

*Full Length Research Paper*

# Kinetic modeling of concentrated acid hydrolysis of walnut green skin

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The overall goal of this experiment was to detect whether kinetic modeling can explain effects of temperature, acid concentration, time and solid contents on the production of glucose by concentrated acid hydrolysis of walnut green skin. For this purpose, sulfuric acid concentration of 20, 40 and 60% (w/w), processing temperature of 65, 80 and 90°C, reaction time of 120, 180 and 240 min and solid content of 5, 10 and 15% (w/w) were used as hydrolysis conditions. High performance liquid chromatography (HPLC) was used to analyze the products. The process was modeled by first-order irreversible reaction in series and kinetic constant, relating reaction time to glucose released. To relate temperature with kinetic constant and calculate activation energy, Arrhenius equation was employed. Optimal conditions occurred at 40% H<sub>2</sub>SO<sub>4</sub>, 90°C and 15% solid content for 285 min, which yielded a solution with 10.72 g glucose/L. In these conditions, 45% of the cellulose was hydrolyzed.

**Key words:** Kinetic modeling, fermentable sugar, acid hydrolysis, walnut green skin.

## INTRODUCTION

Green walnut skin is a lignocellulosic biomass that can provide a good source of energy. The USA, China and Iran are major producer of walnut. The increasing production of walnut in Iran has reached a record of 170 ton in the year 2009. The rising green walnut skin needs a good agriculture waste management. Managing the residual of agriculture through energy production from these materials would have high share of energy supply in Iran, and consequently there is need for more research and development on renewable energies (Nagafi et al., 2008).

The lignocellulosic biomass consists of cellulose, hemicelluloses and lignin. Cellulose is a linear, crystalline homopolymer with a repeating unit of glucose held together by beta-glucosidic linkages. The structure is rigid and as a result harsh treatment is required to break it down (Kevin, 2006). In contrast to cellulose, which is a polymer of only glucose, hemicellulose is a heteropolymer of D-xylose, D-glucose, D-galactose, D-mannose and L-arabinose (Shama, 1988). The composition of holocellulose (cellulose + hemicellulose) varies with the

origin and type of the lignocellulosic material (Taherzadeh and Karimi., 2007). The carbohydrate polymers in the lignocellulosic material need to be converted to simple sugars before fermentation through a process called hydrolysis. The most commonly applied method can be classified in two groups: chemical hydrolysis and enzymatic hydrolysis. Cellulose and hemicelluloses can be converted to simple sugars then fermented to ethanol, while lignin remains as a by-product.

Hydrolysis of lignocelluloses by concentrated sulfuric or hydrochloric acids is an old process. Braconnot in 1819 first discovered that cellulose can be converted to fermentable sugar by concentrated acids (Sherrard and Kressman., 1945). Concentrated acid processes are generally reported to give higher sugar yield (example 90% of theoretical glucose yield) and consequently higher ethanol yield, compared to dilute-acid processes. Furthermore, the concentrated acid processes can operate at low temperature, which is a clear advantage compared to dilute acid processes. Reaction times are typically much longer than for dilute acid process (Chandel et al., 2007). Sulfuric acid is the most

investigated acid (Harris et al., 1945), although other acids such as HCl (Hashem et al., 1993) have also been used. However, the concentration of acid is very high in

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**Table 1.** Composition of WGS.

Composition	Percent dry weight
Cellulose	21.5
Hemicellulose	13.25
Extractive M. <sup>1</sup>	18.25
Lignin	26.07
Ash	20.93

<sup>1</sup>Extractives by reaction with mixture of benzene and ethyl alcohol (TAPPI 204 OM-88).

this method (example 30 to 70%), and dilution and heating of the concentrated acid during the hydrolysis process make it extremely corrosive. Therefore, the process requires either expensive alloys or specialized non-metallic constructions, such as ceramic or carbon-brick lining. The acid recovery is an energy-demanding process. In addition, when sulfuric acid is used, the neutralization process produces large amounts of gypsum (Taherzadeh and Karimi., 2007).

Cellulose, hemicellulose and lignin are broken down to glucose, mannose or xylose, and phenolic compounds during acid hydrolysis. Further decompositions occur during these process conditions yielding other unexpected compounds such as furfural from pentose and acetic acid from acetyl groups in hemicellulose. For the fermentation process, the presence of these materials in hydrolysates can hinder or prevent a subsequent fermentation step. Furfural has been reported to be a strong inhibitor for *Saccharomyces cerevisiae*. It decreases significantly the CO<sub>2</sub> evaluation rate, the cell multiplication and the total viable cell number in the early phase of fermentation (Plamqvist et al., 1999; Taherzadeh and Karimi., 1999). The inhibitory effect of acetic acid is pH-dependent (Larrson et al., 1999). Very high concentration of acetic acid increase acidification of cytoplasm and cell death. Two mechanisms have been proposed to explain the inhibitory effect of acetic acid; uncoupling and intracellular anion accumulation (Palmqvist and Hahn, 2000). Therefore, hydrolysis with low concentrations of inhibitors is required.

This work deals with the acid hydrolysis of walnut green skin with concentrated sulfuric acid. Kinetic models were developed to correlate glucose concentration with time. The influence of other variables such as acid concentration, temperature and solid contents has been modeled in kinetic coefficients.

## MATERIALS AND METHODS

### Biomass

Walnut green skin (WGS) was gathered in September 2009 from Spidan village, North Khorasan in Iran. It was air dried, milled to particle size under 50  $\mu\text{m}$  (by vibratory disc mill, Retsch RS 100) and stored in sealed plastic bags at room temperature. For the

determination of the chemical composition of the WGS, preparation of the test specimens was carried out according to TAPPI T 257 om (1985) standard. Extracted materials, lignin and ash contents were determined according to TAPPI standards T 204 om (1988), T 222 om (1988), T 211 om (1988), respectively. The hemicellulose and cellulose contents were determined according to Wise's chloride and Kirschner-Hoffner nitric acid methods. The composition of WGS is shown in Table 1.

### Experimental design strategy

Concentration acid hydrolysis technique was used to hydrolyze WGS. The effect of the following four factors: temperature, acid concentration, reaction time and solid content on fermentable sugars production were studied. For each variable, three levels were considered. The experimental design was based on factorial methods. Each experiment was run three times and only the nearest results were averaged.

### Hydrolysis method

Dried WGS was treated with 20, 40, 60% (wt) sulfuric acid in screw-capped laboratory bottles (Pyrex bottles) at 65, 80 and 90°C for 2, 3 and 4 h with agitation by a laboratory mixer. A distiller was used to prevent water evaporation. Solid to liquid ratio of 5, 10 and 15% was applied. After reaction time, sodium hydroxide (NaOH) was used until its PH become around 7.0 and then liquor is filtered out and the solids were separated by filtering. These were then washed with distilled water until the volume of final solution reached 1000 ml.

### Analysis method

The composition of the hydrolysate from acid hydrolysis (glucose, xylose, mannose, arabinose, galactose, furfural and acetic acid) was determined by high performance liquid chromatography (HPLC) using an HPLC JASCO model. Glucose, xylose, galactose, mannose and arabinose were analyzed by Bio-Rad column Aminex HPX-87P and detected by RI detector at 40°C, while acetic acid and furfural were analyzed by Bio-Rad column Aminex HPX-87H and detected by UV detector at 210 nm.

### Statistical analysis

For analysis of the results, Qualitek-4 (ver. 14.0.2) and Minitab (14.1) software were used and non-linear regression analyses of experimental data were performed with commercial optimization routine using Newton's method (Sigma plot 11 software) by minimizing the sum of squares of deviations between experimental

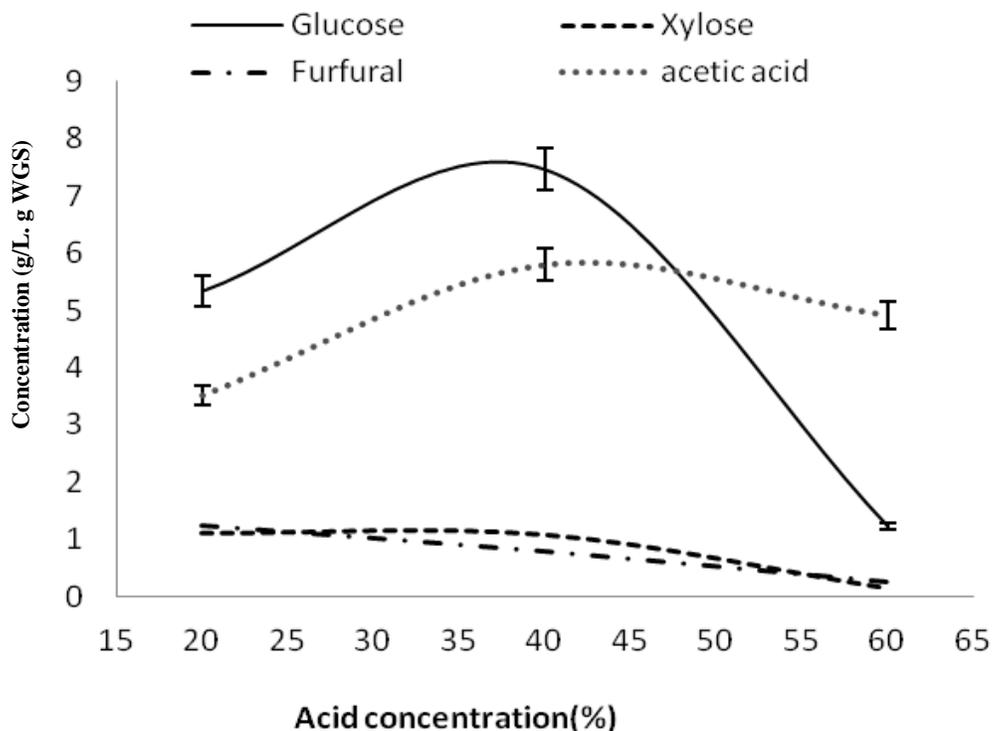


Figure 1. Influence of acid concentration on main products concentration.

and calculated data.

## RESULTS

The effects of acid concentration, temperature, solid contents and reaction time on the amount of released materials in WGS hydrolysis were investigated experimentally. The reported materials are glucose, xylose, furfural and acetic acid. Other released material such as mannose, arabinose and galactose were not considered, because of low concentrations. The effect of acid concentration on the amount of released materials is shown in Figure 1. The glucose concentration was strongly affected by the sulfuric acid concentration. In sever conditions, a sharp decrease was observed in the glucose concentration. This fact suggests that the decomposition reaction may exist, for example to HMF. As can be seen from the results, optimal glucose yield was achieved at medium acid concentration (near 40% acid concentration). It was observed that the concentration of acetic acid first increased and then decreased with acid concentration. Furfural and xylose decreased slightly with acid concentration.

The effect of the temperature on glucose, xylose, acetic acid and furfural is shown in Figure 2. Increasing the hydrolysis temperature significantly affected the glucose production before 80°C and acetic acid production after 80°C. The concentration of these compounds increased

with temperature, but it was low for glucose in the range of 80 to 90°C. Therefore, temperature has a positive effect on single sugar yield. Moreover, an increase in the glucose yield with time was also detected as shown in Figure 3. This increase was sharper at the beginning of the process, as long as the hydrolysis proceeded; it seems that sugar generation rate was reduced. This suggests that decomposition reaction of glucose was negligible.

Another process variable that affects WGS hydrolysis and glucose formation during pretreatment is solid content. A representative plot is displayed in Figure 4 on the effect of solid loading on all products. As solid content increased, the rate of glucose formation and other products increased. All the figures showed that concentration of glucose and acetic acid are more than other compounds. Hence, kinetic modeling of glucose as a fermentable sugar and acetic acid as an inhibitor were studied.

## Kinetic modeling

It is usual to use simplified models to determine the kinetic of hydrolysis of lignocelluloses material. The models proposed in the literature use irreversible pseudo-homogeneous first-order reactions (Malester et al., 1988, 1992; Orozco et al., 2007; Aguilar et al., 2002; Lenihan et al., 2010) as follows:

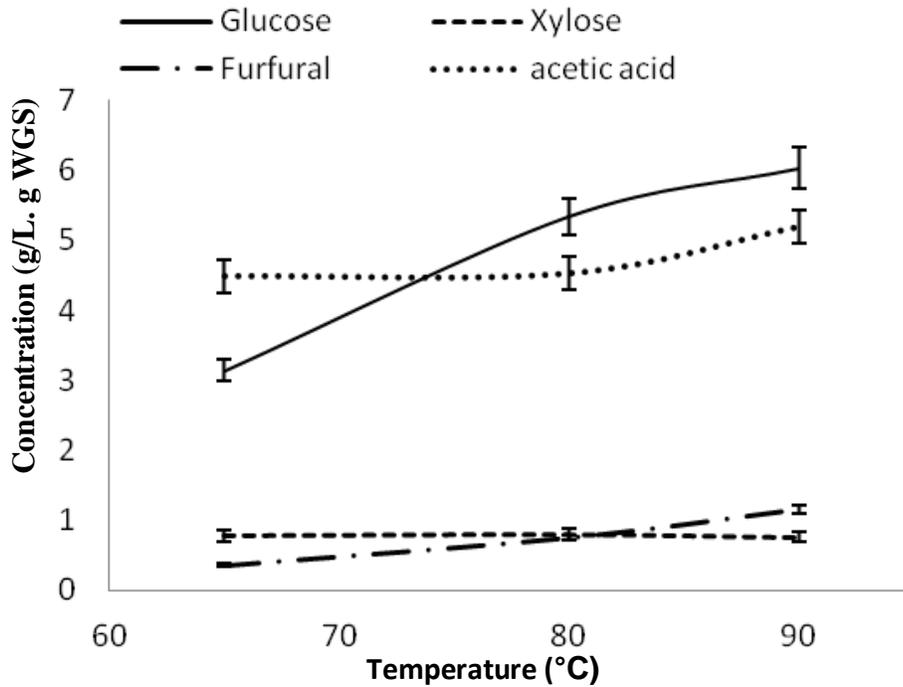


Figure 2. Influence of temperature on main products concentration.

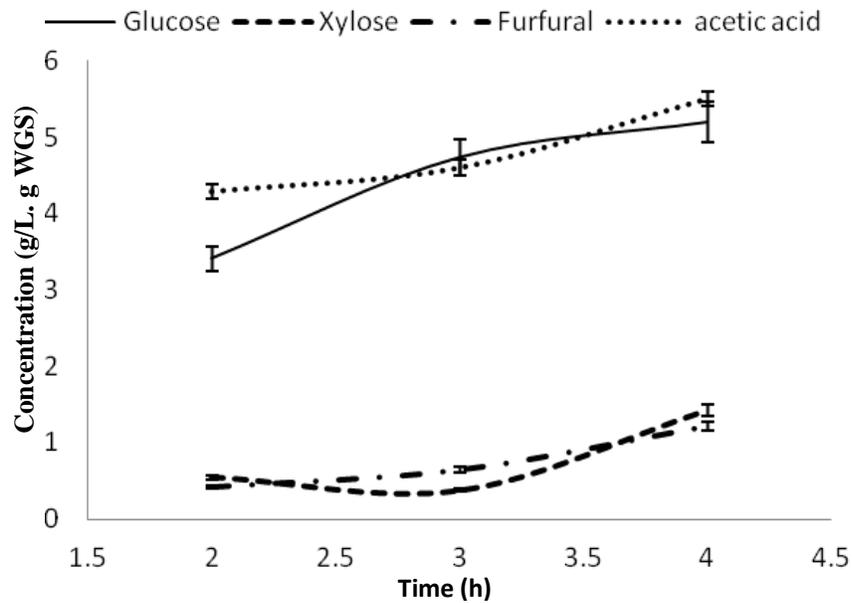
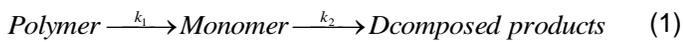


Figure 3. Influence of time content on main products.



Where  $k_1$  is the rate of conversion of polymer (cellulose) to monomer (glucose) and  $k_2$  is the rate of decomposition of monomers. Both have units of the reciprocal of time ( $min^{-1}$ ). From these reaction models and the results of differential equations, the following equation that

represents the monomer concentration as a function of time can be derived (Lenihan et al, 2000; Levenspiel, 1999):

$$M = \frac{P_0 k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (2)$$

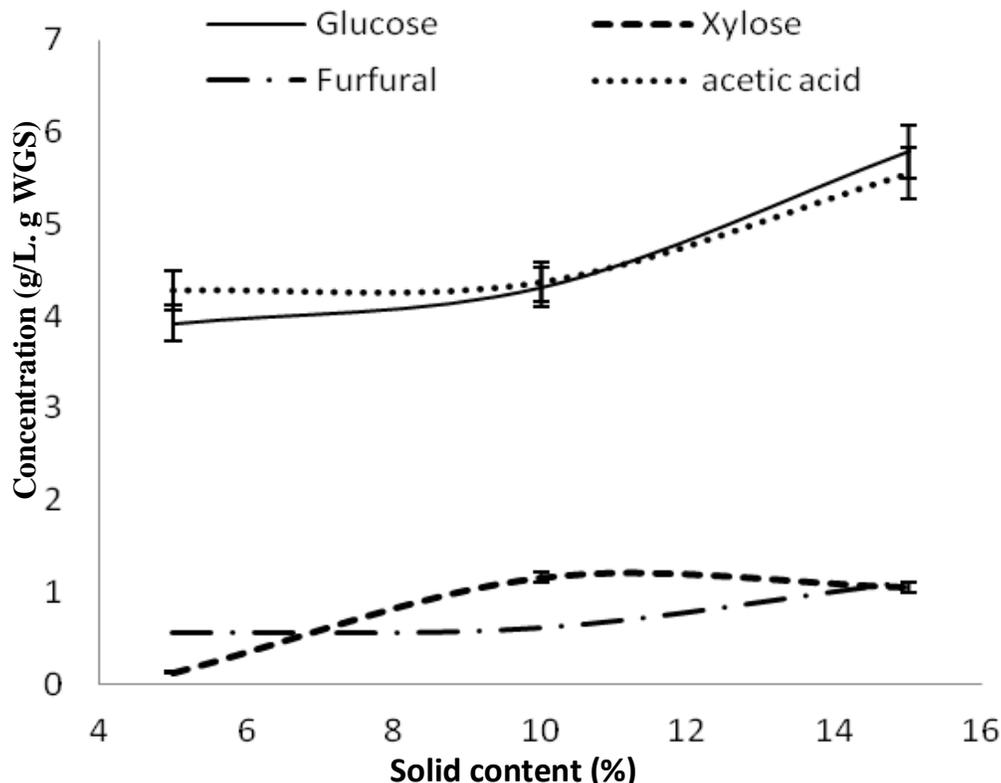


Figure 4. Influence of solid contents on main products.

Where,  $M$  is the monomer concentration (g/L) and  $P_0$  is the polymer concentration (g/L).

An alternative model called "two fraction model" is often used to describe the reaction kinetics and is tested versus the previous model to provide accuracy. This model that was used upon the fitting of experimental data to Equation 2 was not successful implying that only a fraction of the polymer reacts. This is called the fast fraction, and the fraction that does not react or reacts slowly is called the slow fraction. The ratio between susceptible polymers to total is the parameter  $\alpha$ . In case the slow fraction does not react, the following equation is used (Gamez et al., 2004; Herrera et al., 2003; Lenihan et al., 2010):

$$M = \alpha \frac{P_0 k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (3)$$

#### Kinetic modeling of glucose concentration

The modified model described in Equation 3 can be used in the kinetic modeling of glucose concentration, where  $M$  is the glucose concentration (g/L);  $P_0$  is the cellulose concentration corresponding with the quantitative conversion to glucose;  $k_1$  is the rate of the generation reaction

from cellulose to glucose ( $\text{min}^{-1}$ ) and  $k_2$  is the rate of the decomposition reaction from glucose to HMF ( $\text{min}^{-1}$ ). The value of  $P_0$  was calculated as:

$$P_0 = \frac{180 CG_0}{162 WSR} = 23.85 (\text{gr/l}) \quad (4)$$

Where,  $CG_0$  is the initial composition of cellulose (21.5 g cellulose/100 g WGS); WSR is the water/solid ratio (100 g water/ g WGS), and 180/162 is ratio of stoichiometric factors of glucose to cellulose. The kinetic parameters ( $k_1$ ,  $k_2$  and  $\alpha$ ) for glucose production which are calculated based on experimental data regression are shown in Table 2. In addition, the model predictions and experimental data are compared in Figure 5. The statistical parameter ( $R^2$ ) showed a good agreement between experimental and predicted data. Parameter  $\alpha$  in all sets is one. This means that all cellulose was susceptible and the fitting of experimental data to Equation 2 should be successful as well.

As far as the kinetic constant is concerned, most of authors' accept a potential dependence on acid concentration and Arrhenius-type dependence on temperature as shown in Equation 5 (Brennan et al., 1986; Carrasco and Roy., 1992; Ranganathan et al., 1985; Kim et al., 2000; Romero et al., 2010).

**Table 2.** Kinetic parameters and standard deviation of Glucose released for the sulfuric acid hydrolysis of WGS.

Acid concentration (%)	Temperature (°C)	Solid content (%)	$\alpha$	$k_1(10^3) (\text{min}^{-1})$	$k_2(10^3) (\text{min}^{-1})$	$R^2$
20	65	5	1	0.934	6.9E-12	0.98
20	65	10	1	1.109	2.5E-12	0.99
20	65	15	1	1.653	2.008	0.99
20	80	5	1	1.427	2.202	0.99
20	80	10	1	1.52	1.667	0.98
20	80	15	1	2.396	3.225	0.99
20	90	5	1	1.804	1.958	0.99
20	90	10	1	2.002	2.112	0.98
20	90	15	1	2.967	2.795	0.99
40	65	5	1	1.73	1.68	0.99
40	65	10	1	1.887	2.032	0.98
40	65	15	1	2.416	2.887	0.99
40	80	5	1	2.501	2.989	0.98
40	80	10	1	2.703	2.914	0.98
40	80	15	1	3.46	3.049	0.98
40	90	5	1	3.159	2.818	0.98
40	90	10	1	3.408	2.88	0.98
40	90	15	1	4.35	2.80	0.98

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \quad (5)$$

Where,  $k_0$  is the pre-exponential parameter ( $\text{min}^{-1}$ );  $E$  is the activation energy for glucose generation (KJ/mol) and  $T$  is the temperature in Kelvin (Aguilar et al., 2002). The fitting of  $k_1$  was performed for each set of concentration of sulfuric acid and solid content. The resulted parameters ( $k_0$  and  $E/R$ ) are shown in Table 3. The statistical parameter  $R^2$  shows a good agreement between experimental and predicted data for all regressions. Furthermore, the parameter  $k_0$  can be correlated with acid concentration as given in Equation 6. The resulted values of regression parameters ( $n$  and  $a$ ) are shown in Table 4.

$$k_0 = aC^n \quad (6)$$

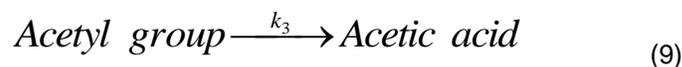
In addition, for considering the effect of solid contents, the parameters  $n$  and  $a$  are correlated with the solid contents ( $S$ ) as follows:

$$n = -0.11 + 0.0620S + 0.0012S^2 \quad R^2 = 0.999 \quad (7)$$

$$a = 14.4 - 1.903S + 0.06547S^2 \quad R^2 = 0.999 \quad (8)$$

### Kinetic modeling of acetic acid concentration

The acetic acid is generated from the hydrolysis of the acetyl groups present in the hemicellulosic heteropolymers. Equation 9 describes the generation of acetic acid in hydrolysis of WGS.

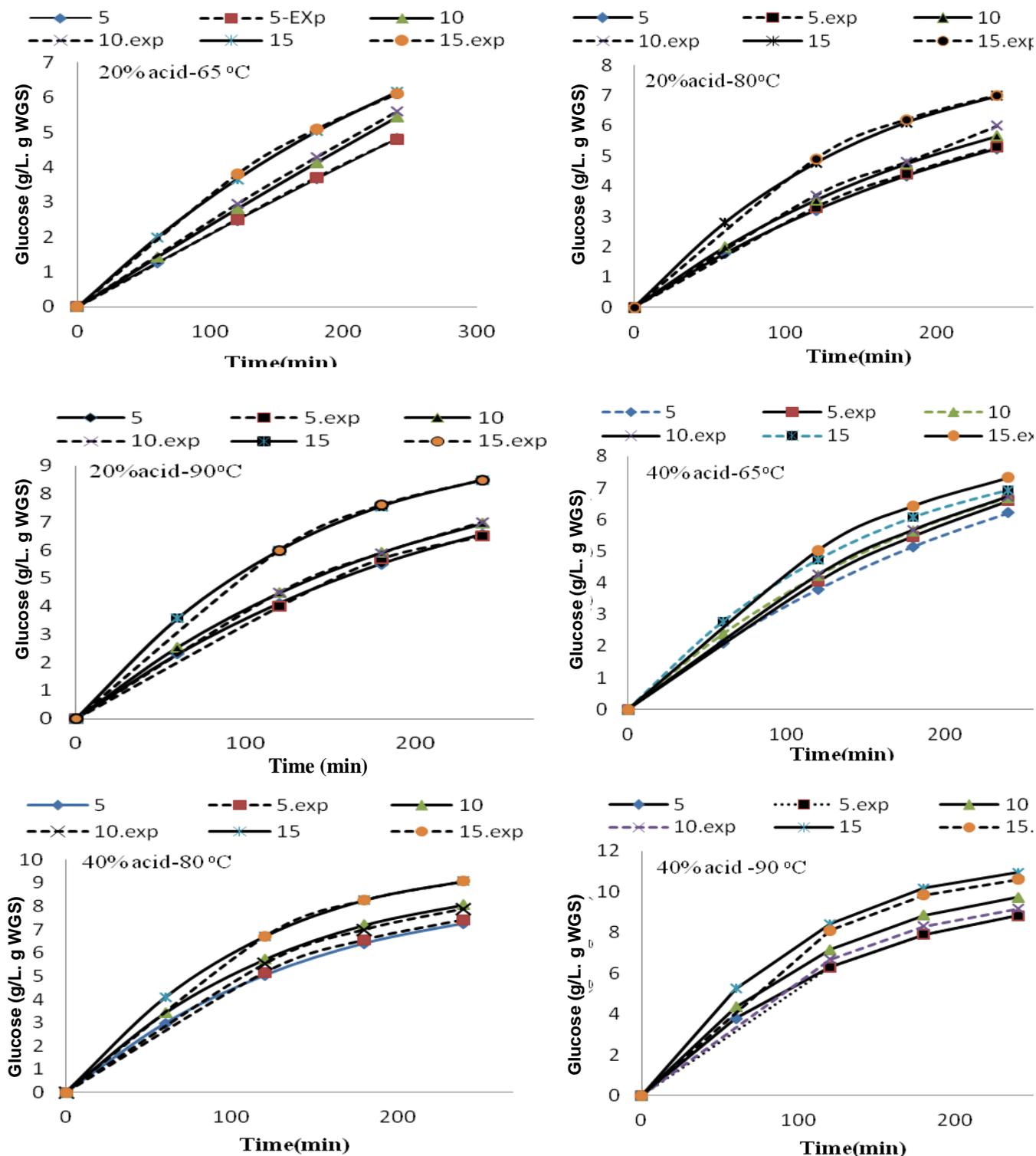


Based on the above reaction, the acetic acid concentration ( $Ac$ ) as a function of time can be calculated as follows:

$$Ac = Ac_0 (1 - \exp(-k_3 t)) \quad (10)$$

Where,  $Ac_0$  is the potential concentration of acetyl groups and  $k_3$  is the rate of acetic acid generation ( $\text{min}^{-1}$ ).  $Ac_0$  was expressed as a regression parameter. Table 5 shows the kinetic and statistical parameters obtained in the fitting of acetic acid generated in hydrolysis of WGS.  $R^2$  confirms good agreement between experimental and predicted data. According to Equation 5,  $k_0$  and activation energy could be calculated, and the results are shown in Table 6.

According to the obtained kinetic parameters ( $k_1$ ,  $k_2$  and  $k_3$ ), maximum concentration of glucose and the time that it was reached could be calculated (Levenspiel, 1999) by Equations 11 and 12. In addition the



**Figure 5.** Experimental and predicted dependence of Glucose concentration on time at several H<sub>2</sub>SO<sub>4</sub> concentration, temperature and solid contents.

concentration of acetic acid as an inhibitor could be calculated by the obtained model. Table 7 shows these results.

$$t_{\max} = \frac{\ln(k_2 / k_1)}{k_2 - k_1} \tag{11}$$

**Table 3.** Parameters obtained in the fitting using the Arrhenius equation for the Glucose released in the sulfuric acid hydrolysis of WGS.

Acid concentration (%)	Solid content (%)	$k_0(\text{min}^{-1})$	$E/R(\text{K}^{-1})$	$R^2$
20	5	7.45	3042	0.98
20	10	7.85	3030	0.98
20	15	7.96	2866	0.98
40	5	10.95	2959	0.98
40	10	10.82	2928	0.98
40	15	10.51	2830	0.98

**Table 4.** Regression parameters  $a$  and  $n$ .

Solid content (%)	$n$	$a$	$R^2$
5	0.235	6.56	0.999
10	0.637	1.955	0.999
15	1.899	0.6237	0.999

**Table 5.** Kinetic parameters and standard deviations of Acetic acid released for the sulfuric acid hydrolysis of WGS.

Acid concentration (%)	Temperature (°C)	Solid content (%)	$Ac_0(\text{g/L})$	$k_3(\text{min}^{-1})$	$R^2$
20	65	5	38.9	0.027	0.97
20	65	10	13.94	0.090	0.97
20	65	15	8.23	0.219	0.97
20	80	5	10.33	0.139	0.97
20	80	10	8.64	0.193	0.97
20	80	15	7.51	0.305	0.97
20	90	5	7.39	0.336	0.97
20	90	10	7.4	0.372	0.97
20	90	15	7.57	0.455	0.98
40	65	5	7.71	0.303	0.97
40	65	10	7.37	0.350	0.97
40	65	15	7.5	0.433	0.97
40	80	5	7.4	0.379	0.97
40	80	10	7.42	0.419	0.98
40	80	15	7.71	0.496	0.98
40	90	5	7.84	0.512	0.98
40	90	10	7.99	0.546	0.98
40	90	15	8.45	0.609	0.98
60	65	5	14.5	0.085	0.97
60	65	10	10.06	0.146	0.97
60	65	15	7.7	0.264	0.97
60	80	5	8.72	0.192	0.97
60	80	10	7.88	0.245	0.98
60	80	15	7.37	0.347	0.98
60	90	5	7.4	0.369	0.98
60	90	10	7.4	0.410	0.98
60	90	15	7.17	0.559	0.98

**Table 6.** Parameters obtained in the fitting using the Arrhenius equation for the Acetic acid released in the sulfuric acid hydrolysis of WGS.

Acid concentration (%)	Solid content (%)	Ln ( $k_0(\text{min}^{-1})$ )	$ER(K^{-1})$	$R^2$
20	5	17.2	6.68	0.89
20	10	17.1	6.58	0.90
20	15	9.71	3.81	0.96
40	5	6.84	2.68	0.90
40	10	5.55	2.25	0.94
40	15	4.16	1.7	0.94
60	5	17.11	6.59	0.98
60	10	14.14	5.47	0.98
60	15	10.58	4.07	0.92

**Table 7.** Composition of the hydrolysates obtained for the optimum conditions of each set.

Acid concentration (%)	Solid content (%)	Temperature (°C)	$t_{\max}$ (min)	Max glucose concentration (g/L)	Yield (%)	Acetic acid concentration (g/L)
20	5	65	27900	23.85	100	38.9
20	5	80	721	8.52	35.7	13.94
20	5	90	569	8.53	35.8	8.22
20	10	65	26600	23.85	100	10.33
20	10	80	639	8.22	34.5	8.64
20	10	90	504	8.22	34.5	7.51
20	15	65	548	7.93	33.3	7.39
20	15	80	360	7.46	31.3	7.4
20	15	90	347	9.03	37.9	7.57
40	5	65	587	8.89	37.3	7.71
40	5	80	365	8.01	33.6	7.37
40	5	90	335	9.27	38.9	7.5
40	10	65	513	8.41	35.3	7.4
40	10	80	356	8.44	35.4	7.42
40	10	90	319	9.508	39.9	7.71
40	15	65	377	8.02	33.6	7.84
40	15	80	308	9.33	39.2	7.99
40	15	90	285	10.72	45.0	8.45

$$C_{\max} = C_0 \left( \frac{k_2}{k_1} \right)^{k_2/(k_2-k_1)} \quad (12)$$

According to the calculation, when the acid concentration and the temperature are low, it is possible to reach 100% yields in a long time. This means that the rate of decomposition is low in those conditions.

## Conclusion

In this study, concentrated acid hydrolysis of walnut green skin was studied. For this purpose, sulfuric acid concentration, process temperature, reaction time and

solid were used in three levels as hydrolysis conditions and HPLC was used to analyze the products. Kinetic modeling of glucose as a fermentable sugar and acetic acid as an inhibitor was studied. Temperature, acid concentration and solid contents were used as independent variables in modeling of kinetic constants. These kinetic models permit the prediction of the reaction time for the maximum concentration of glucose. Typically, 40%  $\text{H}_2\text{SO}_4$  at 90°C in 285 min was selected as the best condition because in this condition, glucose concentration was calculated as 10.75 g/L and 45% of cellulose was hydrolyzed. Acetic acid concentration in this condition was estimated at 8.45 g/L by model.

**NOMENCLATURE:**  $\alpha$  = Ratio between susceptible polymer to total;  $a$  = Regression parameter;  $Ac_0$  = Potential concentration of

acetyl group;  $Ac$  = Acetic acid concentration;  $CG_0$  = Initial composition for Cellulose;  $C_{max}$  = Maximum concentration of Glucose;  $E$  = Activation energy;  $k_1$  = Rate of conversion of polymer;  $k_2$  = Rate of decomposition of monomer;  $t_{max}$  = Time for maximum concentration;  $M$  = The monomer concentration;  $n$  = Regression parameter;  $P_0$  = The polymer concentration;  $R$  = Gas constant;  $T$  = Reaction temperature;  $R^2$  = Regression parameter; WGS = Walnut green skin; WSR = Water solid ratio; g/L = gram / liter; w/w% = Percentage weight/weight; TT = Thousand ton.

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