

# DISSOLUTION KINETICS OF CORNCOB IN LITHIUM PERCHLORATE SOLVENT SYSTEM

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**ABSTRACT:** To improve the economical use of lignocellulosic bio-waste (e.g. corn cob), an efficient pre-treatment route is required to make its content accessible to enzymatic hydrolysis to produce bio-products such as biofuels and bio-chemicals. The use of mineral acidic ( $\text{H}_2\text{SO}_4$ ) and alkaline ( $\text{NaOH}$ ) media for pre-treatment is very efficient but produces toxic effluents that are not environmental benign. However, studies have shown that the use of molten hydrate salts is very efficient and environmentally benign. This study presents results of the investigation of dissolution kinetics of corn cob in lithium perchlorate ( $\text{LiClO}_4 \cdot 2\text{H}_2\text{O}$ ), an environmentally friendly molten hydrate solvent system. Pre-screened milled corncob sample was fractionated in  $\text{LiClO}_4 \cdot 2\text{H}_2\text{O}$  solvent system at solid to solvent ratio of 1:10 and the mixture was stirred continuously at stirring rate of 250 rpm for 10 hours. Samples of the mixture were taken for analysis after every 10-minute interval for the first hour and 1-hour intervals until the end of the experiment. Dissolution kinetic study was carried out at 120 °C-180 °C at 20 °C intervals to understand the effect of temperature on the kinetics. The samples obtained were filtered to separate the liquid and the solid fractions and analyzed with a pre-calibrated high-performance liquid chromatograph. The study reveals that dissolution kinetics of corn cob in the solvent system is fast with rate constant that is enhanced at increasing temperature and could be described by a pseudo-first order dissolution kinetics. The dissolution (activation) energy for the kinetics for glucose, xylose and lignin were 15.0 kJ/mol, 14.2 kJ/mol and 36.54 kJ/mol, respectively. It is apparent that the activation energy associated with lignin is higher than that of glucose and xylose, indicating that more energy will be required to release lignin from corn cob.

**Keywords:** Kinetics; Lignocellulosic biomass; Corn cob; Pre-treatment; Lithium perchlorate

## 1 INTRODUCTION

Implementation of green technology has attracted continuing research efforts into green production of bio-products. Lignocellulosic biomass, the most abundant renewable resource on earth, has been regarded as the significant feedstock material for the process (Brodeur et al., 2011). Lignocellulosic biomass refers to a plant-based material, such as corncob, bagasse, wheat & rice straws, wood chips and etc., that is composed of cellulose, hemicellulose and lignin. Biomass products are abundant and renewable and about 220 billion tons are produced per annum worldwide [1]. Compared to current practice, plant biomass is a natural resource that captures carbon dioxide for its own growth, emits no harmful gases and therefore produces clean energy in processing and application. In addition, biomass products are versatile such that they can be used to generate all sorts of different products i.e. Biofuels, bio-additives, biodegradable plastics, bio surfactants.

Lignocellulosic biomass is generally recalcitrant (it resists biological deconstruction by simple methods) to enzymatic hydrolysis, therefore pre-treatment is necessary to enhance its enzyme digestibility [2]. Pre-treatment process removes the lignin and other complex materials and therefore makes cellulose accessible for hydrolysis. However, the process is not efficient since the pre-treatment solvent as mineral acid produces by-products that are not environmentally benign, thus the use of aqueous pre-treatment method with environmental benign solvents becomes a point of interest in bio-production. Boonsombuti and colleagues reported on pre-treatment of biomass using microwave assisted alkaline process while Ayeni and fellow researchers focused on hydrogen peroxide and lime based oxidative pre-treatment. [4]. Bardone et al. reported the use of dilute acid for pre-treating and hydrolysis; and Nagoor and Arbain wrote a nice review on green solvent (e.g. ionic liquid) for pre-treatment of lignocellulosic biomass [1]. A few research

efforts have been dedicated to investigating the use of green solvents for pre-treatment of lignocellulosic biomass. For instance, Awosusi et al. investigated fractionation of corncob in zinc chlorides [5]. But designing an efficient operation unit for the pre-treatment of the biomass depends on the understanding of the dissolution kinetics of the biomass in these solvents.

As a contribution to this research line, this paper reports on aqueous pre-treatment of corncob using Lithium perchlorate as a solvent with the aim to develop a novel solvent system and understand dissolution kinetics during the process. The overall aim of this study was to improve the economical use of corncob as a feedstock for bio-processing of lignocellulosic materials.

## 2 MATERIAL AND METHODS

### 2.1 Materials

The corncob samples used in this study were collected from a farm in Mukula Village, Limpopo South Africa, dried and stored in sealed plastic bottles to avoid absorption of moisture and contamination. The solvents used was lithium perchlorate ( $\text{LiClO}_4 \cdot \text{H}_2\text{O}$ ) purchased from Sigma Aldrich (Pty) South Africa.

### 2.2 Method

#### 2.2.1 Pre-treatment

The corncob samples were crushed to small size using a grinder and classified into smaller sizes using 2000, 1000  $\mu\text{m}$ , 850  $\mu\text{m}$  and 500  $\mu\text{m}$  sieves. Based on the milling process, the size classification of 850  $\mu\text{m}$  -1000  $\mu\text{m}$  was used in this study. These samples were dried in a conventional oven at 100 °C for 3 hours to remove the moisture content. For pre-treatment, 10 g of the dried samples was measured and added to the 100 ml solvent in a conical flask placed on a heating plate equipped with a magnetic stirrer. The content of the flask was continuously stirred for 3.5 h at a temperature between 70-80°C. After

the pre-treatment, the mixture was separated using a vacuum-assisted filtration system. The filtrate and solid residue were separated using a 47 mm-size filter paper and the non-solvent medium removed by extensive washing of the material with deionized water. Monomeric sugars (glucose and xylose) were analyzed by a HPLC system (model 2695). HPLC system equipped with an Aminex HPX- 87H column was applied with acetonitrile solution as the mobile phase at the total flow rate of 0.6 ml/min and the column temperature was maintained at 60 °C. UV-vis was used to measure soluble lignin and absorbance was measured at 205 nm wavelength because it corresponds to a minimum wavelength in the UV spectrum in a region where lignin components absorb strongly. X-ray diffraction (XRD) measurement was conducted using a D8 ADVANCE diffractometer (Bruker, German) equipped with a Cu K alpha radiation and the scanning was from 5° to 60° with step size of 0.03 at 4 s per step. Crystalline indices of cellulose samples were calculated from the X-ray diffraction results using Equation (1):

$$C_r I = \frac{I_{002} - I_{amp}}{I_{002}} \times 100\% \quad (1)$$

Where  $I_{002}$  is the crystalline region intensity for the crystalline portion of biomass (i.e., cellulose) at about  $2\theta = 22.5^\circ$  and  $I_{amp}$  is the peak for the amorphous portion (i.e., cellulose, hemicellulose, and lignin) at about  $2\theta = 18.3^\circ - 19^\circ$ . To better understand the significant enhancement of enzymatic digestibility of corncob after pre-treatment, the morphological evidence of the untreated and pre-treated samples was investigated by scanning electron microscopy (SEM).

### 2.2.2. Dissolution Kinetics.

Corncob was mixed with  $\text{LiClO}_4 \cdot \text{H}_2\text{O}$  solvent at ratio of 1:10 of corncob to the solvent. The mixture was then incubated for a maximum of 10 h at the stirring rate of 250 rpm. Samples were withdrawn from the mixture every 10 minutes for the first hour and then at 1 hourly until the end of the experiment. The withdrawn samples were filtered to separate the liquid and the solid fractions. Collection of data for the kinetic study during the pretreatment was at 120 °C, 140 °C, 160 °C 180 °C to investigate effect of temperature on the dissolution kinetics during the pre-treatment. The responses considered during the study were the amount of glucose, xylose and the amount of lignin removed from the pre-treated solids. The amount of glucose and xylose was obtained using a pre-calibrated HPLC and the soluble lignin was quantified using a UV-vis. Equation (2) was proposed for the kinetics and consequently, the rate of dissolution was expressed by Equation (3):

$$\frac{dC}{dt} = -kC \quad (2)$$

Where C is either the concentration/yield of glucose, xylose or lignin; k is the dissolution rate constant; t is the pre-treatment time. Integrating Equation (2) between  $C_i$  and  $C_f$ , which are the initial concentration and final concentration of the sugars (xylose & glucose), respectively, from initial dissolution time,  $t_i = 0$ , to final dissolution time ( $t_f$ ), gives Equation (3).

$$\ln \left( \frac{C_i}{C_f} \right) = -kt + z \quad (3)$$

Plotting  $\ln \left( \frac{C_i}{C_f} \right)$  against dissolution time gives a linear plot whose slope is the dissolution rate constant (k). It has been reported that the temperature dependence of the rate constant is characterized by the value of the energy of activation, which is the minimum energy that must be possessed by reacting molecules before the reaction can occur [3,6]. Thus, the dissolution rate constant can be related to temperature via the Arrhenius equation expressed as:

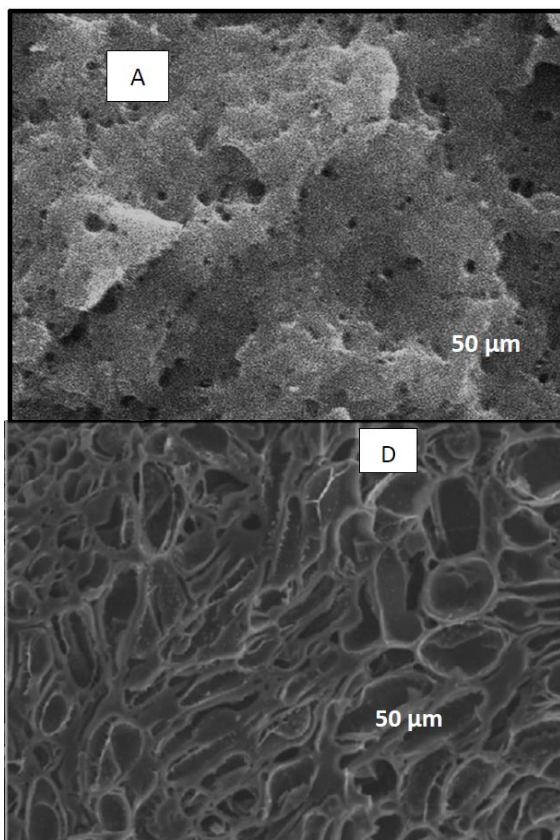
$$k = A \exp \left( -\frac{E_a}{RT} \right) \quad (4)$$

Where A = Arrhenius constant;  $E_a$  = activation energy; R = gas constant = 8.314 kJ/mole·K; T = absolute temperature (K).

## 3 RESULTS AND DISCUSSION

### 3.1. Morphology and crystallinity of the pre-treated samples

The SEM image of untreated corncob sample in Figure 1 (A) reveals rigid, compact fibrillary morphology with thick-walled fibre cells and fibres constituted by parallel stripes, limiting the cellulose accessibility shows a uniform cell wall surface. These cellulosic components are responsible for the cohesive forces within the cell wall that entail structural support to plants [7]. The SEM image of the  $\text{LiClO}_4$  pre-treated corncob shows a rougher surface and more porous than raw corncob (see Figure 1 (D)). This rough surface, characterized with cracks, is essential for enzymatic hydrolysis of cellulose because they can increase surface area and porosity of lignocellulosic biomass [8]. The particle sizes of the pre-treated samples are greatly reduced when compared with that of the raw corncob, which is desirable since it increases the cellulose accessibility. However, agglomerates are also formed in the  $\text{LiClO}_4 \cdot \text{H}_2\text{O}$  pre-treated sample because the hydrogen-bonding network in amorphous cellulose seems to promote the agglomeration of small particles [9]. Compared to the smooth surface of raw material, the bundle structure of cellulose was still retained after treatment, which proved that the crystalline structure of cellulose was not damaged by treatment. However, the surface of reaction residues after treatment became rougher, which implied the dropping of lignin fraction from corncob residue.

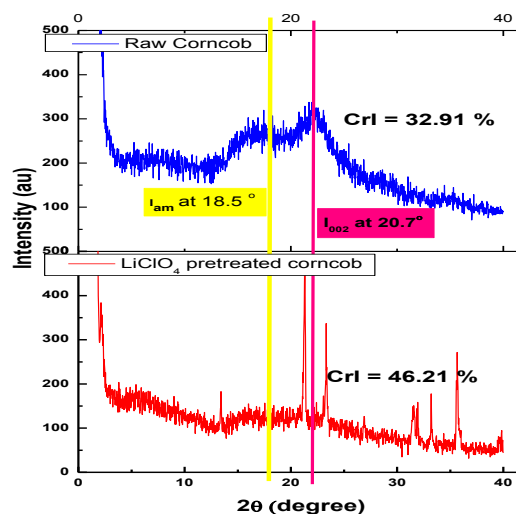


**Figure 1:** SEM micrographs revealing the internal structure of corn cob particles. (A) A section of untreated corn cob (D) LiClO<sub>4</sub> pre-treated corn cob. Scale bars 50 μm

X-ray patterns of the corn cob sample before and after lithium perchlorate pre-treatment are given in Figure 2. The results reveal that pre-treatment with LiClO<sub>4</sub> changed the structure of the corn cob crystalline region since the peak shapes are not identical. According to Chandra and colleagues [10], the intensity of the crystalline peak at maximum 2θ angle is between 22° and 23°, whereas the intensity of the amorphous materials at 2θ angle is between 18° and 19°. It can be observed from the diffractograms of raw corn cob that there are two peaks appearing in the native sample at 2θ ≈ 22° and at 2θ ≈ 18°, which is suggestive of the corn cob samples' crystallinity.

Many studies report that pre-treatment of lignocellulosic biomass results in the reduction of the cellulose crystallinity in the crystalline region. The XRD data was obtained from the solid residue, thus the CrI should increase after pre-treatment due to the removal of amorphous hemicellulose. It should be noted that cellulose CrI is obtained by dividing biomass crystallinity with cellulose content in the biomass, which reflects real changes in crystalline during pre-treatment. Consequently, this modification in cellulose crystallinity structure enhances the enzymatic hydrolysis [11]. The raw corn cob has a biomass CrI of 32.91%, which increased to 46.21% for LiClO<sub>4</sub> pre-treated samples. This indicates the high possibility of lithium perchlorate pre-treatment disrupting the native cellulose crystalline structure [11]. The XRD results also suggest that the increase of CrI could be attributed to release of amorphous cellulose from the corn cob residues by the pre-treatment solvent. The pre-treated cellulose transformed into a disordered structure

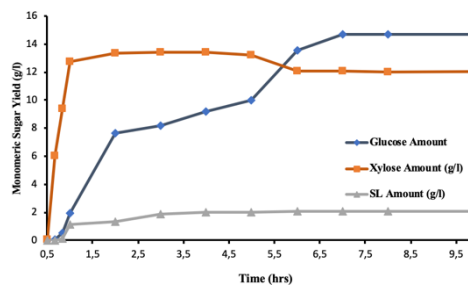
upon displacement of solvent's molecules, leading to a drop in the biomass CrI [12].



**Figure 2:** The X-ray patterns of the corn cob before and after lithium perchlorate pretreatment (a) raw corn cob (b) lithium perchlorate pretreated corn cob

### 3.2. Kinetic study

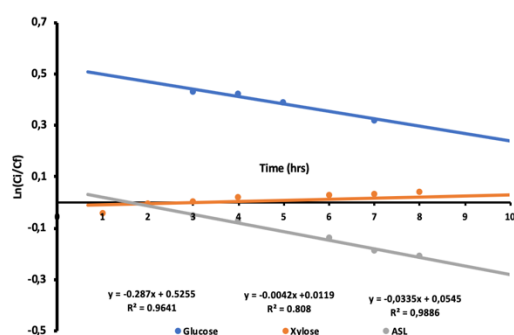
Kinetic modelling of pre-treatment of corn cob using lithium perchlorate solvent system was carried out to obtain a kinetic model that will describe perfectly the dissolution kinetics of the solvent system focussing on the recovery of hemicellulose, cellulose and soluble lignin. Figure 3 shows the concentration profile of glucose, xylose and soluble lignin accessibility at 120°C in LiClO<sub>4</sub>·2H<sub>2</sub>O. Glucose yield increased slightly until it reached equilibrium after 7 h. The xylose yield reached equilibrium after 3 h and began to decrease after 5 h. The decrease in xylose yield after 5 h could be attributed to the decomposition of xylose to its constituent sugars as time progressed, hence the decrease in the concentration of detected xylose. Cellulose, which likely represents the amorphous region, dissolved and started depolymerisation to glucose after 30 minutes to reach equilibrium at 7 h at a concentration of 14.7 g/l. It was observed that the acid-soluble lignin was in a small amount and it dissolves during pre-treatment, thereby inhibiting not the dissolution of either cellulose or hemicellulose.



**Figure 3:** Monomeric sugar yields of total glucose, lignin and xylose at the optimal conditions

A plotted of  $\ln\left(\frac{c_i}{c_f}\right)$  against dissolution time for glucose, xylose and soluble lignin is depicted in Figure 4. From the results, it can be inferred that the model describes well the

dissolution kinetics with coefficient of determination ( $R^2$ ) of 0.9641 for glucose;  $R^2$  of 0.808 for xylose; and  $R^2$  of 0.9886. Consequently, it could be concluded that the dissolution of corncob in the solvent system follows pseudo-first order kinetics. Similar trends were observed for the dissolution at 140°C, 160°C and 180°C (though results are not shown in this article). The estimated kinetic parameters at 120°C, 140°C, 160°C, and 180°C, with their corresponding coefficient of determination, are provided in Table 1. These results show that the rate constant increased as the temperature increased. Chemical reactions are typically expected to proceed faster at higher temperatures, but slower at lower temperatures. This is because thermal energy relates directly to motion and frequency of collision at the molecular level. As the temperature rises, molecules move faster and collide more vigorously, thereby increasing the likelihood of bond cleavages and rearrangements.



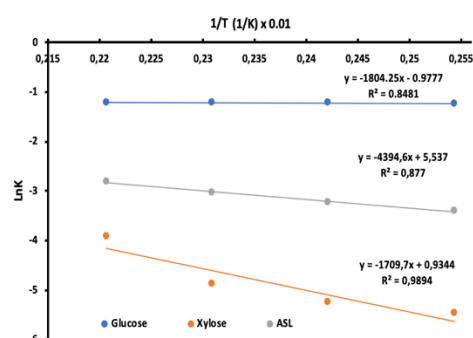
**Figure 4:** Kinetic model for glucose, xylose and SL dissolution at 120 °C: logarithm plots

**Table 1:** Rate constant for glucose, xylose and lignin dissolution and their corresponding R-squared values

T (°C)	Glucose		Xylose	
	$K_G$	$R^2$	$K_X$	$R^2$
120	0.287	0.964	0.004	0.808
140	0.295	0.990	0.005	0.863
160	0.295	0.994	0.006	0.658
180	0.360	0.968	0.020	0.955

Figure 5 depicts the Arrhenius plot used to estimate the activation energy of the dissolution. The apparent activation energies and coefficient of determination ( $R^2$ ) calculated for glucose, xylose and lignin dissolution are presented in Table 2. The resulting  $E_a$  are 15.0 kJ/mol, 14.2 kJ/mol and 36.54 kJ/mol for glucose, xylose and lignin, respectively. It is apparent that the activation energy associated with lignin is higher than that of glucose and xylose, indicating that more energy is required to release lignin from corncob. However,  $E_a$  for xylose and glucose is low, indicating that low quantity of activation energy at high temperature enhances the dissolution rate. However, it should be noted that even a moderate quantity of activation energy could reduce the rate by a factor of  $10^8$

[13].



**Figure 5:** Kinetics of lignin content dissolution, glucose and xylose: Arrhenius plot for the treated biomass. Note: temperature in kelvin (K)

**Table 1:** Calculated activation energies and R-squared value

	$E_a$ (KJ/mol)	$R^2$
Glucose	15.002	0.848
Xylose	14.215	0.877
ASL	36.539	0.989

#### 4. CONCLUSIONS

Kinetics of dissolution of corncob (specifically South African corn cob) in  $LiClO_4 \cdot 2H_2O$  solvent system has been investigated in this study. Morphology and crystallinity of the raw and the treated corncob reveal that  $LiClO_4 \cdot 2H_2O$  is an effective solvent system for fractionation of corncob. The results of the kinetic study indicate that dissolution rate of corncob in the solvent system could be described by pseudo first-order kinetic model and dissolution rate constant increases with increase in pre-treatment temperature keeping all other variables constant.

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