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Thermodynamic Consideration of Hydrolysis of Cellulose to Glucose Under Liquid to Semiliqid Conditions

Prajakta P. Mane
Department of Chemical Engineering, Sinhgad College of Engineering, Pune, Maharashtra, India.

Sanjay M. Chavan
Department of Chemical Engineering, Sinhgad College of Engineering, Pune, Maharashtra, India.

Abstract — There is increase in awareness for deriving energy from renewable sources like biomass. Biomass contains lignin, cellulose, hemicellulose and lignocellulose. These basic carbohydrates can be converted into glucose molecules (as source of energy or fuel) or to other useful products. This can be achieved either by pyrolysis or degradation (by hydrolysis). In this study, we have considered glucose as monomer and all other constituents as polymer of glucose molecule, hence cellulose conversion to glucose is considered as depolymerisation of cellulose for n = 500 to n = 2. For cellulose it can range from few thousands. In this study, when thermodynamic principles(as derived from depolymerisation theory) are applied values of diffusivity found are in the unrealistic range for e.g. n = 5000 and diffusivity around 10-13 m2/sec, while for n = 500 to n = 2 realistic values of diffusion coefficient (10-7m2/sec) are obtained.

Keywords: cellulose; hydrolysis; depolymerisation; glucose.

I. INTRODUCTION

There is increase in awareness for deriving energy from renewable sources like biomass. Biomass contains lignin, cellulose, hemicellulose and lignocellulose. These basic carbohydrates can be converted into glucose molecules (as source of energy or fuel) or to other useful products. This can be achieved either by pyrolysis or degradation (by hydrolysis). There are two types of hydrolysis, one is enzymatic and another one thermal.

Hydrolysis break down food and chemicals that are needed for the body and takes out the nutrients needed for proper functioning of the body. Hydrolysis of cellulose by cellulolytic enzymes has been investigated during current years with the objective of developing a process for production of sugars (glucose and cellobiose). [1] At present modelling of enzymatic hydrolysis of lignocellulose in almost certainly one of the most challenging subjects in (bio) reactor engineering science. [2] Enzymatic hydrolysis of cellulosic materials to manufacture reducing sugars has been pursued food and it is probable for providing plentiful food and energy resources. Enzymatic hydrolysis is becoming a more and more important process because of increased demand for biofuel. Bioethanol production from plentiful and renewable lignocellulose biomass is a capable option to fossil fuel. [3] Hydrolysis is the breakdown of complex nutrients into smaller ones. When adding of water molecule to carbohydrates, proteins or fats break it down into smaller molecules depending on its base. This is very important because without hydrolysis then the nutrients from the food we eat would not be able to be absorbed by our small intestine and we would not be able to make energy. To produce bio ethanol from lignocellulose three steps are of major importance are as below [4]

1) The pre-treatment, in which the raw material is treated with high pressure steam and SO2 to make cellulose accessible to enzymatic hydrolysis.
2) The SSF (simultaneous saccharification and fermentation), in which cellulose is hydrolysed to glucose and fermented to ethanol by yeast and
3) The distillation, in which the ethanol is recovered.

A. Lignocellulose

Lignocellulosic biomass is the most abundant material on the Earth. Its sources including raw materials like agricultural residues (e.g. corn and wheat straw), forestry residues (e.g. sawdust and mill wastes), and municipal solid waste (e.g. waste paper) and various industrial wastes have a great potential to be used in the industrial processes. Lignocellulose is the collective name for the three main components of plant material namely cellulose, hemicellulose and lignin. Hemicellulose provides bonding between cellulose and lignin.

II. HYDROLYSIS

Hydrolysis is a cleavage of chemical bonds by the addition of water. In this process carbohydrate is broken into its component sugar molecules. Generally, hydrolysis or saccharification is a step in the degradation of a material. The reaction mainly occurs between ion and water molecule and they often changes the pH of solution. Under the standard conditions, a few reactions between water and organic compounds take place. The acid or base is considered a catalyst. They are meant to speed up the reaction, but are recovered at the end of it.

Hydrolysis is a chemical process in which a sugar molecule is split into two parts by the addition of a molecule of water. One part of the parent molecule gains a hydrogen ion (H^+) from the additional water molecule. The other group collects the remaining hydroxyl group (OH^-).

It is type of reaction that is used to break down certain polymers, especially those made by step growth polymerization. Such polymeric degradation is usually catalysed by either acid, for e.g. concentrated sulphuric acid (H_2SO_4).

A. Types of Hydrolysis

a) Acid hydrolysis (Traditional method)

In this method concentrated acid is used for hydrolysis of cellulose under high temperature and pressure. This method is not preferred by biofuel industry because they produce toxic by-products that are remaining in fermentation step by affecting the fermenting bacteria/yeast. Acid hydrolysis is faster acting reaction that requires much less residence time.

b) Enzymatic Hydrolysis

Enzymatic hydrolysis of pre-treated lignocellulose materials represents the most useful method to produce simple sugars. Compared to acid hydrolysis, enzymatic hydrolysis is more capable with milder separating conditions, which gives better sugar yield. Enzymatic hydrolysis of pre-treated lignocellulose materials involves enzymatic reactions that convert cellulose into glucose and hemicellulose into pentose and hexoses. [5]

Enzymatic hydrolysis of cellulose into sugar is one of the most expensive steps in biofuel production depending on the cost of enzymes. Enzymes should be successfully used in the hydrolysis, but there are number of obstacles which affect the enzyme performance.

Enzymes are macromolecules that help to accelerate chemical reactions in biological system. Some biological reaction in absence of enzymes may be slower. The most notable characteristic of enzymes is their specificity for a particular material.

In enzymatic hydrolysis processes, there are some important phenomena that finally control the overall rates of reaction. The overall reaction rate that is determined by the three events occurring in sequences are; [5]

- The rate of the mass transfer of the enzymes.
- The rate off diffusion of the enzymes on the substrate surface.
- The rate of the cellulose catalytic action.

In general established mechanism of cellulase system on crystalline cellulose, Endo-glucanases hydrolyses internalβ-1, 4-glycosidic bonds of the amorphous regions, thereby increasing the number of exposed non-reducing end. Exo-glucanases that are cleaves of cellobiose units from the non-reducing end, which in turn is hydrolysed to individual glucose units by β-glucosidases. Cellulase, however have been found to be more disposed to hydrolyse the amorphous region of cellulose. The result was that a linear relation between crystallinity and hydrolysis rate exists whereby higher crystallinity indices that corresponds to slower enzyme hydrolysis rate.

III. THERMODYNAMIC CONCEPTS APPLIED TO HYDROLYSIS

Enzymatic hydrolysis of cellulose is performed by several different enzymes, cellulases. Three distinct classes of cellulases have been found

The endo-glucanases, which act randomly on soluble and insoluble cellulose;

The exo-glucanases, which includes both cellubiohydrolases and glucohydrolases, act on the non-reducing end of cellulose. The former release cellobiose and the later glucose; and

The β-glucosidases act on cellobiose and cellodextrins releasing single glucose units. [3]

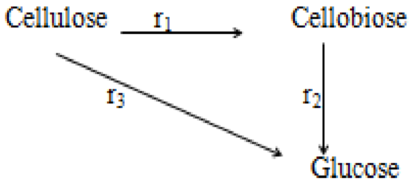

Fig. 1. Endo-glucanases (1), Exo-glucanases (2), and β-glucosidase (3).

The rate of the hydrolysis reactions are influenced greatly by characteristics of the raw material such as degree of polymerization.

Due to the difficulty of finding a strict mechanism for hydrolysis reactions of hemicellulose, simplified models are commonly used to determine the rate of the hydrolysis biomass. [6]

$$M = M_0 e^{-k1t} + \alpha P_0 (k_1/k_2\text{-}k_1)(e^{-k1t} - e^{-k2t}) \qquad (1)$$

M concentration of monomer

P concentration of polymer

Subscript 0 indicates initial conditions

k_1 is rate constant of first step in hydrolysis reaction.

$$k_1 = e^{(\frac{-E_{\sigma 1}}{RT})} \qquad (2)$$

k_2 is rate constant for second step in hydrolysis reaction.

$$k_2 = e^{(\frac{-E_{\sigma 2}}{RT})}$$

t is needed for simplified model for calculating hydrolysis time. [6]

$$t = \frac{1}{k_1}\left(\frac{\alpha P_o}{\alpha P_o - M}\right) \qquad (3)$$

This t is used for calculation of severity factor. [6]

This is proposed model to predict the concentration of monomers respectively.

From rate constant reaction rates are calculate.

$$-r_A = k * C_A * C_E \qquad (4)$$

r_A is reaction rate. C_E is enzyme concentration.

Diffusion coefficient obtained from

$$D_{AB} = \frac{-r_A * z^2 + r_A * L^2 * z}{(C_A - C_A * z + C_{AO} * z) * 2} \qquad (5)$$

By using the calculated diffusion time in the severity factor would take some important characteristics of biomass into consideration and enable the optimisation of important aspects of reaction. [6]

The proposed severity factor:

$$R = \frac{t}{\frac{\rho * (r) * (1 - 0.\sin(\phi))}{2 * M * \phi * D * \Delta C}} * e^{\frac{T - 100}{14.75}} * 10^{-pH} \qquad (6)$$

t is hydrolysis time, T is temperature , ρ is density, Φ void fraction (0.29).

$\frac{\rho * (r) * (1 - 0.\sin(\phi))}{2 * M * \phi * D * \Delta C}$ is time needed for diffusion.

IV. Result and Discussion

Polysaccharides are synthesized by plants, animals and humans to be stored for food, structural support, or metabolized for energy. Cellulose is polysaccharides made up of glucose monomers, and is the most abundant organic polymer on earth. Cellulose shows strong crystalline resistance to hydrolysis.

As number of molecules of glucose increase the hardness, crystallinity, imperviousness of molecule increases for e.g. breaking lignin, lignocelluloses and hemicelluloses into glucose need from days to years under normal conditions. Even with harsh acidic conditions it is reported to take many hours. The percentage of these high polymeric constituents varies with their source. Thus, the conditions for treatment also vary with the source. Practically it has been found to be difficult to consider all such conditions into one/unique process condition to convert them completely into desired products. It has also been found to be difficult to model these conditions into one unique model. Literature is replete with base empirical models.

In this study all other constituents of biomass are considered as polymers of glucose. n is the number of glucose molecules (degree of polymerisation of polymer). Rate constant is depending upon n (degree of polymerisation). If degree of polymerisation of cellulose is decreases rate constant increases. And rate of product (Glucose) is increases.

The extent of carbohydrate chains is among the important factor that extremely affects the hydrolysis. The severity coefficient of such cellulose chain is larger and more difficult to hydrolyse. Larger the cellulose chains, the accessibility to react with derivatives of sugar is low which lower hydrolysis yield.

A. Diffusion coefficient Vs Number of moles

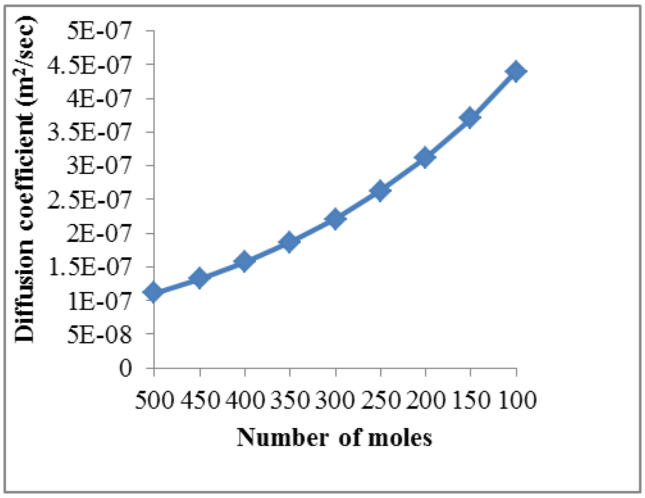

Fig. 2. Diffusion coefficient Vs Number of moles

Here graph represent, as numbers of moles are decreases diffusion coefficients increase. Decreasing surface area affects the diffusion of the molecule. Increase in diffusion coefficient helps to break the hydrogen bonds in cellulose chain. This is improves the hydrolysis of the reaction. This is because of increased susceptibility of the cellulose to hydrolysis. This decreases cellulose degree of polymerization.

B. Severity Parameter vs Number of Moles

The severity parameter factor is important for hydrolysis. This parameter facilitates the combined effects of temperature, time and concentration.

Severity factor combine time, temperature and a simply acidity function such as pH. The severity factor combines the treatment temperature (T) and residence time (t) in one value and provides an approximate indication of the hydrolysis. The ability of the severity parameter to relate performance at different times, temperature and concentration level is very valuable for selecting process condition.

The reaction ordinate (severity parameter) has proven to be extremely useful in sugar release from complex cellulosic material. The initial rate of hydrolysis was shown to be linearly correlated with the degree of polymerization.

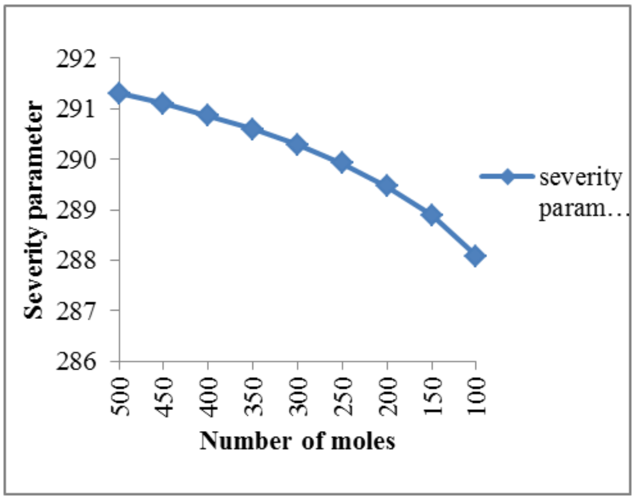

Fig. 3. Severity Parameter Vs Number of Moles

Here graph shows that how the severity parameter is affected by degree of polymerisation.

Under hydrolysis conditions, the degree of polymerisation has been found to change sustainability.

The severity parameter assumes a constant pH during hydrolysis. The severity parameter concept to provide a single reaction ordinate, denoted as (R) that could combine time and temperature in single parameter related to the changes in concentration of monomers in cellulosic material during hydrolysis.

This discussion indicates that the crystallinity is a factor in digestibility of celluloses. However, it is not the only factor in hydrolysis of these materials, due to the heterogeneous nature of celluloses and the contribution of other components such as lignin and hemicellulose.

The specific surface area per gram of substrate sharply increases during the initial stage. However, the cellulose surface area is not a major limiting factor for hydrolysis of pure cellulose. Hydrolysis slow down in the later stages is not due to a lack of surface area, but to the complexity in hydrolysis of crystalline part of cellulose.

V. CONCLUSIONS

As mentioned earlier the glucose is considered as a constituent monomer of biomass, with n as a no of monomer units. For values of n above a peculiar value applicability of the thermodynamic concepts is observed to fail probably because of the reasons as under,

For higher values of n the polymer of glucose is in the form of hard solid material. As value of n decreases this solid form gets transformed from hard solid material to soft solid material to semisolid material to viscose material to semi viscose materials to semi liquid and then ultimately into liquid form.

The thermodynamic concepts (as applicable) for polymerization and depolymerisation are applicable strictly for liquid phase.

When we applied these concepts for above treatment for n more than 500, it gives unrealistic values of diffusion coefficient.

Probably beyond these values of n the polymers of glucose are not in liquid or semi-liquid state.

Thus the basics of thermodynamics as brought from polymerization and depolymerisation seem to be applicable only when n is less than a threshold value at which they are in either semi liquid or liquid state.

Above this threshold value entirely new approach from thermodynamics needs to be investigated.

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