Optimization of Concentrated Acid Hydrolysis of Waste Paper Using Response Surface Methodology\textsuperscript{*1}

Ji Young Jung\textsuperscript{*2}, Myung Suk Choi\textsuperscript{*2}, and Jae Kyung Yang\textsuperscript{*2†}

ABSTRACT

Waste paper stands for the major biodegradable organic fraction of most of municipal solid waste. The potential of waste paper for glucose production was investigated in this current work. The pretreatment was accomplished by first subjecting waste paper to disintegration time (30 s), followed by ink removal of disintegrated waste paper using a deinking agent. Concentrated acid hydrolysis of waste paper with sulfuric acid was optimized to maximize glucose conversion. The concentrated acid hydrolysis conditions for waste paper (disintegrated time: 30 s, deinking agent loading: 15 mL) were optimized by using central composite design and response surface methodology. The optimization process employed a central composite design, where the investigated variables were acid concentration (60 ∼ 80%), loading sulfuric acid (1 ∼ 5 mL) and reaction time (1 ∼ 5 h). All the tested variables were identified to have significant effects ($p < 0.05$) on glucose conversion. The optimum concentrated acid hydrolysis conditions were acid concentration of 70.8%, loading sulfuric acid of 3.2 mL and a reaction time of 3.6 h. This research of concentrated acid hydrolysis was a promising method to improve glucose conversion for waste paper.

Keywords: waste paper, pretreatment, acid hydrolysis, central composite design, response surface methodology

1. INTRODUCTION

In recent years, efforts have increased towards a more efficient utilization of renewable municipal solid waste including waste paper (Holtzapple \textit{et al.}, 1992; Lay \textit{et al.}, 1999, Li \textit{et al.}, 2007; Li \textit{et al.}, 2012). Waste paper was usually recycled into low-grade paper products, such as newsprint, paper towels, toilet paper, and cardboard (Park \textit{et al.}, 2004). The shortening of cellulose fibers with repeated reutilization tends to decrease the quality of the paper products (Deng \textit{et al.}, 2010). Because of this phenomenon, the upper limit of waste paper-to-paper recycling is said to be 65%. This means that the rest of the paper must be disposed of by incineration or landfill. However, because of environmental restrictions, lack of suitable new

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sites, and concerns about the greenhouse effect, incineration or disposal by landfill may become practically impossible in the near future. Finding new uses for recycled paper is a pressing demand. Among paper, perhaps the most limited in its use is computer printout, which is so superabundant in the business districts of civilized countries (Xiao & Clarkson, 1997). Generally, waste computer printout is shredded before disposal, in order to keep office matters confidential; this practice has the unintended consequence of shortening the constituent cellulose fibers beyond utilization (Clarkson & Xiao, 2000; Teghammar et al., 2010). As a consequence, incineration is the usual fate of such materials. However, recent studies have explored other industrial routes. A better way to utilize waste paper would be to converted into bioethanol. Providing that the carbohydrate content of the waste paper is high, it could be converted into bioethanol.

Cellulose, a major building block of waste paper, can be converted enzymatically to reducing sugars including glucose; one use of glucose is fermentation into ethanol. Also, paper sludge after deinking has been traditionally disposed of by burning or landfilling, but could be used as an organic amendment in agricultural soils and filler of erosion control (Chantigny et al., 1999). Basically, the recycling of waste paper can be done by reusing waste paper after pulping them by a machine called pulper and followed by removal of printing ink, a treatment specifically called ‘deinking’ (Holtzapple et al., 1992).

In order to break down holocellulose for conversion of waste paper to glucose, the cellulose and hemicellulose must be broken down to corresponding monomers (sugars). The hydrolysis step may be carried out either enzymatically or by acid treatment (Romero et al., 2010). Enzymatic hydrolysis is conducted at mild conditions but requires a pretreatment of the raw material to improve the enzymatic digestibility (Sun and Cheng, 2005) and longer retention time (Ingram et al., 1999). Moreover, the production and recovery of enzymes may affect this option from an economic point of view (Iranmahboob et al., 2002). Acid hydrolysis may be carried out either at diluted or concentrated acid conditions. Diluted acid hydrolysis attacks polysaccharides, especially those from the hemicellulose fraction which is easier to hydrolyze than cellulose. In addition, no acid recovery steps are required and acid losses are not important. On the negative side, the yield of glucose from cellulose is low. Concentrated acid hydrolysis enables high ethanol yield because of almost quantitative conversion of cellulose into glucose, although acid recovery is required as well as more resistant reactors.

Acid hydrolysis needs the optimization of process parameters, including concentration of sulfuric acid, reaction time, and reaction temperature, loading substrate for efficient hydrolysis. Ritter et al. (Ritter et al., 1945) showed that the yield of lignin from wood treated with 72% sulfuric acid for 1 hr. showed a nearly constant low value when the temperature was varied from 15 to 30°C. These same workers reported that with a 2 hr. treatment with 72% sulfuric acid, results showed a maximum yield of reducing sugars at 35°C. For these reasons it was considered well to begin experiment on saccharification of cellulose using a temperature of 30°C. Sulphuric acid is the most commonly used in lignocellulosic residues hydrolysis (Baudel et al., 2005; Larsson et al., 1999) although other mineral acids like hydrochloric acid (Lavarack et al., 2002), nitric acid (Rodriguez-Chong et al., 2004) or phosphoric acid (Romero et al., 2007) have also been assayed. Acid hydrolysis residue included inorganic compound such as ash and lignin. These residue is used primarily as an organic amendment rather than as fertilizers,
because of mineral nutrient contents. The inorganic compound is affect on the soil improvement (Bolan & Duraisamy, 2003).

Optimization of hydrolysis conditions involves varying one factor at a time and keeping other variables constant (Mathew & Nair, 2006). On the other hand, response surface method can effectively use variables simultaneously and determine optimum conditions required (Giovanni, 1983). Response surface methodology is a statistical technique used to model and optimize multiple variables, and it can be used to determine the optimum conditions by combining experimental design with interpolation of first or second order polynomial equations in a sequential testing procedure. Central composite design (CCD) and response surface methodology (RSM) were used to design a systematic experimental method. CCD is well suited for fitting a quadratic surface which usually works well for process optimization. RSM is able to map a response surface over a particular region of interest (Chun et al., 2011). To our knowledge, there are no reports on combined concentrated acid hydrolysis and RSM of waste paper (Um et al., 2011; Rahman et al., 2007; Laopaiboon et al., 2010; Karimi et al., 2006; Sun et al., 2005).

In this research, RSM was applied to determine the optimum concentrated acid hydrolysis conditions. Furthermore, the extent of glucose production was evaluated at the operating conditions determined by RSM analysis.

2. MATERIALS and METHODS

2.1. Raw Material

Three different types of waste paper were tested: newspaper, old corrugated containers, and computer printout. The waste papers were cut using a standard office shredder to rectangles 0.6 cm wide and 1.5 cm long, and were used for pretreatment and concentrated acid hydrolysis (Park et al., 2002). The moisture content of waste paper (newspaper, old corrugated containers, and computer printout) were 3.8%, 6.3% and 5.4%, respectively.

2.2. Pretreatment of Waste Paper

Pretreatment was conducted in order to understand the effects of disintegration time and loading deinking agent on computer printout pretreatment efficiency. The pretreatment procedure employed in this study is shown schematically in Fig. 1. To produce pretreated computer printout, 100 g of shredded computer printout, 10% NaOH (10 mL) and tap water (1450 mL) were
mixed in a pulp disintegrator (GF7-P61, Han- 
young Co. Ltd., KOREA). The disintegration 
time was then carried out for 30 s, 60 s, 90 s, 
120 s and 150 s. After this, the disintegrated 
computer printout was incubated for 1 hr in a 
60°C water bath. The amount of deinking agent 
required to achieve frothing, and hence deinking 
agent (nonionic surfactant) was 5 to 25 mℓ, 
which is normally added to commercial dein-
kling agent (provide by Ssangyong paper, Osan-
si, Korea).

The disintegrated computer printout was di-
luted in a 5,050 mℓ flotation cell to a consis-
tency of 1.5% and conditioned in the presence 
of the collector. The flotation was then carried 
out for 20 min. at a stirring speed of 1400 rpm. 
Subsequently, the float (toner particles) and 
nonfloat (cellulose fibres) products were care-
fully filtered, dried and stored for analysis of 
yield and cellulose recovery.

2.3. Concentrated Acid Hydrolysis of 
Waste Paper

2.3.1. Concentrated Acid Hydrolysis

Concentrated acid hydrolysis (Table 1) was 
performed according to the method originally 
described by Saeman et al. (1945). A first step 
(concentrated acid hydrolysis) with 60 ∼ 80% 
(w/w) H₂SO₄ at 30°C for 1 ∼ 5 hr. was used. 
The media consisted of 300 mg pretreated com-
puter printout/1 ∼ 5 mℓ H₂SO₄ liquor on dry 
basis. In a second step, the reaction mixture was 
diluted to 4% (w/w) H₂SO₄ and autoclaved at 
121°C for 1 hr. After reaction was completed, 
solids were separated from aqueous solution by 
filtration. The filtrate was analyzed for glucose.

2.3.2. Design of Experimental

The effect of three independent variables (acid 
concentration, loading sulfuric acid and reaction 
time) on the response (glucose conversion) was 
studied using a factorial central composite design 
(CCD) of response surface methodology (RSM), 
which is a collection of mathematical and sta-
tistical techniques for designing experiments, 
analysing the effects of variables, developing 
models and optimising the process variables for 
the optimum response (Ferreira et al., 2009). The 
experimental data were fit using a low-order 
polynomial equation to evaluate the effect of 
each independent variable to the response, which 
were later analysed to determine the optimum 
process conditions. For fitting second-order 
models, CCD was one of the most commonly 
used RSM (Ferreira et al., 2009). CCD consists 
of 2^k factorial points, 2^k axial points (± α), and 
6 centre points, where k is the number of in-
dependent variables. Each of the variables were

<table>
<thead>
<tr>
<th>Coded levels of experimental factors</th>
<th>X(1) : Acid concentration (%)</th>
<th>X(2) : Loading sulfuric acid (mℓ)</th>
<th>X(3) : Reaction time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-a</td>
<td>60</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>-1</td>
<td>65</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>0</td>
<td>70</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>1</td>
<td>75</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>a</td>
<td>80</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>
Optimization of Concentrated Acid Hydrolysis of Waste Paper Using Response Surface Methodology

investigated at five coded levels (-a, -1, 0, 1, a), as listed in Table 1, and the complete experimental design matrix for this study was shown in Table 2. A total of twenty experiments, including eight for factorial design, six for axial points and six repetitions at the central point, were performed.

2.3.3. Statistical Analysis

The CCD experimental results were analyzed using Design-Expert software version 6.0.6, from STAT-EASE, Inc., Minneapolis, USA. Each coefficient in regression equation was calculated and the possible interaction effects of the process variables on the response were obtained. Their significance was checked by variance analysis (ANOVA). Three-dimensional plots were drawn using the RSREG (SAS: statistical analysis system, SAS institute, U.S.A) to illustrate the effects of independent variables on the response. Lastly, two additional replicates were conducted to verify the validity of the predicted optimum values by the program.

Optimization (maximizing glucose conversion) of the fitted polynomial was determined using numerical optimization contained in the RSREG (SAS: statistical analysis system, SAS institute U.S.A). After optimizing the conditions using RSM, it was validated by extruding the waste paper at the identified optimum acid concentration, loading sulfuric acid and reaction time.

2.4. Analytical Methods

The chemical composition of waste paper was determined by the National Renewable Energy Laboratory (NREL) using standard biomass analytical procedures. The glucose content was determined by American Society for Testing and Materials (ASTM) using standard test method for determination of carbohydrates in biomass by gas chromatography. The gas chromatography (Model YL 6100, Younglin, KOREA) system was equipped with a DB-225 capillary column (5 m, 0.25 mm ID, 0.25 mm film thickness) (J&W Scientific, Folsom, CA). Nitrogen was used as the carrier gas. An initial column temperature of 190°C was held for 1.0 min. before ramping at 10°C per min. up to 220°C where it was kept steady for 14 min. The injection port temperature was set at 200°C, and the FID temperature

<table>
<thead>
<tr>
<th>Run</th>
<th>Experimental design</th>
<th>X(1)</th>
<th>X(2)</th>
<th>X(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1 -1 -1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>-1 1 -1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>3</td>
<td>-1 -1 1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>-1 1 1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>1 -1 -1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
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<tr>
<td>6</td>
<td>1 1 -1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
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<td>7</td>
<td>1 -1 1</td>
<td>1</td>
<td>-1</td>
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<td>8</td>
<td>1 1 1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>0 -2 0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0 2 0</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>0 0 -2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>0 0 2</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>-2 0 0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>2 0 0</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>0 0 0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>0 0 0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>0 0 0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td>0 0 0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>0 0 0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>0 0 0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

1) Coded value of acid concentration (%).
2) Coded value of loading sulfuric acid (㎖).
3) Coded value of reaction time (hr).
Table 3. Retention times for monosaccharide alditol acetates on DB-225 capillary column

<table>
<thead>
<tr>
<th>Monosaccharide</th>
<th>Alditol acetate derivative</th>
<th>Retention time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arabinose</td>
<td>Arabitol acetate</td>
<td>4.11</td>
</tr>
<tr>
<td>Xylose</td>
<td>Xylitol acetate</td>
<td>4.64</td>
</tr>
<tr>
<td>Mannose</td>
<td>Mannitol acetate</td>
<td>6.69</td>
</tr>
<tr>
<td>Galactose</td>
<td>Galactitol acetate</td>
<td>7.08</td>
</tr>
<tr>
<td>Glucose</td>
<td>Glucitol acetate</td>
<td>7.52</td>
</tr>
<tr>
<td>Inositol</td>
<td>Inositol acetate</td>
<td>7.92</td>
</tr>
</tbody>
</table>

was set at 250°C. Total column flow was 50 ml/min., sample linear velocity through the column was 78 cm/s, column flow was 3.0 ml/min., and 2 µl samples were injected with a split ratio of 15:1. The retention times for each monomer can be found in Table 3.

The glucose conversion after concentrated acid hydrolysis was calculated by Eq. (1):

\[
\text{% Glucose conversion} = \left( \frac{\text{Weight of glucose in acid hydrolysate (g)}}{\text{Weight of glucose in pretreated computer printout (g)}} \right) \times 100
\]

3. RESULTS and DISCUSSION

3.1. Chemical Composition of Waste Paper

The waste paper was divided into: corrugated paper and paper bags, newspaper, coated paper, cardboard and uncoated, wood-free paper (Jannick et al., 2007). The chemical composition of waste paper was shown in Table 4.

Newspaper was found to contain, cellulose (57.1%), hemicellulose (8.4%), lignin (17.2%) and ash (6.2%). The results obtained here were similar to earlier studies, where lignin and holocellulose content in newspaper were found to be 16～22% and 60～75%, respectively (Lee et al., 2000; Torget et al., 2000). Also, Table 4 shows the chemical composition of the old corrugated containers. Experimental results show that about 47.5% of the oven-dry cardboard weight corresponds to cellulose, a proportion lower than the one reported for Yáñez et al. (59.7%) (Yáñez et al., 2004). Computer printout main contained 68.2% holocellulose (59.2% cellulose and 9.0% hemicellulose) and 17.5% ash content. Among three sources of waste paper including computer printout, newspaper and old corrugated containers, computer printout gave the highest values of cellulose. Carbohydrate (cellulose and hemicellulose) was higher than that reported for other lignocellulosic material like wood, agriculture residue (Chen et al., 2007; Mamma et al., 1995; Gnansounou et al., 2005; Li et al., 2010, Wiselogel et al., 1996). The high cellulose content in the computer printout made it a substrate of choice for glucose production.

3.2. Pretreatment of Computer Printout

Computer printout was defined as that paper used in plain paper copiers; waste computer printout denotes plain paper copiers after printing in a printer or copy machine. Computer printout contain toner or ink-related compounds on the surface of paper (Park et al., 2004). The ink fixed on the repeating units of cellulose backbone block the sequential hydrolysis of paper and inhibited the hydrolysis kinetics significantly (Kuhad et al., 2010). To determine their effects on yield and cellulose recovery, computer printout were used for pretreatment. The purpose of this pretreatment was to remove the toner and ink-related compounds in computer printout. At first attempt at pretreatment, the disintegration condition was tested at room temperature during five different disintegration time 30～150 s. Fig. 2 shows the yield and cellulose recovery resulting from pretreatment at different
Table 4. Chemical composition of waste paper\textsuperscript{1,2,3}

<table>
<thead>
<tr>
<th>Composition</th>
<th>Newspaper (% dry weight)</th>
<th>Old corrugated containers (% dry weight)</th>
<th>Computer printout (% dry weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractives</td>
<td>9.7 ± 0.3\textsuperscript{2}</td>
<td>8.8 ± 0.4\textsuperscript{2}</td>
<td>9.2 ± 0.8\textsuperscript{2}</td>
</tr>
<tr>
<td>Cellulose as glucose</td>
<td>57.1 ± 0.1</td>
<td>47.5 ± 0.1</td>
<td>59.2 ± 0.2</td>
</tr>
<tr>
<td>Hemicellulose\textsuperscript{3} as</td>
<td>8.4</td>
<td>10.6</td>
<td>9.0</td>
</tr>
<tr>
<td>Xylose</td>
<td>5.5</td>
<td>6.8</td>
<td>7.6</td>
</tr>
<tr>
<td>Galactose</td>
<td>0.8</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>Arabinose</td>
<td>0.8</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Mannose</td>
<td>1.3</td>
<td>2.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Acid insoluble lignin</td>
<td>14.3 ± 0.2</td>
<td>14.5 ± 0.1</td>
<td>3.0 ± 0.1</td>
</tr>
<tr>
<td>Acid soluble lignin</td>
<td>2.9 ± 0.0</td>
<td>3.6 ± 0.0</td>
<td>3.4 ± 0.0</td>
</tr>
<tr>
<td>Ash</td>
<td>6.2 ± 0.2</td>
<td>12.7 ± 0.2</td>
<td>17.5 ± 0.3</td>
</tr>
<tr>
<td>Protein</td>
<td>0.5 ± 0.1</td>
<td>0.9 ± 0.1</td>
<td>0.4 ± 0.1</td>
</tr>
</tbody>
</table>

\textsuperscript{1}Data in the table was based on oven dry samples.
\textsuperscript{2}Mean values of triplicate samples with standard deviations.
\textsuperscript{3}Hemicellulose : xylose + galactose + arabinose + mannose.

disintegration time. The recovered computer printout samples have significantly reduced yield ($p < 0.05$) and cellulose recovery compared to the untreated computer printout. During disintegration, yield was decreased by 7.6%, and 12.1% of cellulose recovery. The yield ranged between 93.0 and 92.4%, cellulose recovery ranged between 49.6 and 41.9%. The maximum cellulose recovery in disintegrated computer printout was obtained at disintegration time 30 s. In flotation deinking lines, ink removal exceeds 80~90% but a modest ink separation selectivity (Zhu et al., 2005) results in high losses (15~30%) of mineral fillers and cellulosic material (Beneventi et al., 2007).

In flotation deinking process, mechanisms governing inter fibre and bubble/fibre interaction in aerated pulp slurries and their contribution to the fibre yield during the flotation deinking process, are not fully understood.

Experimental data showing the effects of various loading deinking agent on yield and cellulose recovery are summarized in Fig. 3. As this

Fig. 2. Effect of disintegration time on the pre-treatment.

Fig. 3 suggests, yield of disintegrated computer printout decreased with increased loading deinking agent. The cellulose recovery attained their maximum at approximately 15 mL of deinking agent per 100 g of computer printout. The practice of caustic pulping originates from the success in the deinking of computer printout. However, the computer printout was printed with oil-based inks. Such inks were removed from the paper by a saponification reaction (McKinney, 2005)
3.3. Modeling and Optimization of Concentrated Acid Hydrolysis

The conditions of the system were optimized using the CCD based on the model obtained and the input criteria. The optimization of concentrated acid hydrolysis was carried out based on the three variables (acid concentration, loading sulfuric acid and reaction time) which were in the range of experimental runs.

The experimental design and corresponding responses of the dependent variables (glucose conversion) are listed in Table 5. Central composite design was used to develop correlation between the concentrated acid hydrolysis variables to the glucose conversion. The glucose conversion was found to range between 30.9 and 94.4%. Runs 15～20 at the centre point were used to determine the experimental error.

According to the sequential model, sum of squares, the models were selected based on the highest polynomials order and were not aliased. For responses of glucose conversion, the quadratic model was selected, as suggested by used software. The final empirical models in terms of coded factors are given by Eq. (2) where $Y$ was glucose conversion:

$$
Y = \beta_0 + \beta_1X(1) + \beta_2X(2) + \beta_3X(3) + \beta_{11}X(1)^2 + \beta_{12}X(1)X(2) + \beta_{22}X(2)^2 + \beta_{13}X(1)X(3) + \beta_{23}X(2)X(3) + \beta_{33}X(3)^2
$$

where $X(1)$, $X(2)$ and $X(3)$ were the acid concentration, loading sulfuric acid and reaction time, respectively. The experimental data were used to calculate the coefficients of the second-
The response surface regression and models were expressed in terms of coded variables, without taking into account the statistically non-significant terms at \( \alpha = 0.05 \). In other words, only the model terms with \( p \)-values less than 0.05 were determined to be significant to the model equations. The coefficients \( \beta_i \) are displayed in Table 6. The quality of the models developed was evaluated based on the correlation coefficient \( R^2 \), and also the standard deviation values. The \( R^2 \) was found to be 0.7830. This indicates that 78.3\% of the total variation in glucose conversion was attributed to the experimental variables studied. The regression model for the glucose conversion was presented in Eq. (3). Additionally, the \( p \)-values suggest that the variables \( X(1) \) had significant effects on the glucose conversion.

\[
Y = -2926.694167 + 83.507167X(1) + 45.730000X(2) - 4.245000X(3) - 0.615033X(1)^2 + 0.630000X(1)X(2) - 14.825833X(2)^2 + 0.455000X(1)X(3) + 1.000000X(2)X(3) - 4.363333X(3)^2
\]

The effects of the three variables (acid concentration, loading sulfuric acid and reaction time) on glucose conversion were analyzed using RSM. The data analysis was developed by fitting the experimental data in a smooth curve, which was plotted by calculation of the specific predicted response. Three-dimensional response surface and contour plots were generated to investigate the interactive effects of any two variables on the response by evaluating two variables at a time while holding the other one constant at central level. A three-dimensional plot can give a clearer geometrical representation of the nature and extent of the interaction between the variables and response within the experimental range studied. The relationship between the response and controlled variables was visualized using the response surface or contours plots. Graphic representation of the response surface shown in Fig. 4(a∼c) helps visualize the effects of various variables. Response surfaces plots of glucose conversion was obtained using predicted values from the fitted model, by keeping one of the independent variables fixed at the optimum value while modifying the other two variables.

Fig. 4(a) represents the three-dimensional response surface plot of glucose conversion at a reaction time of 3.6 hr to investigate the interactive effect of acid concentration and loading sulfuric acid. At different acid concentration, the glucose conversion reaches a maximum value at approximate 70.8%. At different acid concentration and loading sulfuric acid, the glucose conversion reaches a maximum value at approximate 3.6 hr and slightly decreases above that value (Fig. 4(b) and Fig. 4(c)). This study has revealed that concentrated acid hydrolysis at a moderate acid concentration around 70.8\% maximum glucose conversion within the range 68∼78\% and reaction time from 2 to 5 hr.

Table 6. Regression coefficients for the response surface and \( p \)-values

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Parameter estimate</th>
<th>( p )-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta_0 )</td>
<td>-2926.694167</td>
<td>0.0207</td>
</tr>
<tr>
<td>( \beta_1 )</td>
<td>83.507167</td>
<td>0.0133</td>
</tr>
<tr>
<td>( \beta_2 )</td>
<td>45.730000</td>
<td>0.6928</td>
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<tr>
<td>( \beta_3 )</td>
<td>-4.245000</td>
<td>0.9706</td>
</tr>
<tr>
<td>( \beta_{11} )</td>
<td>-0.615033</td>
<td>0.0099</td>
</tr>
<tr>
<td>( \beta_{12} )</td>
<td>0.630000</td>
<td>0.6874</td>
</tr>
<tr>
<td>( \beta_{22} )</td>
<td>-14.825833</td>
<td>0.0118</td>
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<tr>
<td>( \beta_{13} )</td>
<td>0.455000</td>
<td>0.7708</td>
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<tr>
<td>( \beta_{23} )</td>
<td>1.000000</td>
<td>0.8979</td>
</tr>
<tr>
<td>( \beta_{33} )</td>
<td>-4.363333</td>
<td>0.3677</td>
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</table>

R-square 0.7830
The optimal conditions for concentrated acid hydrolysis were extracted by Design-Expert software though a graphical optimization. Taking efficiency into consideration, the optimum operating parameters were found to be: $X(1) = 70.8\%$, $X(2) = 3.2 \text{ mL}$, $X(3) = 3.6 \text{ hr}$. Under these conditions, confirmation experiments were conducted in five replicates. The observed mean glucose conversion was found to be largely consistent with the predicted values. At the same time, it is further confirmed the rationality and practicability of optimal conditions for concentrated acid hydrolysis in this work. In these conditions, the model predicted glucose conversion of 94.4%.

To confirm these results, experimental runs were conducted under optimized conditions and glucose conversion of 92.1% was attained. These results showed that the model fitted well the experimental data and thus described well the region studied.

4. CONCLUSION

The use of waste paper for the production of glucose seems feasible approach for energy conservation and waste minimization. Concentrated acid hydrolysis of pretreated computer printout (disintegration time: 30 s, loading deinking agent: 15 mL) was successful in enhancement of glucose conversion. The optimum concentrated acid hydrolysis condition for glucose conversion was determined to be acid concentration 70.8%, loading sulfuric acid 3.2%
and a reaction time 3.6 hr. The experimental value was well within the estimated value of the model. By operating the pretreatment at optimum conditions, it avoids using the longest possible time and highest sulfuric acid loading, subsequently reduces the overall production cost.

The research is needed to make this process economically feasible. Ultimately the optimal hydrolysis conditions for the glucose recovery at the laboratory scale may potentially be scaled up to the production level.

This research of concentrated acid hydrolysis was an economical method to improve glucose conversion for waste paper.

ACKNOWLEDGEMENT

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