

Monte Carlo Simulation to Study Non-Isothermal Acid Hydrolysis of Lignocellulosic Material in Ethanol Production

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Abstract—High temperature hydrolysis is one of important steps to produce lignocellulosic ethanol using chemical process. Since the heating of the reactant needs considerable time, during the heating, the reaction has started. As a result, the hydrolysis usually runs at non-isothermal condition. This research explores the use of Monte Carlo simulation to deeply study the progress of non-isothermal hydrolysis by calculating the chain length distribution of the polysaccharide at various times. The accuracy of the Monte Carlo simulation was tested by comparing the results with the ones obtained by kinetics model via simultaneous differential equations for hydrolysis of relatively short chain polymers. It turned out that Monte Carlo simulation results are in good agreement with the ones of the kinetics models. It is observed also that Monte Carlo simulation can be easily applied for long chain polysaccharide, while the kinetics model is not feasible.

Keywords—Chemical Hydrolysis, Kinetic Modeling, Lignocellulosic Ethanol, Monte Carlo Simulation, Non-Isothermal.

I. INTRODUCTION

STUDIES on lignocellulosic ethanol, one of renewable energy source alternatives for liquid transport fuels, are developing rapidly, such as study on the potential lignocellulosic raw material [1], [2], the efficient process condition [3]–[5], and the economic process condition [6], [7]. Likewise, studies on the homogeneous kinetic models of dilute-acid hydrolysis [8] as well as heterogeneous one [9], and enzymatic hydrolysis [10] have been conducted at various conditions. Commonly, the kinetic approaches describe the yield of monosaccharide, which represents the ratio of monosaccharide formed to the theoretical monosaccharide can be formed, for examples: investigation of the mechanism of acidic hydrolysis of cellulose [11]; kinetics of enzymatic hydrolysis of cellulose [10]; modeling using Monte Carlo simulation method of enzymatic hydrolysis of amilose and amylopectin of wet milled waxy, corn hybrids, and ground yellow dent corn [12]; influence of cellulose polymerization degree and crystallinity on kinetics of cellulose degradation [13]; kinetic models of xylose, glucose, arabinose, furfural, 5-

(hydroxymethyl)-2-furaldehyde and acetic acid of dilute-acid hydrolysis of wheat straw [8]. However, chain length distribution during acid hydrolysis of lignocellulosic biomass polysaccharide has not been explored. Actually, the hydrolysis of both hemicellulose and cellulose does not directly convert polysaccharides to sugars monomer but to hydrocellulose (a product with a reduced degree of polymerization) [11], [14], [15]. In addition, the kinetic models developed usually obtained from isothermal condition. According Demirbas (2008) [3], acid hydrolysis of lignocellulosic material can occur at high temperatures. In those hydrolysis, the reaction has in fact started during heating-up to the desired temperatures. So, non-isothermal kinetic model will be of importance. In the present work, we developed a simulation model of acid hydrolysis at non-isothermal condition. To be more detailed, the aim of this research was to model the chain length distribution of lignocellulosic polysaccharides during acid hydrolysis at non-isothermal condition, using Monte Carlo method. Previous study show Monte Carlo simulation can be applied in predicting chain length distribution of a number of types of chemical reactions [16]–[20]. In this study, the Monte Carlo simulation was developed based on the imagination that water molecules attack the bonds of two glucose units, so that new sugar polymer formed [11], as shown in Figure 1. In order to verify the validity of the Monte Carlo simulation, the results of the simulation of relatively short molecules were compared to the ones obtained from kinetic models (simultaneous differential equations solved by Runge-Kutta method). The Monte Carlo simulation was then applied to the hydrolysis of long molecules, where kinetic modeling via simultaneous differential equations becomes very complicated.

II. METHODS OF SIMULATION

A. Kinetic of acid hydrolysis of lignocellulosic material

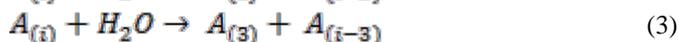
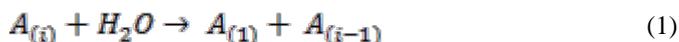
The structure of lignocellulosic material is composed of cellulose, hemicellulose, and lignin. Cellulose is crystalline glucose polymer and hemicellulose is a complex amorphous polymer. In acid hydrolysis of lignocellulosic material, the acid release protons that break the heterocyclic bonds between the sugar monomers in the polymeric chains. Accordingly, analysis of the cellulose and hemicellulose contents can be

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carried out using a quantitative acid hydrolysis under standard conditions [21] that stoichiometrically converts cellulose and hemicellulose to sugar. The sugars of the hydrolyzate solutions produced by acid hydrolysis can be analyzed using Fehling method calibrated by standard glucose solution [15]. Using those methods, the amount of sugar obtained at various time of hydrolysis and initial amount of polysaccharide can be analyzed. The amounts are usually expressed as glucose equivalent. Based on those, the conversions at various times of hydrolysis can be calculated. Most of kinetic modeling of hydrolysis assumes a pseudo one step reaction, polysaccharide to sugars. Usually, the acid hydrolysis reaction in the literatures considers a pseudo-homogeneous irreversible first-order reaction. The first model used successfully was proposed by Saeman [22] based on the hydrolysis of cellulose from fir wood using sulphuric acid catalyst. Later, the model was also applied to the hydrolysis of the hemicellulosic fraction [8], [23].

In this study, a more realistic model was applied. The acid hydrolysis of lignocellulosic material may be simplified as a consecutive depolymerization of glucose polymers as follows:



in which i is the degree of polymerization of the polymer.

It obvious that polymers $A_{(j)}$ are formed as the products of hydrolysis of longer polymers, and simultaneously degraded to shorter polymers. Assuming homogeneous reaction and the reaction is first order to the polysaccharide (the water is in excess) as well as applying material balances in batch reaction, the differential equation for polymer $A_{(j)}$ can be formulated as follows:

$$\frac{dA_j}{dt} = 2k \sum_{i=j+1}^{N_{INIT}} A_i - k(j-1)A_j \quad (5)$$

In which A_j = concentration of polymer $A_{(j)}$, k = reaction rate constant (assumed to be the same for all chain length), $j = 1, 2, 3, \dots$, N_{INIT} , in which N_{INIT} is the degree of polymerization of initial polysaccharide. Hence, the kinetics modeling results in N_{INIT} simultaneous differential equations. For large N_{INIT} (long polysaccharide) the equations became complicated. Theoretically, the degree of polymerization of cellulose depends on the type of plants, and is estimated to be from 400 to 27000 glucan units [13], [15], [24]. In this simulation, the reaction rate constant is influenced by temperature and was expressed by Arrhenius equation. In the Arrhenius equation, the activation energy of hydrolysis of lignocellulosic material of forest and agricultural biomass with 12.04 M sulfuric acid as catalyst are about 76.6 and 68.9 kJ/mol, respectively [25]. Meanwhile, the empirical equation of temperature as function

of time can be formulated based on the experimental data.

The set of equations can be solved numerically, for example by Runge-Kutta method [26], so the concentration of each polymers and monomer at various times can be obtained. In this simulation, the values of initial polymer concentration (C_0), N_{INIT} , pre-exponential factor (A), activation energy (E), reaction time (Δt) were taken to be 1 mol/L, 80, 6.10^6 min^{-1} , 80 kJ/mol, and 0.1 min, respectively, and the time dependence of the temperature is expressed as follow:

$$T = 140 + 5.55t^{0.91} \quad (6)$$

Based on the Runge-Kutta results (concentrations of monomer and polymers at various times), the total mol of depolymerization products at certain time (C_{total}), the the ratio of C_{poly} to C_0 , and the chain length distribution population (the ratio of C_{poly} to C_{total}) can be then calculated.

B. Monte Carlo simulation

In this paper, the Monte Carlo simulation was applied to the acid hydrolysis of lignocellulose polysaccharide. The algorithm was designed not only to simulate the kinetic behavior of depolymerization but also to obtain the chain length distribution. Imagination of the acid hydrolysis mechanism of lignocellulosic biomass as the basis of the Monte Carlo simulation is schematically shown in Figure 1.

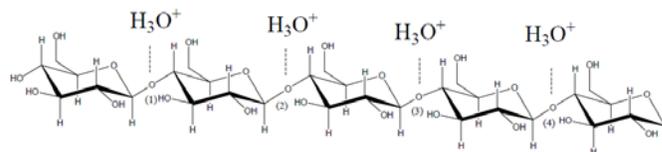


Fig. 1. Attacks of hydronium ion on cellulose molecule [11].

As mentioned previously, the reaction is imagined occurs between the inter-glucose bond and water molecule. Since the amount of water is in excess, the reaction is first order to the inter-glucose bond. It means that if the number of the bond is N_{BOND} , the number of reaction per unit of time should be equals to $k \cdot N_{BOND}$. Hence the average time interval between reactions is:

$$\Delta t = \frac{1}{kN_{BOND}} \quad (7)$$

Supposed that the initial number of the bonds is N_{BOND} , the initial average time interval follows equation (7). If the number of bonds at certain time is N , the probability of reaction in the interval Δt is:

$$P = \frac{N}{N_{BOND}} \quad (8)$$

For non-isothermal condition, the correction due to the change of k value needs to be incorporated. If the maximum value of maximum temperature is T_{max} , with the corresponding value of k be k_{max} , and the number of bonds is N_{BOND} , then the average time interval between reactions (Δt_R) can be applied

by equation (9).

$$\Delta t_R = \frac{1}{k_{max} N_{BOND}} \quad (9)$$

If the time interval chosen is Δt , the number of bonds is N and the temperature is T , with the corresponding value of reaction rate constant k , the probability of reaction in the time interval of Δt is:

$$P = \left(\frac{\Delta t}{\Delta t_R} \right) \left(\frac{k}{k_{max}} \right) \left(\frac{N}{N_{BOND}} \right) \quad (10)$$

The Monte Carlo simulation can be then developed based on equations (9) and (10). The simulation started with number of polysaccharide molecules of N_{mol0} , and the degrees of polymerization of all initial molecules N_{INIT} . The number of bonds can be easily calculated as:

$$N_{BOND} = N_{mol0} \cdot N_{INIT} \quad (11)$$

The bonds are assigned indexes $I = 1, 2, 3, \dots, N_{BOND}$. All of the bonds are then assigned status, 1 if exist and 0 if does not exist. Hence, all initial statuses are 1, except bonds of indexes of $N_{INIT}, 2N_{INIT}, 3N_{INIT}, \dots, N_{BOND}$ (status = 0). The ratio of N/N_{BOND} can be simulated by generating random integer number in the interval of 1 to N_{BOND} , say i . If bond index i exist (status = 1), reaction occurs, if does not exist (status = 0), the reaction does not occur. If bond index i reacts, its status is changed to 0. The change of status during time interval Δt can be simulated by the following steps:

1. Calculated k at the corresponding temperature.
2. Calculated $y = (\Delta t / \Delta t_R) (k / k_{max})$.
3. Generated random number γ' in the interval of 0 to 1.
4. If γ' less or equal to y , forward to step 5, else reaction does not occur, so no status change.
5. Generated random number γ'' in the interval of 0 to 1.
6. Generated random integer number i in the range of 1 to N_{BOND} using the formula: $i = 1 + \gamma'' (N_{BOND} - 1)$
7. If bond index exist (status = 1), reaction occurs and the status of the bond be changed to 0, else (status = 0) reaction does not occur.

Starting from $t = 0$, the statuses of all of the bonds at various times can be simulated. The degree of polymerization of each molecule can be then known as the number of integers between two non-existing bonds. The number of molecules with certain degree of polymerization (N_i) can be then counted. The ratio of the concentration of the molecule with degree of polymerization i to the concentration of the initial polysaccharide can be approximated as N_i / N_{BOND} . The program to conduct the Monte Carlo simulation is presented as follows.

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C      BATCH HYDROLISIS
C      NON-ISOTHERMIC
C      MONTE CARLO METHOD
C      A(J) + H2O -----> A(1) + A(J-1)
C      A(J) + H2O -----> A(2) + A(J-2)
C      A(J) + H2O -----> A(3) + A(J-3)
C      .
C      .
C      .
C      A(J) + H2O -----> A(J-1) + A(1)
C      MAY 20, 2012
C      DIMENSION ISTAT(500000),FMOL(50000)
C      DEGREES OF POLYMERIZATION OF INITIAL POLYMERS
C      NINIT=80
C      MAXIMUM (FINAL)TEMPERATURE OF REACTION, K
C      TMAX=493.
C      MAXIMUM REACTION RATE CONSTANT, MOL/L/MIN
C      TEMP=TMAX
C      CALL AKREAC(TEMP,AK)
C      AKMAX=AK
C      TIME OF SIMULATION, MIN
C      TEND=40.
C      NUMBER OF INITIAL POLYMER
C      (NMOL0*NINIT MUST BE LESS THAN DIMENSION OF ISTAT)
C      NMOL0=500
C      NUMBER OF INITIAL BONDS
C      NBOND=NINIT*NMOL0
C      MINIMUM REACTION TIME AT INITIAL CONCENTRATION, MIN
C      DELTR=1./AKMAX/FLOAT(NBOND)
C      TIME INCREMENT (DELT MUST BE LESS OR EQUAL TO DELTR)
C      DELT=0.001
C      IF (DELT .LE. DELTR) GOTO 15
C      WRITE(*,10)
C      10 FORMAT(2X,'DELT TOO LARGE, USE SMALLER DELT!')
C      GOTO 290
C      15 IF (DELT .GE. 0.2*DELTR) GOTO 20
C      WRITE(*,18)
C      18 FORMAT(2X,'DELT TOO SMALL, USE LARGE DELT!')
C      GOTO 290
C      PROBABILITY OF REACTION
C      20 PROB=DELT/DELTR
C      NUMBER OF SIMULATION STEPS
C      NSIM=INT(TEND/DELT+0.001)
C      TIME INCREMENT FOR EVALUATION
C      DELTP=5.
C      NEVAL=INT(DELTP/DELT+0.001)
C      INITIAL STATUS OF BONDS(1=EXISTED, 0=NOT EXISTED)
C      DO 30, I=1,NBOND
C      ISTAT(I)=1
C      30 CONTINUE
C      DO 40, I=NINIT,NBOND,NINIT
C      ISTAT(I)=0
C      40 CONTINUE
C      SIMULATION STARTS HERE
C      ISIM=0
C      IEVAL=0
C      INDEX OF REACTING BOND
C      50 TIME=FLOAT(ISIM)*DELT
C      TEMP=413.+5.5*TIME**0.91
C      IF (TEMP .GT. TMAX) THEN
C      TEMP=TMAX
C      ENDF
C      CALL AKREAC(TEMP,AK)
C      RATIO=AK/AKMAX
C      GAMA=RANDOM()
C      Y=PROB*RATIO
C      IF (GAMA .GT. Y) GOTO 60
C      IREAC=1+RANDOM()*FLOAT(NBOND-1)
C      IF (ISTAT(IREAC) .EQ. 0) GOTO 60
C      ISTAT(IREAC)=0
C      60 ISIM=ISIM+1
C      IEVAL=IEVAL+1
C      IF (IEVAL .EQ. NEVAL) GOTO 90
C      GOTO 50
C      90 CALL POPULATION(NINIT,NMOL0,NBOND,ISTAT,FMOL)
C      WRITE(*,250) TIME
C      WRITE(*,255)
C      WRITE(*,260)
C      WRITE(*,270)
C      TOTAL=0.
C      DO 120, I=1,NINIT
C      TOTAL=TOTAL+FMOL(I)
C      120 CONTINUE
C      DO 130, I=1,10
C      WRITE(*,280) I, FMOL(I), FMOL(I)/TOTAL
C      130 CONTINUE
C      WRITE(*,270)
C      IEVAL=0
C      IF (ISIM .LT. NSIM) GOTO 50
C      250 FORMAT (/2X, 'TIME = ', F7.2, ' MIN')
C      255 FORMAT (2X, '-----')
C      260 FORMAT(4X, 'NPOLY', 4X, ' CI/CO ', 4X, ' POP(I) ')

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270 FORMAT(4X, '-----', 4X, '-----', 4X, '-----')
280 FORMAT(5X, I4, 3X, F9.3, 6X, F6.4)
290 STOP
END

SUBROUTINE POPULATION(NINIT, NMOL0, NBOND, ISTAT, FMOL)
CALCULATING DISTRIBUTION BASED ON COUNTED NUMBER DATA
DIMENSION ISTAT(500000), JSUM(20000), FMOL(20000)
DO 640, I=1, NINIT
JSUM(I)=0
640 CONTINUE
ISTART=0
DO 700, I=1, NBOND
IF(ISTAT(I).EQ. 1) GOTO 700
IEND=I
NPOLY=IEND-ISTART
JSUM(NPOLY)=JSUM(NPOLY)+1
ISTART=IEND
700 CONTINUE
DO 720, I=1, NINIT
FMOL(I)=FLOAT(JSUM(I))/NMOL0
720 CONTINUE
RETURN
END

SUBROUTINE AKREAC(TEMP, AK)
AK=6.E6*EXP(-80000/8.314/TEMP)
RETURN
END

```

III. RESULTS AND DISCUSSION

The results of Monte Carlo simulation are compared to the ones of differential equation approach solved by Runge-Kutta method, for relatively short chain initial molecules ($N_{INIT} = 80$), in which differential equation approach is still feasible. The simulation run at initial concentration, $C_0 = 1$ mol/L, Arrhenius parameters of pre-exponential factor = 6.10^6 min^{-1} , and activation energy = 80 kJ/mol, temperature formula as a function of time (min), $T \text{ (K)} = 413 + 5.5t^{0.91}$. The Monte Carlo simulation used $N_{mol0} = 500$. The results are shown in figures 2 and 3. From those figures, it can be seen that the Monte Carlo simulation produces close approximates compared to the differential equation approach. It was observed also that differential equation approach was not feasible for relatively long chain initial molecules (degree of polymerization of more than 1000), since it took relatively long time to be conducted in an ordinary personal computers. Meanwhile, the Monte Carlo simulation can be still feasible for relatively long chain molecule (tried to be run up to $N_{INIT} = 100000$).

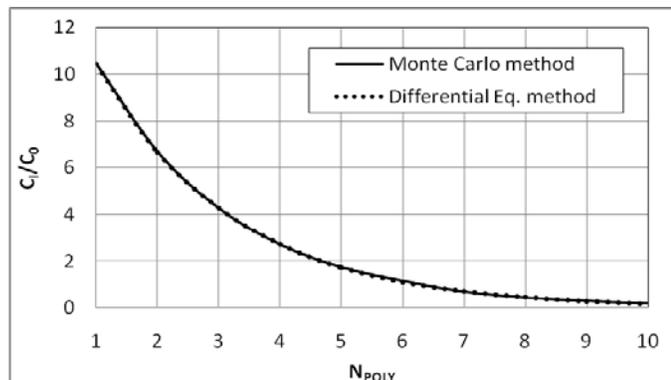


Fig. 2. The chain length distribution of acid hydrolysis of lignocellulosic material by the kinetic model via simultaneous differential equations (spotted line) as well as the Monte Carlo method (solid line) at reaction time of 35 min.

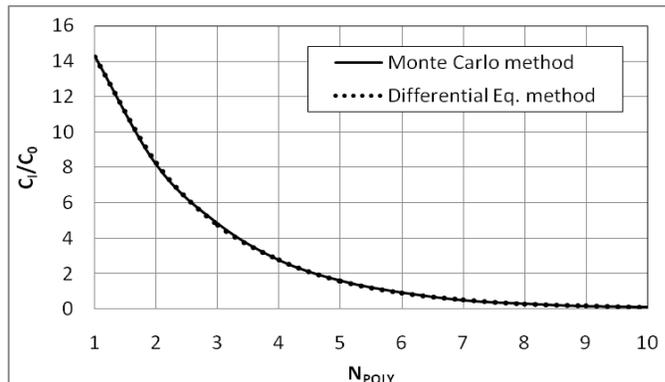


Fig. 3. The chain length distribution of acid hydrolysis of lignocellulosic material by the kinetic model via simultaneous differential equations (spotted line) as well as the Monte Carlo method (solid line) at reaction time of 40 min.

The results of Monte Carlo simulation for $N_{INIT} = 1000$, $N_{mol0} = 500$, initial concentration, $C_0 = 1$ mol/L, Arrhenius parameters of pre-exponential factor = 6.10^6 min^{-1} and activation energy = 80 kJ/mol, temperature formula as a function of time (min), $T \text{ (K)} = 413 + 5.5t^{0.91}$ are presented in figure 4. It can be seen that the Monte Carlo simulation results at relatively long chain initial molecules are conceivable.

The conversion to sugars can be obtained easily computed from the simulation results. For example, if the laboratory chemical analysis detects the amount of sugars in the form of monosaccharides and disaccharides expressed as glucose equivalent (say N_1 moles), as well as the initial amount polysaccharides (say N_0 moles), the conversion is usually calculated as $x = N_1/N_0$. The simulated conversion can be easily calculated as: $x = (\text{number of monosaccharide} + 2 \text{ (number of disaccharide)})/N_{BOND}$. Comparison of the Monte Carlo simulation results and the relevant experimental data can be used to evaluate the more realistic kinetics model and their more fundamental parameter. The currently available parameters are usually obtained from simple kinetics models assuming pseudo direct reaction from polysaccharide to sugars. For example, the research of dilute-acid hydrolysis of Lantana camara with condition of concentration acid as catalyst of 1% v/v, reaction time of 45 min, and temperature of 140 °C, the sugar yield obtained of 16,29%. Likewise, for biomass of olive tree with condition of concentration acid as catalyst of 1% v/v, reaction time of 10 min, and temperature of 180 °C, the sugar yield obtained of 26,23% [27]. This sugar yield number calculated with the Monte Carlo method is about 16% and 26% for Lantana camara and olive tree biomass, respectively, with the values of degree of polymerization of 400-825 [24] and the activation energy of 80 kJ/mol [25]. The more realistic models are expected to enable deeper understanding of the reaction as well as to give more accurate quantitative information to support the design of equipment for industrial scale. Monte Carlo simulation can also be modified to more complicated mechanisms of hydrolysis, for example by considering degradation of sugars, as well as the present of several types of sugars.

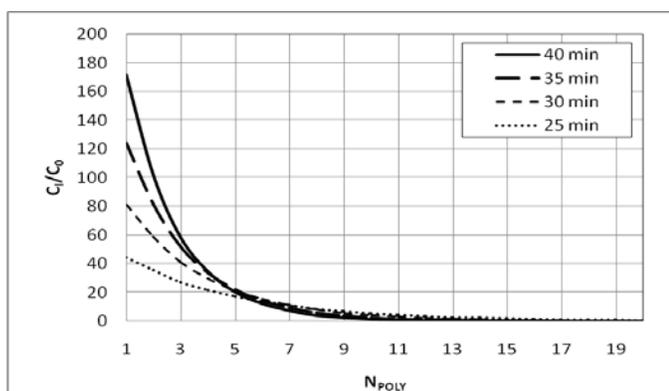


Fig. 4. The chain length distribution of acid hydrolysis of lignocellulosic material at non-isothermal condition by the Monte Carlo method at initial degree of polymerization (N_{INIT})=1000, initial number of molecules (N_{mol0})=500, at various times of reaction.

IV. CONCLUSIONS

The Monte Carlo simulation successfully simulated to predict chain length distribution of polysaccharides in acid hydrolysis of lignocellulosic biomass for ethanol production. For initially low degree of polymerization polysaccharide, in which kinetics modeling via simultaneous differential equations is still feasible, the Monte Carlo simulation results are in good agreement with the ones from kinetics model via simultaneous differential equations, as well as with the experimental data obtained by another researcher. Likewise, at initially high degree of polymerization polysaccharide (tried up to 100000), the Monte Carlo simulation is still applicable, whereas the simultaneous differential equation approach is not feasible.

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