



Modelling of low temperature dilute sulfuric acid pre-treatment of South African grass

Nicholas W. Burman, Craig Sheridan, Lizelle van Dyk, Kevin G. Harding*

Industrial and Mining Water Research Unit (IMWaRU), University of the Witwatersrand, Johannesburg, Private Bag 3, Wits, 2050, South Africa
Centre in Water Research and Development (CiWaRD), University of the Witwatersrand, Johannesburg, Private Bag 3, Wits, 2050, South Africa
School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, Private Bag 3, Wits, 2050, South Africa

ARTICLE INFO

Keywords:

Dilute acid hydrolysis
Pretreatment
Lignocellulose
Bioethanol
Kinetics

ABSTRACT

Dilute acid hydrolysis is an effective method of pre-treatment of lignocellulosic biomass. Although there are many studies modelling this pre-treatment at high temperature (120–210 °C), no studies were found modelling this reaction at low temperature. In this study, a long grass species was pre-treated with dilute sulfuric acid (pH 1, 2 & 3) at low temperatures (35 °C, 65 °C, 90 °C). The hydrolysis of xylan was found to obey a bi-phasic model in which there are two fractions of xylan, with significantly different hydrolysis rates. The rates of hydrolysis of the fast reacting fraction was found to obey Arrhenius type temperature dependence ($E_a = 155.06 \text{ kJ/mol}$, $A_0 = 1.65 \times 10^{19}/\text{min}$), which agrees with findings of similar studies at higher temperatures. A negligible rate of hydrolysis was determined for the slow fraction which differs from previous studies. The proportion of the slow reacting fraction (50%) which is lower than previously determined (55%–100%).

1. Introduction

Currently there has been a drive to produce biofuel and other biochemicals from biomass as an alternative to fossil fuels, which has a finite supply and contributes to global warming (Uihlein and Schebek, 2009). Enzymatic hydrolysis of the cellulose contained in biomass produces monomeric glucose sugars, which can undergo a range of biochemical reactions (fermentation, dehydration, oxidation, etc.) to form various bio-chemicals such as bioethanol, succinic acid, hydroxymethylfurfural (HMF) and furfural (Menon and Rao, 2012). Food crops such as sugar cane and corn have successfully been used to produce bio-ethanol on an industrial scale, with 71 billion kg produced in 2015 (E4TECH, 2015). Although effective, the use of food crops has been found to increase food prices and have a negative impact on food security. Other problems associated with the use of food crops include: overall carbon emission; net energy loss; land degradation and lack of available land (Lange, 2007).

Ligno-cellulosic biomass such as, agricultural waste, forestry residue and energy crops are an abundant and cheap source of cellulosic biomass. A recent study has also identified *Salicornia bigelovii* (halophyte plant) as a suitable feedstock for bioethanol production (Bañuelos et al., 2018). Indigenous South African grass have been identified as a good

feedstock for lignocellulosic biochemical production in the Highveld region of South Africa due to a large availability of unused feedstock (Burman et al., 2018; Westensee et al., 2018).

Lignocellulosic biomass consists of a ligno-hemicellulosic matrix which surrounds cellulose fibrils. The presence of this ligno-hemicellulosic matrix prevents cellulase enzymes from accessing the cellulose fibril. To overcome this, biomass needs to undergo pre-treatment which disrupts the ligno-hemicellulosic matrix making the cellulose accessible to cellulase enzymes (Wyman et al., 2005).

Various pre-treatment methods have been investigated including physical (milling, comminution), physico-chemical (steam explosion, AFEX, wet oxidation), biological (white rot hydrolysis), and chemical (dilute acid hydrolysis, alkaline, Ionic liquids, organic solvents, ozone) (Taherzadeh and Karimi, 2008). Dilute acid hydrolysis is currently the most favorable pre-treatment method for industrial applications (Alvira et al., 2010; Maurya et al., 2015; Taherzadeh and Karimi, 2007), with sulfuric acid being the most used type of acid, due to high hydrolysis yields (Mosier et al., 2005).

Pre-treatment using dilute sulfuric acid hydrolyses the hemicellulose content of the biomass, leaving the cellulose content largely intact, and easily accessible for enzymatic hydrolysis. The rate of dilute sulfuric acid hydrolysis was found to display Arrhenius type reaction

* Corresponding author at: Industrial and Mining Water Research Unit (IMWaRU), University of the Witwatersrand, Johannesburg, Private Bag 3, Wits, 2050, South Africa.

E-mail address: kevin.harding@wits.ac.za (K.G. Harding).

<https://doi.org/10.1016/j.biteb.2018.08.014>

Received 16 July 2018; Received in revised form 17 August 2018; Accepted 19 August 2018

Available online 12 September 2018

2589-014X/© 2018 Elsevier Ltd. All rights reserved.

Table 1
Summary of studies modelling xylose hydrolysis according to first order Arrhenius type kinetics.

Reference	Model type	Substrate	Temperature (°C)	% acid (w/w)	Acid	Compounds modelled
(Saeman, 1945)	Mono-phasic	Hardwoods, Softwoods	170–190	0.40–1.6	Sulfuric acid	Glucose, xylose, galactose, arabinose, manose
(Bhandari et al., 1984)	Mono-phasic	Corn stover	160–240	0.49–1.5	Sulfuric acid	Glucose, xylose
(Lavarack et al., 2002)	Mono-phasic	Sugarcane bagasse	80–200	0.25–8.0	Sulfuric acid, hydrochloric acid	Xylose, glucose, arabinose, furfural
(Yat et al., 2008)	Mono-phasic	Switchgrass, hardwoods	160–190	0.25–1.0	Sulfuric acid	Xylose
(Jin et al., 2011)	Mono-phasic	Corn stover	90–100	1.0–3.0	Sulfuric acid	Xylose
(Kim et al., 2013)	Mono-phasic	Xylo-oligomers	140–180	0.30	Maleic acid, oxilic acid, sulfuric acid	Xylose, furfural
(Kobayashi and Sakai, 1956)	Bi-phasic	Hardwood	74–147	1.0–6.0	Sulfuric acid	Xylose
(Nee and Yee, 1976)	Bi-phasic	Sugarcane bagasse	125–165	0.5–2	Sulfuric acid	Xylose
(Maloney et al., 1985)	Bi-phasic	Hardwood	100–170	0.4–1.7	Sulfuric acid	Xylose
(Esteghlalian et al., 1997)	Bi-phasic	Switchgrass, hardwood corn stover	140–180	0.6–1.2	Sulfuric acid	Xylose
(Aguilar et al., 2002)	Bi-phasic	Sugarcane bagasse	100–128	2.0–6.0	Sulfuric acid	Xylose, glucose, acetic acid, furfural
(Lavarack et al., 2002)	Bi-phasic	Sugarcane bagasse	80–200	0.25–8.0	Sulfuric acid, hydrochloric acid	Xylose, glucose, arabinose, furfural
(Schell et al., 2003)	Bi-phasic	Corn stover	165–195	0.7–1.39	Sulfuric acid	Xylose, furfural, oligomers
(Rodriguez-Chong et al., 2004)	Bi-phasic	Sugarcane bagasse	100–128	2.0–6.0	Nitric acid, sulfuric acid, hydrochloric acid	Xylose, glucose, arabinose, acetic acid, furfural

kinetics (Kobayashi and Sakai, 1956). This has been studied by either assuming that the hemicellulose reacts in a monophasic fashion in which all hemicellulose reacts at the same rate of reaction, or that the hemicellulose reacts in a biphasic fashion in which there are two different fractions of hemicellulose with very different rates of reactions. A summary of the conditions under which rates of reaction have been studied is presented in Table 1 for the both monophasic and biphasic models.

As can be seen in Table 1 the rate of hydrolysis have been well studied at high temperatures (120–210 °C) with acid concentrations ranging from 0.25–6% wt/wt H₂SO₄ (Aguilar et al., 2002; Esteghlalian et al., 1997; Kim et al., 2013; Lavarack et al., 2002; Maloney et al., 1985; Nee and Yee, 1976; Yat et al., 2008). Typical reaction times are in the range of 0.5–90 min. Although the rate of reaction is well studied at high temperatures, no studies have been found for low temperature (< 90 °C) hydrolysis.

The benefits of performing hydrolysis at lower temperatures include, reduced heating requirements, reduced reactor operating pressures, increased potential for passive heating systems, cheaper material of construction for reactors and potential for implementation of passive heating processes. The benefits of lower operating temperatures could result in reduced operating and capital costs.

The aim of this study is to: determine the compositional structure of a mixed sample of *Digitaria eriantha* and *Eragrostis* (indigenous South African Highveld grasses); model the rate of hemicellulose hydrolysis during dilute H₂SO₄ pre-treatment of this biomass; and determine the kinetic parameters for the rate of reaction of the hydrolysis, at temperatures between 35 °C and 90 °C and pH ranging from 1 to 3.

2. Methods and materials

In this work the structural composition of the biomass was determined, before hydrolysis pre-treatment experiments were carried out. Liquid hydrolysis samples from hydrolysis experiments were analyzed for sugar concentration. A kinetic model was developed to model the hydrolysis of grass over time and predict the rate of hydrolysis over a range of temperatures and pH.

2.1. Structural determination of grass

Grass was sourced from a local roadside grass cutter in Gauteng, South Africa and was classified as a mixture of *Digitaria eriantha* and *Eragrostis*. The structural determination of this mixture was determined using the gravimetric method proposed by Li et al. (2004). In this method the extractive content was determined gravimetrically through soxhlet extraction using acetone as a solvent. Hemicellulose content was determined gravimetrically through hydrolysis of hemicellulose portion in NaOH. The combined acid insoluble lignin (AIL) and ash content was determined through hydrolysis of hemicellulose and cellulose portion in H₂SO₄. Acid soluble lignin (ASL) content was determined using spectrographic methods as described by Mani et al. (2010) (Sluiter et al., 2012). Ash content was determined through proximate analysis on a thermogravimetric analyzer (Perkin Elmer STA 6000) using the method as described by (Mani et al., 2010). Cellulose and AIL content was determined through closure of mass balance assuming the biomass consists of only extractives, hemicellulose, cellulose, ASL, AIL and ash.

2.2. Hydrolysis pre-treatment

Pre-treatment experiments were carried out in 3 L constructed glass reaction vessels. These were constructed using glass jars fitted with airtight lid. A sampling port was included, by fitting PVC tubes through the lid, to take samples and prevent the contamination of the reacting mixture. These reacting vessels were placed inside an orbital shaking incubator which was operated at 100 RPM. The solid loading of the

Download English Version:

<https://daneshyari.com/en/article/10224643>

Download Persian Version:

<https://daneshyari.com/article/10224643>

[Daneshyari.com](https://daneshyari.com)