Modelling of Low Temperature Dilute Sulfuric Acid Pre-treatment of South African Grass

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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 (Ea = 155.06 kJ/mol, $A_0 = 1.65 \times 10^{19}$/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%).

Keywords: Dilute Acid Hydrolysis, Pretreatment, Lignocellulose, Bioethanol, Kinetics

1. Introduction

Currently there has been a drive to produce biofuel and other bio-chemicals 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 kilograms 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 cops 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 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 H_2SO_4 (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 minutes. 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 H_2SO_4 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 - 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 H_2SO_4. 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 reactor was 10 g/L with a liquid volume of 2.5 L. Duplicate factorial experiments were carried out at pH 1, pH 2 and pH 3 at temperatures of 35°C, 65°C and 90°C. For 65°C and 90°C samples were taken after the first day and then every second day for up to 19 days. For 35°C samples were taken every 4 days. A portion of the sample was used for measuring the pH with the balance stored frozen until the end of the experiment when they were analyzed.

2.3. Kinetic Model Development

The simplest kinetic models assume that hydrolysis occurs straight from poly-saccharide substrate to mono saccharide product without the formation of any oligosaccharide intermediates. This is applied to cellulose and hemicellulose individually (Negahdar et al., 2016). The first kinetic model proposed assumed the hydrolysis of hemicellulose occurs via two consecutive pseudo-homogenous first order reactions, first forming xylose and then forming degradation products as presented in Equation (1).

$$Xylan \qquad (1)$$

where the concentration of hemicellulose, xylose and degradation products can be expressed as

(2)

(3)

(4)

The rate constants were found to obey Arrhenius type temperature dependence, as described by Equation (5) (Saeman, 1945)

(5)

Where $A_{0,i}$ is the pre-exponential factor (min^{-1}), Ca is the concentration of acid (wt %), n_i is an empirical exponent, Ea_i is the activation energy (kJ/mol), R is the universal Gas Constant ($8.314x10^{-3}$ kJ/mol.K), T is the temperature (K)

This model was expanded by Koboyashi and Sakai (1956) to include two different fractions of xylan, which have very different rates of reactions. Both the fast and slow reacting fractions undergo hydrolysis to form xylose in a biphasic fashion as shown in Equation (6).

(6)

The rate of change of xylan and xylose can now be expressed as

(7)

(8)

Where subscripts *f* and *s* are used to denote the fast and slow reacting fractions of xylan.

The fraction of fast and slow reacting xylan is typically determined experimentally with the percent of the fast reacting fraction (α) ranging between 55% and 100%, although it is most frequently found to be between 70% - 80% (Negahdar et al., 2016).

The rate constant has been expanded in some studies to account for the neutralizing ability of the biomass. This neutralizing capacity is due to the ion exchange between the cations associated with the bound and free anions contained in the biomass and the hydronium ions in the acid solution. This can be represented by the simplified equation (Springer and Harris, 1985)

(9)

It was found that the most, but not all, inorganic cations were exchanged for hydronium ions, and the pH of the acid can be accurately predicted by determining the concentration of cations before and after hydrolysis (Springer and Harris, 1985).

Other studies have accounted for the neutralizing capacity of the biomass and calculated an actual acid concentration, C_a, from the original acid concentration, C, by the equation (Esteghlalian et al., 1997)

(10)

Where C is the original acid concentration (% wt/wt) and NC is the neutralizing capacity of the biomass (g H_2SO_4 neutralized/gram biomass). This neutralizing capacity is determined experimentally by the addition of biomass to an acid solution.

In the model to be used in this study, it was assumed that the hydrolysis of grass would obey the bi-phasic model as proposed by Kobayashi and Sakai (1956) (Equation 6). The concentration of potential xylose units remaining was evaluated by integrating Equation (3) to give Equation (11).

(11)

Where: X_r is the percentage of equivalent xylose units remaining in the solid residue (X_i) relative to initial equivalent xylose units in the biomass (X_0); $X_{f,0}$, $X_{s,0}$ are the initial percentages of fast reacting and slow reacting fractions; t is the time (min); k_f, k_s are reaction rate constants for the fast and slow reacting fractions of the biomass (assumed to have Arrhenius type temperature dependence as according to Equation (5).

Xylan is expressed in terms of equivalent xylose units, so to account for the difference in molecular weights between xylan (132 g/mol) and xylose (150 g/mol). The initial equivalent xylose units (X_0) in the biomass can be calculated according to

— (12)

Where $C_{xylan,total}$ is the concentration of xylan in biomass (% wt/wt), and solid loading is the solid loading of biomass in the reaction liquid (g/L).

The equivalent xylose units remaining in the solid residue can be calculated according to

(13)

Where X_t is the measured xylose concentration (g/l) at time t (min).

The fraction of fast reacting xylose units is assigned a value α such that

(14)

(15)

As the fraction of fast reacting and slow reacting xylan is considered to be a physical property of the biomass (Shen and Wyman, 2011), it is assumed that, for a specific biomass, there can only be one value for α for all operating conditions. The fraction of fast reacting biomass was determined through trial and error fitting of the equivalent xylose remaining (X_r) data over time.

The proposed kinetic model (Equation 11) was fitted to the data using Scilab's least square non-linear error minimization function ("lsqnonlin") to optimize the values of k_f and k_s. The values of k_f and k_s were determined for each set of experimental conditions, and are presented in the results section.

2.4. Determination of kinetic parameters

Once values for k_f and k_s were determined, kinetic parameters (A_0, Ea, n_i) were obtained by linearizing Equation (5)

— – (16)

$\ln(k_f)$ can then be plotted against 1/T to give a straight line where the gradient is equal to Ea/R and the intercept is given by $\ln(A_0) + n.\ln(C_a)$. This can be plotted for each different acid concentration tested, each of which would have the same gradient but different intercepts.

This system of linear equations can be solved using the linear regression "\ operator" in Scilab, to give the gradient (Ea/R) and the intercept ($\ln(A_0) + n\ln(C_a)$) of each different acid concentration tested. The intercepts determined can be plotted against $\ln(C_a)$ to give another

straight line, where the gradient is equal to the empirical exponent, n, and the intercept equal to $\ln(A_0)$. Linear regression can once again be performed using Scilab's "\ operator" to determine the values for n and A_0. Values for Ea, A_0, and n are presented in in the results section.

2.5. Analytical methods

Liquid hydrolysate samples, from the hydrolyses pre-treatment experiment, were filtered through 0.25 µm filters before being analyzed by HPLC. The Agilent Zorbax Carbohydrate Column was used for quantification of Xylose, Glucose and Cellbiose using 75% acetonitrile as the mobile phase at a flow rate of 1.4ml/ min at 35°C and a sample injection volume of 20 µl. A Biorad Aminex fermentation monitoring column was used for quantification of hydroxymethylfurfural, furfural, glycerol and acetic acid using 0.05M H_2SO_4 at a flow rate of 0.8ml/min at 65°C and a sample injection volume of 20 µl.

As furfural is a degradation product of xylose the equivalent concentration of xylose that would yield the measured concentration of furfural was determined, and added to the measured concentration of xylose (X) to give a total concentration of xylose (X_{tot}) according to

— (17)

where: X_{tot} is the total equivalent concentration of xylose(g/L); X is the measured concentration of xylose (g/L); F is the measured concentration of Furfural (g/L). 150/96 is included so as to account for the difference in molecular weight between xylose (150 g/mol) and furfural (96 g/mol).

To account for the neutralizing ability of lignocellulosic biomass the pH was monitored throughout the process, and the wt% H_2SO_4 was calculated from the pH. After the effects of

the neutralizing ability of the grass had subsided there was only minor variation in the pH. The pH was thus taken to be the average pH over the duration of the experiment.

3. Results and discussion

3.1. Structural composition of grass

The average composition of the grass (mixed sample of *Digitaria Eriantha* and *Eragrosti)* is given in Table 2 and compared to the composition of switchgrass found in literature (Lee et al., 2007)

The structural composition of the grass was found to be comparable to the mean of switch grass compositions reported in literature (Lee et al., 2007). There was a discrepancy between the hemicellulose content (36.0% determined experimentally vs 28.5% form literature) and Acid soluble lignin (24.5% determined experimentally vs 16.2% from literature). All other fractions were found to be within 3% of the values in found literature.

3.2. Kinetic Model

The remaining xylose determined experimentally and predicted by the model at different temperatures is presented in Figures (1) – (3). The shows the degradation of hemicellulose over time. The error bars represent the standard deviation between data calculated from duplicate experiments.

As can be seen in Figure 1, at 90°C and pH 1 and 2, the rate of reaction hydrolysis of the xylan is relatively fast up until 50% of the xylan is remaining, after which point the rate of hydrolysis slows considerably. Therefore, it is assumed that the fraction of fast reacting xylan is 50%. Only approximately 30% of the xylan is hydrolysed at 90°C and pH 3, by the time the experiment stopped. The model predictions seem to fit experimental data well.

As can be seen in Figure 2, at 65°C and pH 1 there is limited hydrolysis of xylan with just less than 25% of the xylan undergoing hydrolysis. At 65°C and pH 2 there is only very

limited hydrolysis (~10%). At 65°C and pH 3 there is a negligible amount of hydrolysis observed.

As can be seen in Figure 3, at 35°C and pH 1, there is limited hydrolysis of xylan (max 3%). At 35°C and pH 2 and 3 negligible hydrolysis was observed.

Although no hydrolysis was observed at some experimental conditions, there may have been low levels of hydrolysis occurring at these experimental conditions, but low concentrations of xylose (<0.1 g/L) were not detected by the HPLC method used.

The rate constants for k_f and k_s at each experimental condition are presented in Table 3.

For some experimental conditions (65°C at pH 2 and pH 3, 35°C at pH 1, pH 2 and pH 3) no rate of reaction was determined for the fast reacting fraction. These are milder experimental conditions, where a slower rate of reaction would be expected.

By comparing the values in for k_f and k_s in Table 4, the rate of reaction for the slow reacting fraction were found to be orders of magnitude smaller, and hence negligible, compared to the rate of reaction of the fast reacting fraction. No value was determined for all the rates of reaction of the slow fraction, except for 65°C at pH 2 and 35°C at pH 1. These results are counter intuitive as it would be expected that a rate of reaction be determined for the following, more severe, experimental conditions of 90°C at pH1 and pH2, and 65°C at pH 1.

As the rate of reaction of the slow reacting fraction, was often found to be negligible, it was decided to evaluate the model assuming that the slow reacting fraction did not react i.e. $k_s = 0$ in all cases. The kinetic model was thus modified from Equation (11) to:

(18)

The values for k_f were once again determined through optimization in Scilab.

The remaining xylose predicted by the modified model was compared to the remaining xylose predicted by the original model. The difference between the two models was found to be negligible in all cases. The rate of reactions determined in the modified model were compared to the rate of reactions determined in the original model and were found to be identical. The rate of reaction of the slow reacting fraction can thus be assumed to be negligible. The hemicellulose can thus be considered to consists of a reactive and an unreactive fraction.

There is a large range of r^2 values found (presented on graphs). There was a good correlation between experimental data and model predictions for all acid concentrations at 90°C. The correlation was found to be 0.80 at pH 1, 0.88 at pH 2 and 0.92 at pH 1. This good correlation between the model and the data indicates an acceptable accuracy of the model.

At 65°C, r^2 values ranged between 0.32 at pH 2 and 0.4 at pH 1, indicating a low correlation between experimental data and model predictions. It must be noted that the correlation for pH 1 at 65°C would be higher (0.80 instead of 0.43) if the last point at 20 days was excluded. If it is assumed that this point is an outlier, then there is an acceptable level of accuracy in the model at pH 1 and 65°C. The level of model accuracy at pH 2 and 65°C is not acceptable. It should be noted that the peaks in the RID signal detected by the HPLC at low xylose concentrations using this HPLC method was very small, which allows for large inaccuracy. The inaccuracy in the model may be due to this lack of accuracy in concentrations of xylose determined by the HPLC method.

The correlation between experimental data and model prediction at 35°C and pH1 was poor ($r^2 = 0.02$), indicating lack of accuracy of the model at the these conditions. This inaccuracy may be due to a lack of accuracy of the HPLC method at low xylose concentrations, as discussed above.

3.3. Determination of kinetic parameters

The fitted kinetic parameters determined experimentally are of similar magnitude to those determined in previous studies (Table 4). Discrepancies in the kinetic parameters may be due to the different temperature ranges in which previous studies we conducted as well as different substrates considered in each study.

These kinetic parameters determined (presented in table 4) were then used to predict the rate of hydrolysis of grass over a range of temperatures and acidity (Figure 4).

The model has only been used to predict reaction rates 10°C above and below the range in which a rate was determined experimentally. Both temperature and pH can be seen to have a major effect on the rate of reaction, with the rate of reaction increasing with both the temperature and the pH.

A comparison between the predicted rate of reaction literature was conducted. Esteghlalian et al. (1997) (Esteghlalian et al., 1997) was chosen for comparison as their conditions are the most similar to this study (Figure 5).

The kinetic parameters determined in this study and Esteghlalian et al (1997) predict rates of reaction for the fast reacting fraction of grass of the same order of magnitude. No comparison was made for the slow reacting fraction as it was assumed that it was non-reactive at these conditions. The values determined by Esteghlalian et al (1997) predict faster rates under all temperatures and acid concentrations. Esteghlalian et al (1997) values were between 1.8 and 26 times greater, than the values determined in this study, with the largest discrepancy being at low acid concentration and high temperature, and the lowest discrepancy being at high acid concentration and low temperature.

4. Conclusion

The hydrolysis of xylan at low temperatures was found to exhibit a reaction mechanism in which there were two portion of xylan, one which undergoes hydrolysis, and another which undergoes hydrolysis at such a slow rate its can be assumed to be negligible. The rate of hydrolysis of the reacting fraction was found to obey Arrhenius type temperature dependence (Ea = 155.06 kJ/mol, $A_0 = 1.65\times10^{19}$/min). The rate of hydrolysis of fast reacting fraction is similar to that determined in previous studies, however, the proportion of fast reacting fraction was found to be 50% which is lower than previously determined (55%-100%). It is recommended that the kinetic parameters determined in this study be utilized to perform a rigorous techno-economical evaluation of the feasibility of low temperature dilute H_2SO_4 pre-treatment.

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6. References

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List of Tables

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

Table 2 Experimentally determined composition of mixed sample of *Digitaria Eriantha* and *Eragrosti* compared with switchgrass composition reported in the literature.

Table 3: Reaction rate constant for the fast reacting and slow reacting fraction at various pH and temperatures (/min)

Table 4: Kinetic Parameters determined experimentally compared to other studies

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, Sulphuric acid, Hydrochloric acid	Xylose, Glucose, Arabinose, Acetic Acid, Furfural,

Table 2 Experimentally determined composition of mixed sample of *Digitaria Eriantha* and *Eragrosti* compared with switchgrass composition reported in the literature.

	Experimentally Determined		From Literature (Lee et al., 2007)	
	Mean	SD	Mean	SD
Hemicellulose	36.0%	19.7%	28.5%	3.5%
Cellulose	36.6%	18.6%	37.3%	4.4%
Acid Soluble Lignin	1.3%	0.05%	3.5%	0.3%
Acid Insoluble Lignin	24.5%	1.7%	16.2%	0.5
Ash	3.5%	0.59%	5.9%	1.0%
Extractives	1.7%	0.3%	3.1 %	

Table 3: Reaction rate constant for the fast reacting and slow reacting fraction at various pH and temperatures (/min)

Temperature (°C)		35°C	65°C	90°C
pH 1	k_f	4.93×10^{-9}	9.72×10^{-7}	3.25×10^{-5}
	k_s	2.89×10^{-18}	nv	nv
pH 2	k_f	nv*	7.84×10^{-8}	8.42×10^{-6}
	k_s	nv	8.59×10^{-18}	nv
pH 3	k_f	nv	nv	1.17×10^{-6}
	k_s	nv	nv	nv

*nv – no value

Table 4: Kinetic Parameters determined experimentally compared to other studies

Source	A_f (min^{-1})	Ea_f (kJ/mol)	n_f	A_s (min^{-1})	Ea_s (kJ/mol)	n_s	X_f	Substrate
This Study	1.65×10^{19}	155.06	0.74	-	-		0.5	South African grass varieties
(Esteghlalian et al., 1997)	1.90×10^{21}	169	0.4	4.20×10^{23}	210.7	2	0.768	Switch Grass
(Yat et al., 2008)	2.48×10^{13}	115	1.75	-	-	-	1	Switch Grass
(Maloney et al., 1985)	2.67×10^{16}	128.1	1	1.63×10^{19}	156	1	0.684	Paper Birch
(Nee and Yee, 1976)	6.40×10^{5}	53	1.02	10.7×10^{0}	23.5	0.363	0.65	Bagasse
(Aguilar et al., 2002)	3.93×10^{12}	99.15	1	-	-	-	1	Bagasse
(Kim et al., 2013)	6.88×10^{12}	89.4	1.74	-	-	-	1	Xylo-oligomers
(Lavarack et al., 2002)	5.86×10^{9}	88.1	0.79	8.76×10^{7}	73.5	0.79	0.58	Bagasse

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Figure 4: Predicted model reaction rate using determined kinetic parameters and experimentally observed reaction rates

Figure 5: Rate of reaction at various pH and temperature conditions vs. literature (Esteghlalian et al. 1997)

Figure 1

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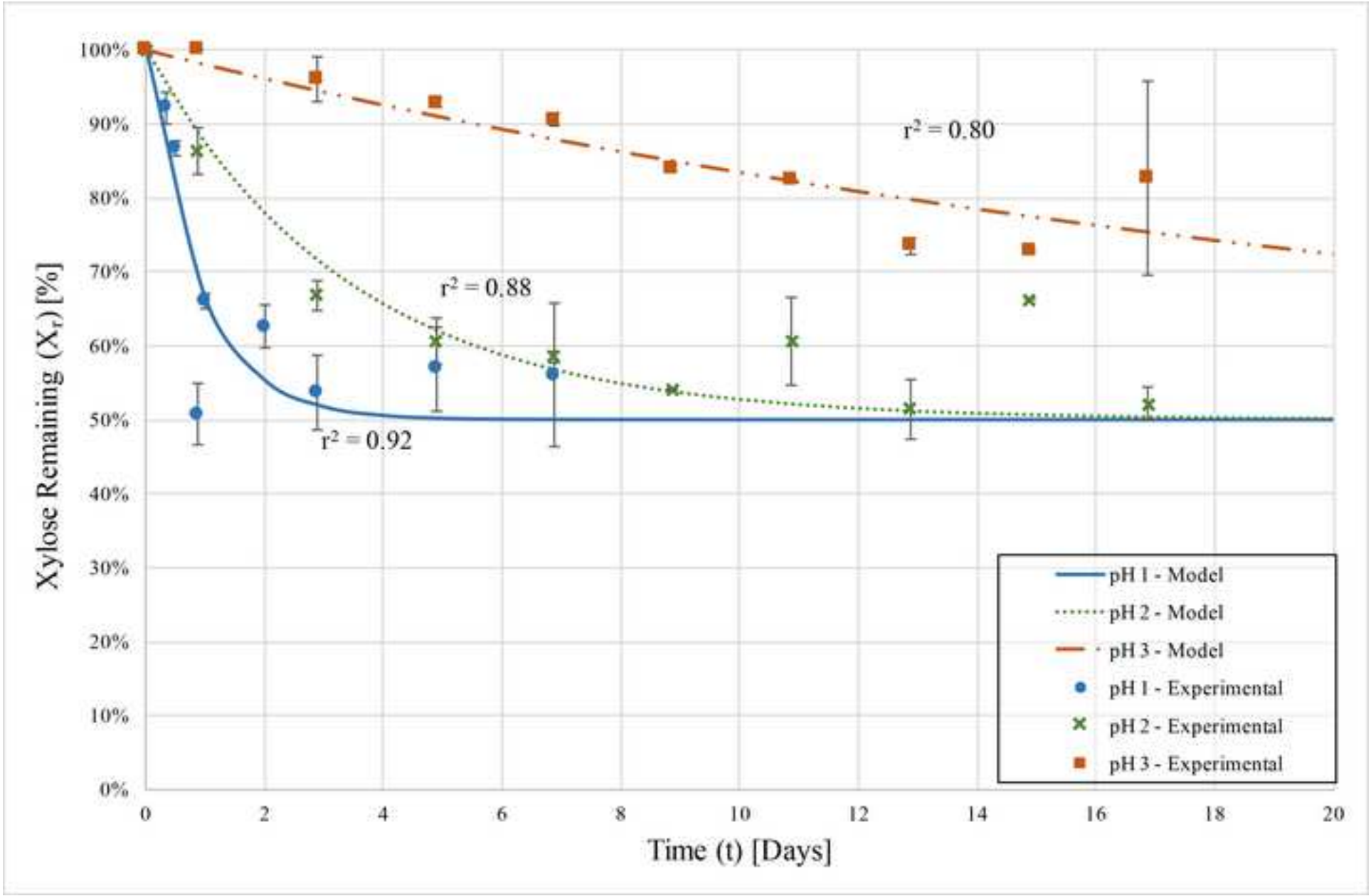

Figure 2

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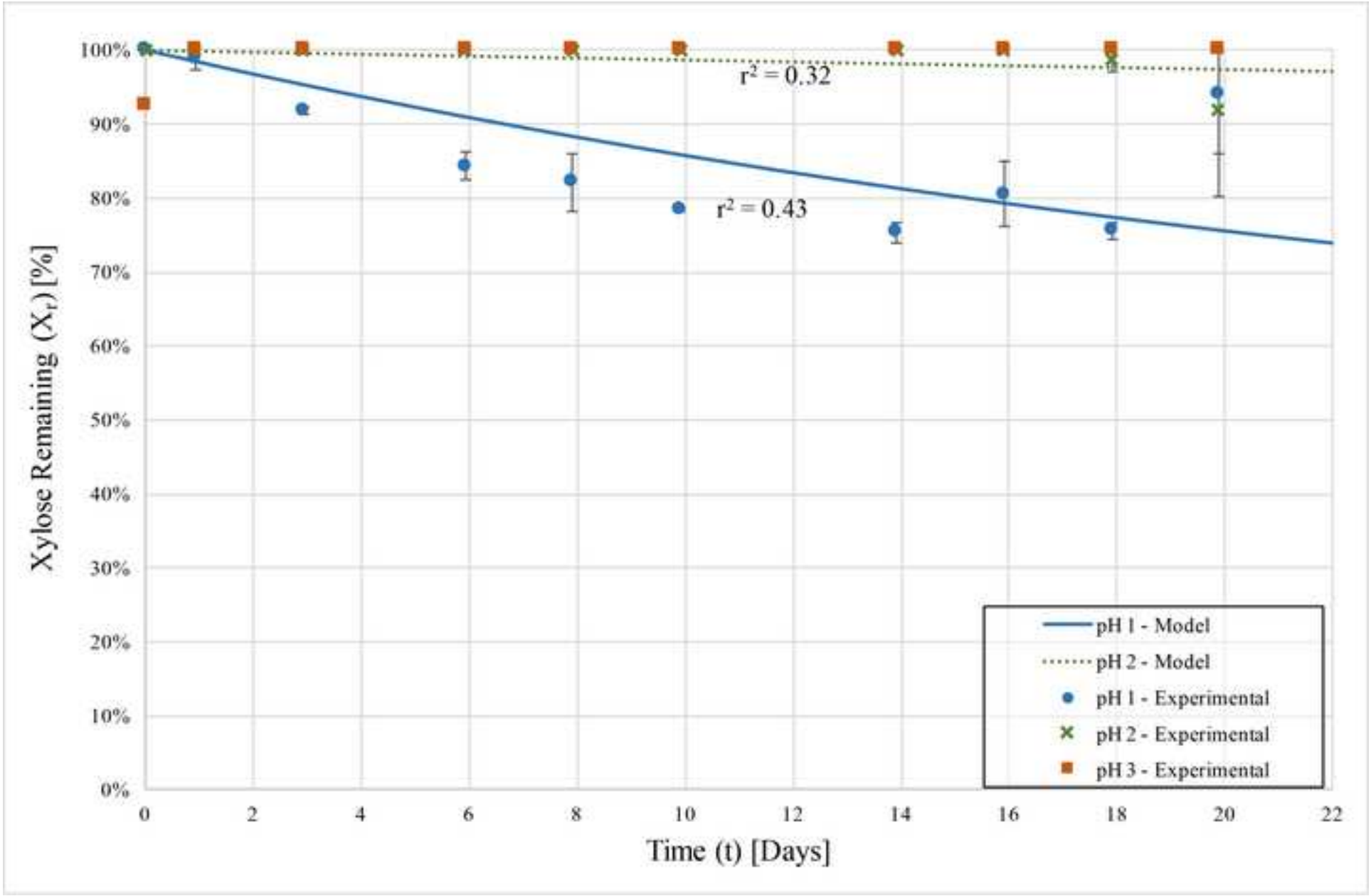

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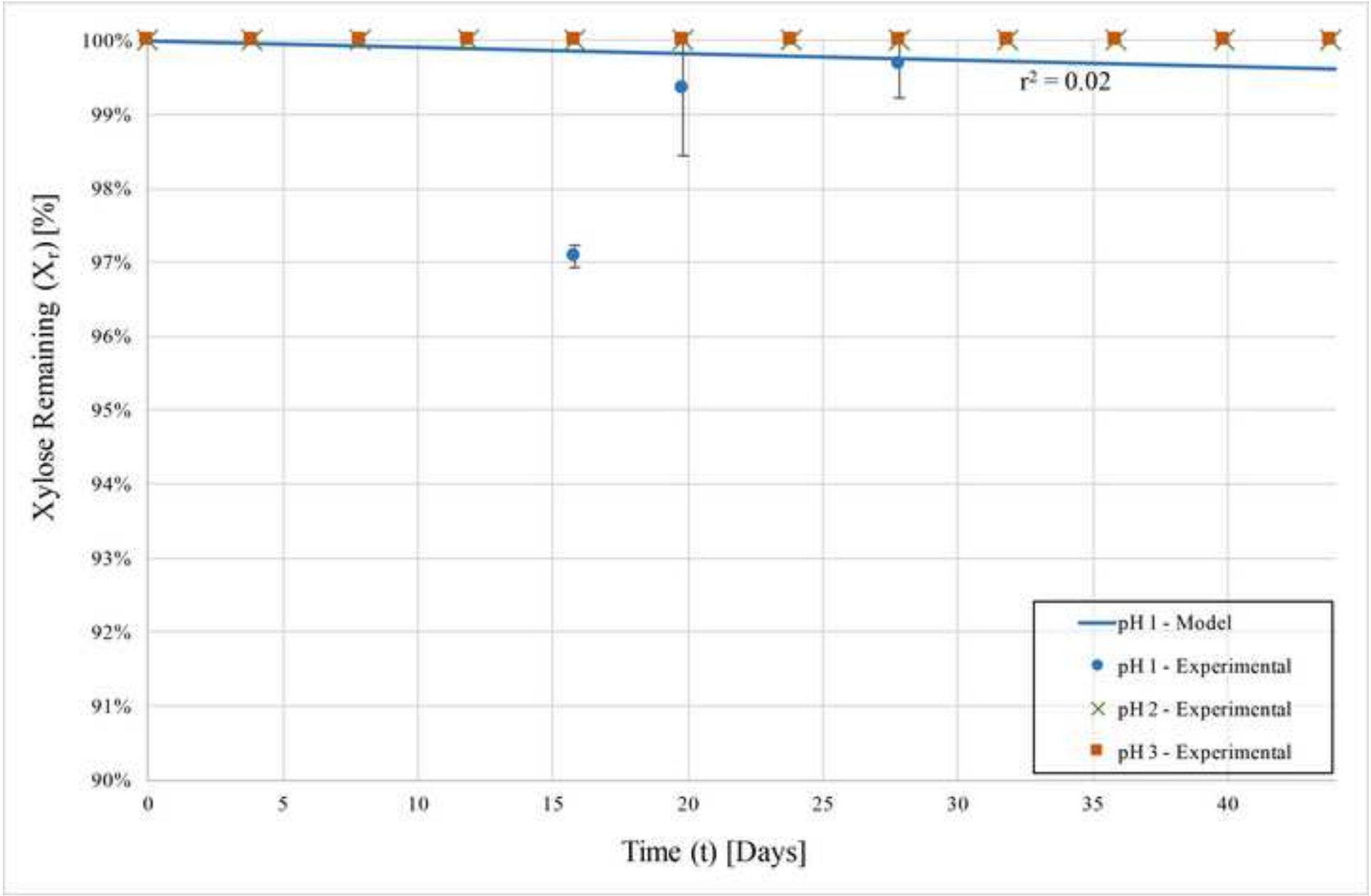

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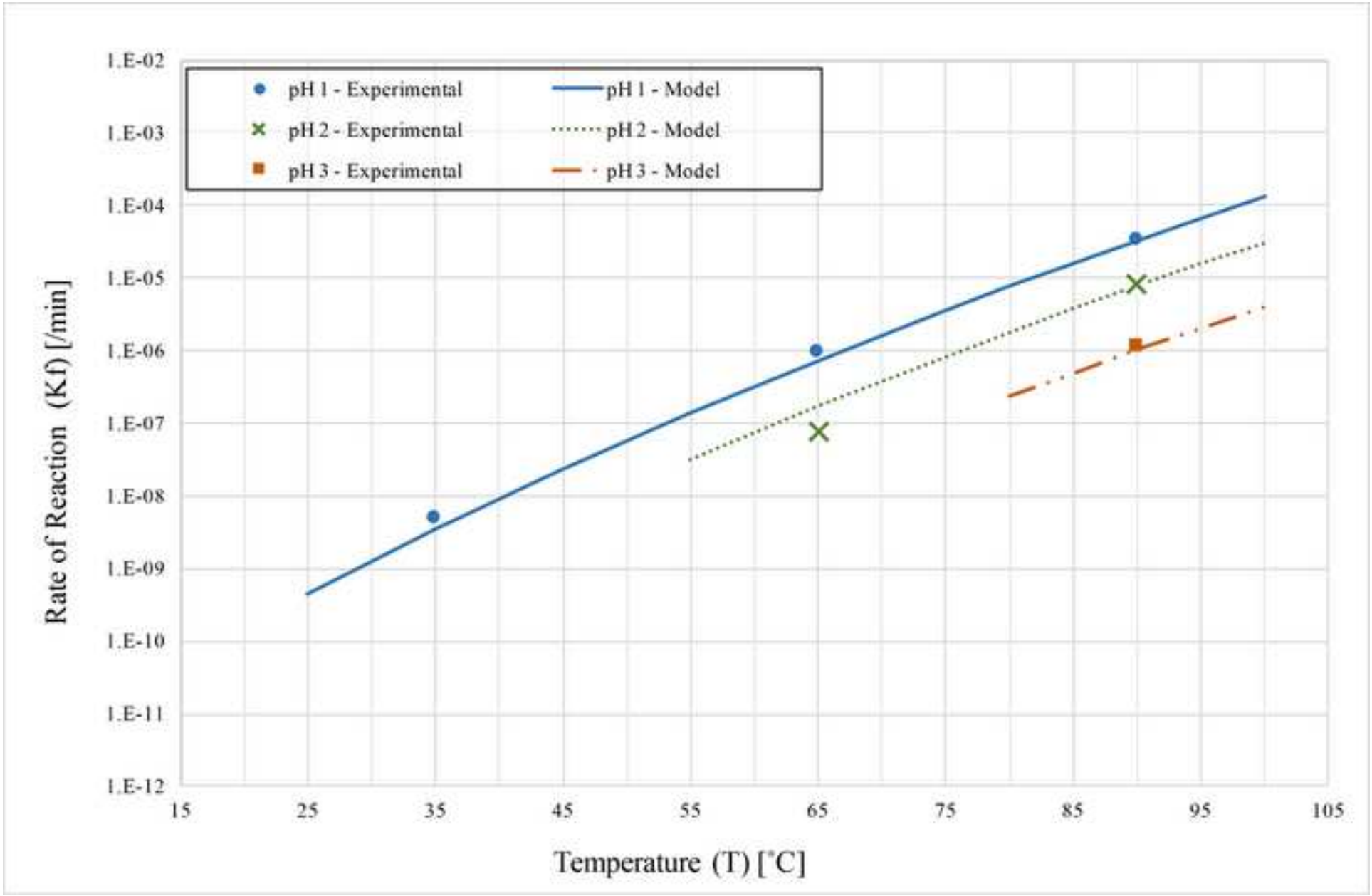

Figure 5

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