these known methods. Thus, one of the most promising pretreatment processes for LCM is the usage of liquid hot water (LHW) that has been gaining increasing attention as both an environmentally friendly solvent and attractive reaction media for a variety of applications. Its distinctly different behavior compared to water at ambient conditions is due to the dramatic changes in physical properties, namely dielectric strength and ionic product, which in turn can easily be altered by changing temperature and pressure [9]. Several biopolymers can react with LHW in short residence times and with high rates of conversion.

A common approach to measure the treatment intensity in LHW is the usage of the so-called severity factor, which was defined by Overend and Chornet [10]:

$$R_0 = t \exp\left(\frac{T - 100}{14.75}\right) \tag{1}$$

where t is the residence time in [min] and T is the temperature in [°C]. Since R_0 depends on temperature and time, it can be used to measure the combined effect of both variables in a given treatment. The severity factor has already been used by numerous researchers being engaged in LHW treatments of several biomasses [1,3–5,7,11,12].

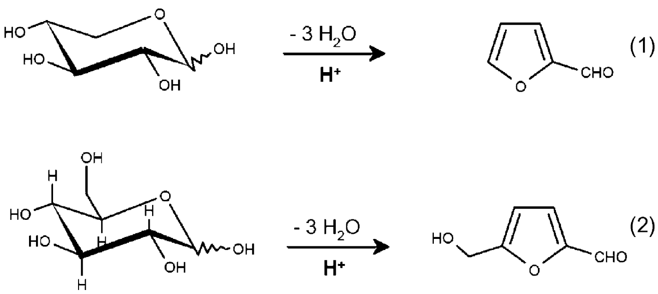

Fig. 1. Degradation pathways of xylose to furfural (1) and glucose to HMF (2).

Depending on the availability in the respective geographical region, different LCMs have been investigated so far. In this work, the substrate of choice was rye straw. Rye is a widespread crop in Germany that is, amongst other things, used as lignocellulosic resource for the production of bioethanol by now. Advantages of rye are in particular its cheap cultivation, the high dry matter yield per hectare, and the high yield stability.

The aim of this work was the hydrolysis of rye straw in LHW as a pretreatment process for the utilization of lignocellulosic material. The success of the pretreatment was rated by means of the solubilization of the biomass and the formation of undesired degradation products as these two aspects significantly influence the further processing, e.g. the enzymatic conversion and fermentation to bioethanol.

2. Modeling

2.1. Modeling of the temperature profile

The severity factor described in the previous chapter can only be used if the temperature remains constant during the reaction. Since this is not the case due to significant heat-up times, a modified severity factor was used, which considers the temperature in dependency on the residence time in the reactor.

$$R_0 = \int_0^t \exp\left(\frac{T(t) - 100}{14.75}\right) dt \tag{2}$$

where t is the residence time [min] expressed as the quotient of the reactor volume and the volumetric feed flow and $T(t)$ is the temperature [°C] in dependency on the residence time considering the heat-up period.

The residence time depending on the reactor length in the case of the CF experiments can be calculated by means of the known reactor geometry, the feed mass flow, which is measured during the experiments, and the density of the feed solution at operating conditions. The densities were taken from literature data [13], whereas the properties of pure water were assumed to be valid since the feed solution was highly diluted (99% water).

The temperature profile in the reactor was calculated as follows: the reaction zone consisted of three parts, two preheaters (length 12 m, part 1), one oven (length 18 m, part 3), and a short unheated pipe section of approximately 1 m in between (part 2) (see chapter 3). These three parts were considered separately; the model is based on an energy balance of a differential element.

The following energy balance is obtained:

$$\dot{H}_{in} + \dot{Q}_r + \dot{Q}_W = \dot{H}_{out} \tag{3}$$

with $\dot{H}_{in}$ the fluid enthalpy at the inlet, $\dot{H}_{out}$ the fluid enthalpy at the outlet, $\dot{Q}_W$ the heat flow volume between the outer wall of the piping and the fluid and $\dot{Q}_r$ is the reaction enthalpy released during substrate hydrolysis.

Due to the low solid loading of the feed, the reaction enthalpy was neglected:

$$\dot{Q}_r = 0 \tag{4}$$