Kinetics and Mechanism of the Decomposition of Cellulose and Cellulose Model Compounds in Sub and Supercritical Water(亜臨界・超臨界水中におけるセルロースおよびセルロースモデル化合物の分解速度および反応機構に関する研究)

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論文内容要旨

Biomass in the form of wood comprises of 150 x 10^9 tons of forests, which are one-third of the land on Earth. Of this, 1.3 x 10^9 tons of wood are harvested annually. This makes biomass a widely available renewable resource if it can be converted to useful chemicals like sugars and alcohols. 40 - 60% of wood is comprised of cellulose which makes cellulose is an important model compound for biomass. From literature survey, it is known that cellulose will decompose under acidic, alkaline and neutral conditions via the formation of oligosaccharides and glucose. A detailed study has been made on the decomposition of cellulose under acidic and alkaline conditions, however such a study has not been conducted under neutral conditions and at high temperatures and short residence times.

In this dissertation, a detailed study was conducted on the decomposition of cellulose and its model compounds such as cellopentaose, cellotriose and cellobiose in subcritical and supercritical water. Glucose decomposition at similar conditions was also studied because it is known to be an important intermediate compound of cellulose decomposition. The aim of this study was to elucidate the reaction pathways, kinetics and mechanism of the decomposition of these compounds which would model cellulose decomposition giving us information on the cellulose decomposition pathways and mechanism. The temperature studied was 300-400 °C, pressure of 25 - 40 MPa and residence time of between 0.02 and 2 seconds. The main chapters of this research are as follows: In **Chapter 1** is the introduction which also explains the objectives of this study.

In **Chapter 2,** the literature review on the previous work related to this study.

Chapter 3 Degradation Kinetics of Dihydroxyacetone and Glyceraldehyde in Sub and Supercritical Water

The motivation behind this study was the need to elucidate the decomposition pathway and mechanism and evaluate the kinetics of glucose decomposition. Glyceraldehyde and dihydroxyacetone are known to be decomposition products of glucose and so their reaction pathways and kinetics were used in obtaining the information on glucose decomposition. The experimental setup which was used for these and other water soluble compounds is shown in Figure 1. Distilled water which was fed by pumps, 1 and 2, was preheated above the

reaction temperature and mixed at the tee joint with the aqueous solution of the reactant fed by pump 4, at room temperature. At a distance from the mixing tee, a chromel-alumel thermocouple was set to measure the mixture temperature. The mixture then passed through the stainless steel reactor which was immersed in a heated molten salt bath kept at the reaction temperature to assure constant temperature throughout the reactor. At the end of the reactor, the reactant mixture was cooled directly by water at room temperature and indirectly via a water jacket, to assure quick quenching of the reaction temperatures. The mixture then passed through a back pressure regulator which controlled the system pressure, and was finally collected in a sampling vessel for analysis by HPLC. The residence time was fixed by setting a constant flow rate (g/min) for both the preheated water and the aqueous solution. The flow rate was corrected by considering the corresponding density (assuming pure water) at the reaction temperature and pressure giving the actual flow in mL/min. Using this flow rate and the reactor volume which was calculated from the known reactor tube diameter and reactor length, the residence time could be calculated. The residence times could therefore be altered by changing the reactor length.

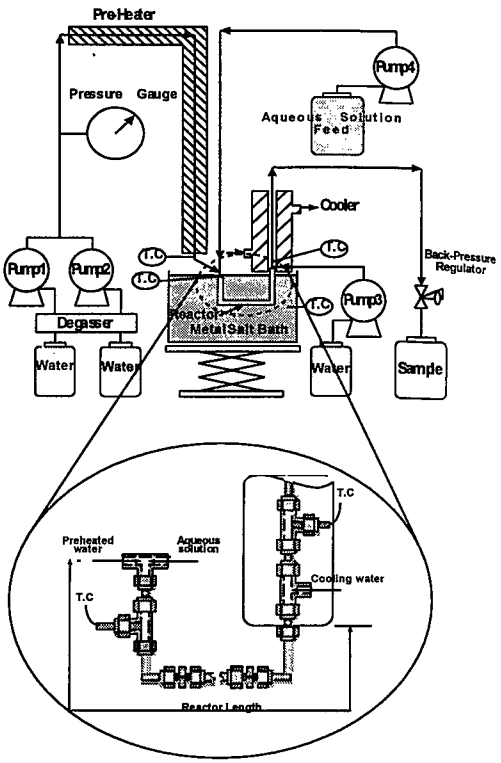

Figure 1 Experimental setup for water soluble reactants

The reactions of glyceraldehyde gave both dihydroxyacetone and pyruvaldehyde and yields of dihydroxyacetone were always higher than those of pyruvaldehyde. The reactions of dihydroxyacetone gave glyceraldehyde and pyruvaldehyde while the yields of pyruvaldehyde were always higher than those of dihydroxyacetone. This pathway involves the reversible isomerization between glyceraldehyde and dihydroxyacetone and their subsequent dehydration to pyruvaldehyde. A model was formulated on the basis of this pathway and the kinetic rate constants involved calculated using the experimental results. As the conditions changed from subcritical to supercritical, the Arrhenius relationship became discontinuous near the critical point of water. At the temperature of 400 ^{o}C, the kinetic constants showed a general increase with increase in pressure.

Chapter 4 Reaction Pathway and Kinetics of Glucose Decomposition in Sub and Supercritical Water

In this chapter, the aim was to elucidate the detailed decomposition pathway and mechanism of glucose and evaluate the kinetics. The experiments were performed in the same reactor shown in Figure 1. The products of glucose decomposition were fructose, a product of isomerization, 1,6 anhydroglucose, a product of dehydration, erythrose and glyceraldehyde, products of C-C bond cleavage. In order to elucidate the detailed reaction pathway, separate experiments were performed on the products fructose, erythrose and 1,6 anhydroglucose. Fructose underwent similar reactions as glucose except that it did not form 1,6 anhydroglucose and isomerization to glucose was negligible. 1,6 anhydroglucose and erythrose decomposed to form mainly acetic and formic acids. Results from Chapter 3 were incorporated and this led to the pathway shown in Figure 2. The mechanism for the

products formed from the C-C bond cleavage could be explained by reverse aldol condensation and double bond rule of the respective intermediates formed during the Lobry de Bruyn Alberda van Ekenstein transformation which is responsible for the glucose to fructose isomerization. The differential equations resulting from the proposed pathways were fit to experimental results to obtain the kinetic rate constants. A high selectivity towards the formation of erythrose from 50 to 77 mole% basis was observed when the conditions changed from 350 °C, 25 MPa to 400 °C 30 MPa respectively. This may lead to the development of a continuous process for the manufacture of erythrose. Erythrose can be reduced by hydrogenation over platinum catalyst to yield erythritol, a food sweetener which is toothfriendly, safe for diabetics and has a low calorific value (0.3Kcal/g). At supercritical conditions of 400°C, glucose decomposition rate was found to decrease with increasing in pressure. This is also important considering the fact that cellulose shows high hydrolysis rates in the supercritical conditions, and a maximization of glucose yield may be achieved.

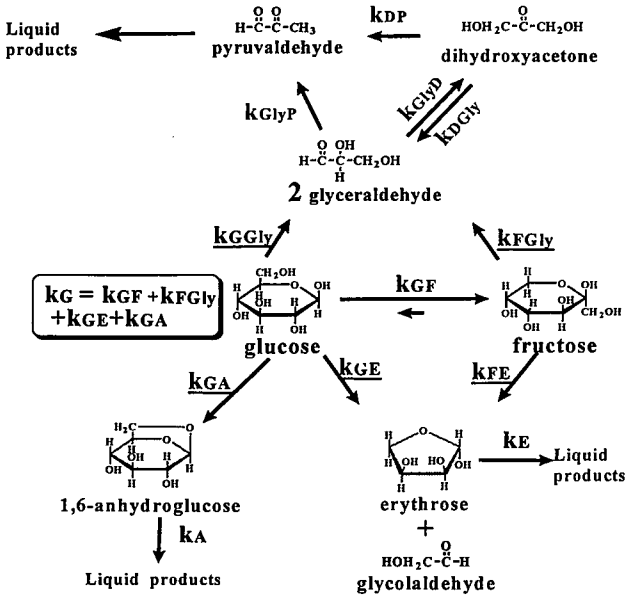

Figure 2 Glucose decomposition pathway

Chapter 5 Mechanism and Kinetics of Cellobiose Decomposition in Subcritical and Supercritical Water

Cellobiose is a disaccharide of glucose linked by β(1-4) glycosidic bonds similar to cellulose which makes it an important model compound of cellulose. The study in this chapter was to elucidate the decomposition pathways and mechanism and evaluate the kinetics of cellobiose decomposition in sub and supercritical water. The reactor used is that shown in Figure 1. The decomposition pathway is shown in Figure 3. Cellobiose was found to decompose via hydrolysis of the glycosidic bond and via pyrolysis of the reducing end. Pyrolysis products were glycosyl-erythrose (GE) and glycosyl-glycolaldehyde (GG) which were confirmed by FAB-MS. Hydrolysis products were glucose, erythrose and glycolaldehyde from cellobiose, GE and GG. respectively as well as glucose decomposition products. The mechanism of pyrolysis of cellobiose was via the ring opening of the reducing end followed by its reverse aldol condensation The differential equations from the

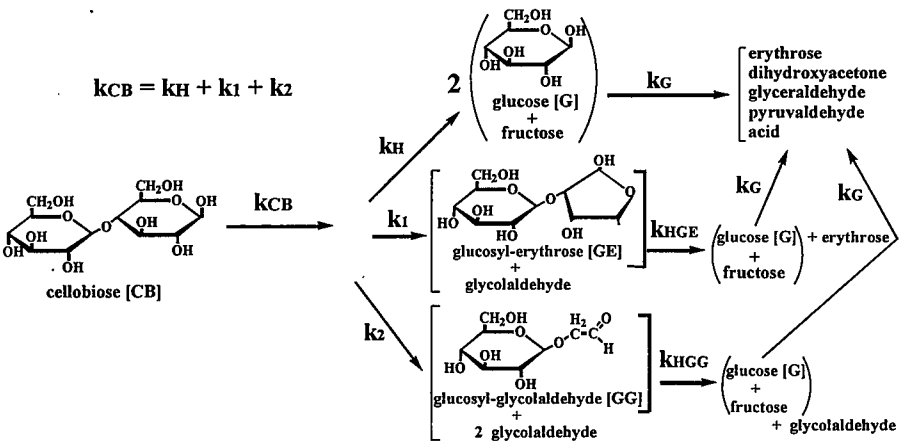

Figure 3 Cellobiose decomposition pathway

reaction pathway in Figure 3 and the kinetics from glucose decomposition in Chapter 4 were used to fit the experimental results and evaluate rate constants of hydrolysis (k_H) and pyrolysis rate constants (k_1, k_2). In the supercritical region, at 400 °C, there was a decrease in the pyrolysis rates and a corresponding increase in hydrolysis selectivity by 10% as the pressure increased from 30 to 40 MPa.

Chapter 6 Monte Carlo Simulation of Cellulose and Cellulose Model Compounds Decomposition in Subcritical and Supercritical Water

In this Chapter, the reaction pathway obtained for cellobiose in Chapter 5 was assumed for the decomposition of the model compounds cellotriose and cellopentaose. The resulting pathway was difficult for solving by differential equations and the Monte Carlo simulation was used. The kinetics for cellobiose and glucose decomposition from the previous Chapters 4 and 5 were used in the Monte Carlo simulation. The hydrolysis rate was evaluated which resulted in a good prediction of cellotriose and cellopentaose decomposition products. The hydrolysis rate was found to decrease with increase in the degree of polymerization of the reactant. This may be due to the structural conformation of the reactant at different reaction conditions in which steric hindrance and inductive effects play a role. The final work in this Chapter was the cellulose slurry experiments. The setup is similar to that of Figure 1, the difference being the slurry pump in place of the aqueous solution pump. The slurry pump was able to supply to the inlet of the reactor a constant concentrated slurry of up to 2 wt%. Results show that the conversion rate was extremely high in supercritical water with very high selectivity towards hydrolysis of the glycosidic bonds. HPLC analysis of the liquid sample show that cellulose decomposes via oligosaccharides such as cellopentaose, cellotriose, cellobiose, glucose and its decomposition products. The Monte Carlo simulation was therefore applied to predict the product distribution of cellulose decomposition by using the decomposition pathway of cellobiose, the kinetics from the previous Chapters 4 and 5 and the hydrolysis rates evaluated in this chapter for cellotriose and cellopentaose. The results of the simulation are shown in Figure 4. An analysis of the results shows that though the order of magnitude of the prediction is close to the experimental results, an accurate prediction was not possible. This is may be attributed from the fact that: 1) the kinetics evaluated earlier were for homogeneous type reactions and therefore may not be accurate for reactions occurring in cellulose slurry. 2) the density used is that of pure water while the 1wt% cellulose slurry entering the reactor has a higher density which results in an error in our residence time calculations 3) Heat and mass transfer limitations occurring at the mixing point have not been accounted for in the simulation.

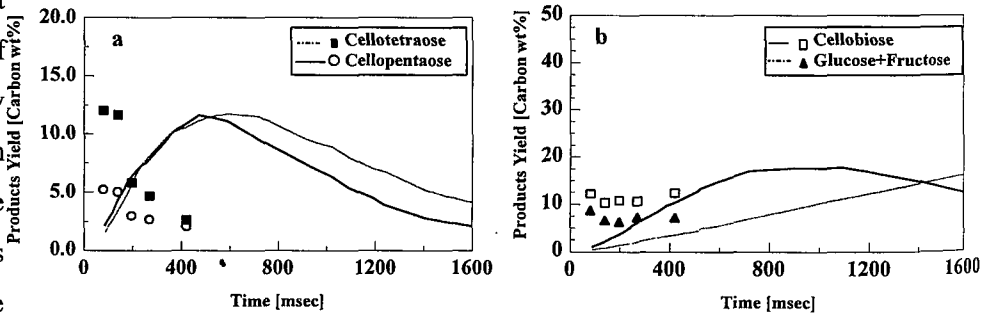

Figure 4 Monte Carlo simulation of cellulose decomposition products in supercritical water a) cellotetraose and cellopentaose b) cellobiose and (glucose + fructose)

In **Chapter 7**, the main conclusions of this work were summarized.

審 査 結 果 の 要 旨

セルロースはこの地球上で最も大量に生産されるバイオマスで、化石燃料に代る再生可能な資源として極めて重要なものである。

本論文は、セルロースの工業原料への効率的な変換プロセスの開発を目的とし、亜臨界および超臨界水中でのセルロースおよびそのモデル化合物の分解反応実験を行い、その反応機構の解明と分解速度の定量化を行ったもので、全編7章よりなる。

第1章は緒論であり、本研究の背景と目的を述べている。

第2章では、本研究に関連した既往の研究を調査し、本研究の方針を明確にしている。

第3章では、グルコースの一次熱分解生成物であるグリセルアルデヒドとその異性体であるジヒドロキシアセトンの亜臨界・超臨界水中での分解実験を行い、その反応の経路と機構を明かにし、各反応経路の速度定数を決定した。

第4章では、グルコースとフラクトース及びグルコースの分解生成物であるエリスロースと1、6アンヒドログルコースの亜臨界・超臨界水中での分解実験を行い、グルコースの分解反応経路と機構を明かにした。グルコースとフラクトースの異性化反応機構を詳細に検討した結果、エリスロース、グリコアルデヒド、グリセルアルデヒドの生成はこの異性化反応過程の中間体の分解反応から説明が可能なことを見い出した。さらに、生成物分布の解析からエリスロースを高収率で得られる条件を見い出し、グルコースを原料としたエリスロースの高速連続製造プロセスの提案を行った。第3章の結果と併せて、得られた各反応経路の速度定数を用いることにより、グルコース分解生成物分布の予測を可能にした。

第5章では、セルロースオリゴマーの二量体であるセロビオースの亜臨界・超臨界水中での分解実験を行い、その反応の経路と機構を明かにした。セロビオースの分解は前章の結果に加えてグルコシド結合の加水分解によるグルコースの生成と還元末端の熱分解によるグリコシルエリスロース、グリコシルグリコアルデヒドの生成と、さらにこの二つの熱分解生成物の加水分解によるグルコースとエリスロース、グリコアルデヒドの生成を新たに考慮することにより、定量的に生成物分布を予測しうることを示した。

第6章では、セロトリオース、セロペンタオース、セルロースの亜臨界・超臨界水中での分解実験を行い、その結果を用いてモンテカルロシミュレーションによる生成物分布の相関を試みた。セロトリオース、セロペンタオースについては、各々の加水分解速度定数のみをフィッテングパラメータとすることにより、生成物分布を予測しうることを示した。一方、セルロースについては、6量体以上のオリゴマー等の高分子量側の生成物の分析の困難さや反応中の相変化の様相が未確定のため、定量的な相関結果は得られなかった。

第7章は総括である。

以上要するに本論文は、セルロースの変換プロセスの開発を目標に、亜臨界および超臨界水中でのセルロースおよびそのモデル化合物の分解反応実験を行い、その反応機構の解明と分解速度の定量化を行ったもので、化学工学及び化学工業の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。