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CONVERSION OF SECONDARY PULP AND PAPER SLUDGE TO GLUCOSE BY HYDROTHERMAL TREATMENT

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A Thesis Submitted in Partial Fulfillment of the Requirements
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อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. ธวัชชัย ชรินพาณิชกุล, 116 หน้า

กากตะกอนเยื่อและกระดาษทุติยภูมิเป็นสิ่งที่เหลือตกค้างทั่วๆไปมาจากกระบวนการบำบัดน้ำเสียจากอุตสาหกรรมกระดาษ ส่วนประกอบหลักของกากตะกอนเยื่อและกระดาษทุติยภูมิ คือ เซลลูโลส, เฮมิเซลลูโลส, ลิกนิน และแคลเซียมคาร์บอเนต ($CaCO_3$) เซลลูโลสและเฮมิเซลลูโลสจะถูกเปลี่ยนไปเป็นน้ำตาลกลูโคสโดยกรรมวิธีไฮโดรเทอร์มอลทรีตเมนท์ ในงานวิจัยนี้ กรรมวิธีไฮโดรเทอร์มอลทรีตเมนท์ของกากตะกอนเยื่อและกระดาษทุติยภูมินั้นจะถูกดำเนินการในเครื่องปฏิกรณ์แบบท่อทำเหล็กสเตนเลส มันถูกพบว่าผงแห้งของกากตะกอนเยื่อและกระดาษทุติยภูมิที่มีขนาด ต่ำกว่า 595, ระหว่าง 595-841 และ ใหญ่กว่า 841 ไมโครเมตร มีจำนวนแตกต่างกันของ แคลเซียมคาร์บอเนต ผลของอุณหภูมิ, เวลาในการทำปฏิกิริยา, ขนาดของอนุภาค, ปริมาณแคลเซียมคาร์บอเนต และตัวเร่งปฏิกิริยาแบบกรด (CH_3COOH) ที่มีผลต่อผลิตผล กลูโคส และ 5-HMF ซึ่งจะทำการทดลองภายใต้สภาวะอุณหภูมิที่ 220-260 องศาเซลเซียส, เวลาในการทำปฏิกิริยา 0-40 นาที และทุกสภาวะจะมีการเพิ่มอุณหภูมิในอัตราเร่ง 10 องศาเซลเซียส / นาที จำแนกชนิดและปริมาณของกลูโคส และ 5-HMF ในผลิตภัณฑ์ที่เป็นของเหลวจะตรวจวัดด้วยเครื่อง HPLC วิเคราะห์ปริมาณคาร์บอนทั้งหมดในผลิตภัณฑ์ที่เป็นของเหลวด้วยเครื่อง TOC การตรวจสอบของของแข็งที่เหลือด้วยกล้องจุลทรรศน์อิเล็กตรอน (SEM), วิเคราะห์ Ca^{2+} ในผลิตภัณฑ์ที่เป็นของเหลวด้วยเครื่อง (ICP) ปฏิกิริยาที่เป็นไปได้จากเซลลูโลสจะได้รับการเสนอและปรึกษา ผลผลิตน้ำตาลกลูโคสที่สูงที่สุดที่ได้รับจากกากตะกอนเยื่อและกระดาษทุติยภูมิที่ 220 องศาเซลเซียส และเวลาในการทำปฏิกิริยา 20 นาที และพบว่า $CaCO_3$ ต้องแยกจากสารตั้งต้นก่อนกรรมวิธีไฮโดรเทอร์มอลทรีตเมนท์จะช่วยให้เซลลูโลสสามารถสลายตัวได้มากยิ่งขึ้น

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต..
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก....................................
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NAWAPON CHARIYAPRASERTSIN: CONVERSION OF SECONDARY PULP AND PAPER SLUDGE TO GLUCOSE BY HYDROTHERMAL TREATMENT. ADVISOR: ASSOC.PROF.TAWATCHAI CHARINPANITKUL, D. Eng., 116 pp.

Secondary pulp and paper sludge is typical residue supplied from water treatment process of paper industry. The main components of secondary pulp/paper sludge are cellulose, hemicellulose, lignin and calcium carbonate ($CaCO_3$). The cellulose and hemicellulose could be converted to glucose by hydrothermal treatment. In this work hydrothermal treatment of the secondary sludge has been conducted in a stainless-steel tubular batch reactor. It was found that dried powder of secondary pulp/paper sludge with nominal size of lower 595, 595 - 841, over 841 μm contains different amount of $CaCO_3$. Effect of temperature, holding time, particles sizes, $CaCO_3$ and Acid catalyst (CH_3COOH) on the glucose and 5-HMF yields has been examined under designated conditions of 220-260 ºC, holding time 0-40 min, In every experiments, heating rate is set constant at 10 ºC/min. Identification and quantification of glucose and 5-HMF in the aqueous phase is performed with high-performance liquid chromatography (HPLC). Content of total organic carbon in liquid products is determined by total organic carbon analyzer (TOC), while concentration of Ca^{2+} ion could be quantified by using an Inductively coupled plasma spectroscopy (ICP). Fresh feed of pulp and residual solid is subjected to the scanning electron microscopy (SEM). Plausible reaction pathway of cellulose would be proposed and discussed. The highest glucose yield could be obtained from secondary sludge at 220 ^{o}C and 20 min of holding time. It was found that $CaCO_3$ must be separated before hydrothermal treatment to gain higher cellulose conversion.

Department: Chemical Engineering Student's Signature……………………………..
Field of Study: Chemical Engineering Advisor's Signature…………………………….
Academic Year: 2012 .

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CHAPTER I

INTRODUCTION

1.1 Background

Biomass is a renewable energy source and biological material from living, or living organisms. As an energy source, biomass can either be used directly, or converted into other energy products such as bio-fuel. In the first, biomass is material from plant and use for generate electricity from steam turbines and gasifiers or generate heat by combustion directly. Examples forest residues (such as dead trees, branches and tree stumps), yard clippings, wood chips and even solid waste from municipal. And the second, biomass composes plant or animal matter that could be converted into fibers or other industrial chemicals, including bio-fuels. Industrial biomass can be grown from many types of plants, such as rice, sugarcane, cassava, soil bean, corn, bamboo and a variety of tree species, ranging from eucalyptus to oil palm (palm oil). Biomass ethanol is the major renewable energy source. It would provide an alternative liquid-fuel which is derived from domestic resource and then utilized as partial substitute for petroleum based fuel in many developing countries. Ethanol can be produced from three main types of biomass material: (a) sugar bearing materials (such as sugarcane, molasses, sweet sorghum, etc.): (b) starches (such as cassava, corn, potatoes, etc.) and (c) cellulose (such as wood, agricultural residues, etc.). In Thailand, the main raw materials for produce ethanol are molasses, rice, sugarcane, cassava, soil bean and corn but all of them are valuable agriculture products [1] Moreover, Thai people use E20, E85 gasoline as main fuel for transportation. Ethanol are used approximately 1.5 million liters per day and would increase to 2 million liters per day on next year.

Figure 1.1 Biomass materials: Molasses, rice, sugarcane, cassava, soil bean and corn

1.2 Motivation

The consumption of paper is increasing annually in many countries and society and it make waste from pulp and paper mills increasing as well, especially pulp and paper sludge. There are two kinds, primary sludge and secondary sludge. The primary sludge mainly consists of fibers, fines, fillers and other organic matter. Almost of it lost from the pulp and paper making process. There are suspended in water and easily to dewater by filtration or use alum to coagulate them, but the secondary sludge is not the same. The secondary sludge is residue from biological treatment section by aerobic bacteria. The secondary sludge is difficult to dewater than primary sludge because of consistency. On the other hand, the production of secondary sludge growth depends on the activated sludge from pulp and paper mills and the pulp and paper production increasing [2] Secondary pulp/paper-mill sludge is the residue produced in the biological treatment process of wastewaters from the pulp and paper industries by aerobic bacteria. The waste water is a liquid suspension that concentration is approximately 2 wt% solids, and there are biodegradable organic compounds, inorganic compounds and a little bit of heavy metals. Secondary pulp and paper mills sludge can considered be the waste biomass and can use biological and thermo-chemical processes both, same with other types of biomass, Secondary pulp/paper-mill sludge is a source of renewable energy. This idea would decrease gas emission a little bit in carbon-neutral lifecycle which cause of the Green house effect [3, 4] In the paper recycle processes in Japan, Secondary pulp and paper sludge that is produced from low-grade cellulose including organics, and in-organics with the content 40 wt% water and 60 wt% solids that is the average value of pulp and paper mills in Japan [3] The estimated amount of pulp and paper sludge in 1999 was more than 1.7 Mt/ y [5] In North America, secondary pulp and paper sludge is produced 4 kg from 100 kg of paper production at a paper mill [6] Generally, the pulp and paper sludge is reused by land-filling and incineration as fuel [7], but incineration is poor in economic because of the high cost of sludge dewatering to 20–40 % consistency or higher that is a factor affect to use land-filling or incineration and the energy for evaporate water in the sludge before feed in incineration or combustion process by a recovery boiler. The sludge disposal or management costs could be 60% of the total wastewater treatment plant operating costs [8] In addition to Thailand 2550, the estimated amounts of pulp and paper sludge were approximately 1 million ton per year and tend to increase over time. Land-filling is the mainly method to operate the sludge but it is the significant cause of gas emission in carbon-neutral lifecycle and global warming problem.

Hydrothermal process is an environment friendly technology. Unlike the hazardous products of combustion, such as CO, NOx, etc, hydrothermal reaction converts biomass to harmless products. Under hydrothermal water conditions, biomass and oxygen oxidize to form of CO_2 or H_2O. Nitrogen in biomass, mainly converts N_2. Sulfur, chlorine, and phosphorous are oxidized to inorganic acids that are neutralized to salt by adding suitable base. Hydrothermal technology suitable for wide range of feedstock such as wet biomass, sewage sludge, and high sulfur coals [9] In the hydrothermal literature, it is well-known that cellulose in the absence of any catalyst can be converted into glucose in high yields and produced liquid products such as cellulosic oligomers, cellobiose, glucose, fructose, 5-hydroxymethylfurfural, or acids [10] Mechanism of reaction, cellulose is hydrolyzed into oligomers or monomer glucose and then into various saccharides including cellobiose and monosaccharides (glucose and fructose) as reaction time progresses and then the sugar groups can be decomposed to others form of acids or dehydration products depending on the conditions such as temperature, residence time, and whether a catalyst is used or not.

1.3 Objective of the research

1.3.1 To produce liquid products from secondary pulp/paper sludge, especially glucose by hydrothermal treatment.

1.3.2 Study the effects of reaction temperature, holding time, raw material size, $CaCO_3$ and catalyst.

1.4 Scope of the research

1.4.1 Pulp and paper sludge will be used as a biomass feedstock under hydrothermal method.

1.4.2 The experimental conditions for hydrothermal treatment process of secondary pulp/paper sludge will be focused by variation of following parameters.

- Effect of reaction temperature in a range of 200 – 260 °C.
- Effect of holding time in a range of 0-40 min.
- Effect of classified pulp and paper sludge size in a range of over 840, 595-840 and lower 595 μm.
- Effect of $CaCO_3$ adding in a range of 0-0.6 g.
- Effect of catalyst CH_3COOH concentration in a range of 0.25-1 % wt.

1.4.3 Find the optimal condition parameter of reaction temperature, holding time, and sludge power size.

1.4.4 Study on the effect of catalyst in hydrothermal process that would increase glucose yields.

1.5 Expected benefits

1.5.1 The optimal condition, which converse secondary pulp and paper sludge to glucose and another products for renewable energy.

1.5.2 To gain additional experimental data to support biomass technology in Thailand for the future renewable energy sources.

CHAPTER II

FUNDAMENTAL THEORY

2.1 Biomass

Biomass is a biological organic material from living which is commonly planted to produce energy or heat. The heat can be used directly, for heating, cooking, and industrial processes, or indirectly, to produce electricity. Biomass consists of carbon, hydrogen and oxygen based. Nitrogen and small quantities of other atoms, including alkali, alkaline earth and heavy metals can be found. Metals and magnesium are often found in the functional molecules of porphyrins and chlorophyll. Moreover, this renewable energy source may also include biodegradable wastes that can be used as an energy source. Biomass is presumably our oldest source of energy after the sun. Since people have burnt wood to heat their homes and cook their food for thousands of years ago. Particularly, biomass differences from organic materials such as fossil fuels, which have been transformed by geological processes into substances such as coal and petroleum. Environmentally, biomass is used as a replacement of fossil fuel, even though when they are burnt, the same amount of carbon dioxide (CO_2) is released into the atmosphere but when they are used for the energy production, it could be noted that a net amount of greenhouse gases are decreased because of the offset of methane (CH_4 is a much stronger greenhouse gas than CO_2) that would have otherwise entered the atmosphere. Thereby, biomass has some advantages over fossil fuels. Moreover, since they contain little amount of sulfur and nitrogen, that is why they cannot cause the acid rain. By the way, they can remove carbon dioxide, one of the greenhouse gases from the atmosphere when they have photosynthesized.

According to the photosynthesis process as shown in equation 2.1, the sun always gives plants the energy and then plants would convert water and carbon dioxide into oxygen and sugars. Eventual, the whole organic matter contains stored in their leaves, stems and roots.

$$6H_2O + 6CO_2 + \text{Radiant Energy} \longrightarrow C_6H_{12}O_6 + 6O_2 \qquad (2.1)$$

Figure 2.1 shows the physical structure of the whole plants, these sugars found in cellulose, hemicelluloses and lignin, they area starting point for the major fractions in all of the terrestrial plants. For this reason, biomass is a renewable energy source because its supplies are not limited.

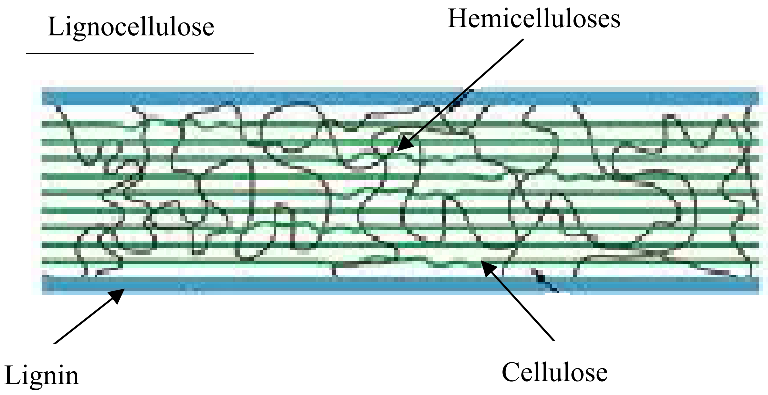


Figure 2.1 The essential element of plants [11]

From the industrial point of view, biomass can be grown from many kinds of plants such as miscanthus, switchgrass, hemp, corn, poplar, willow, sorghum, sugarcane, eucalyptus and oil palm. This particular plant is not only used to the end products, but it also affects the processing of the raw material. Even though fossil fuels have their origin in ancient biomass, they are not considered biomass as the generally accepted definition because they contain carbon that has been "out" of the carbon cycle for a very long time. Their combustion therefore disturbs the carbon dioxide content in the atmosphere.

The non-combustion processes convert raw biomass into a variety of gaseous, liquid, or solid fuels that can be used directly in a power plant for energy generation. The carbohydrates in biomass, which are comprised of oxygen, carbon, and hydrogen, can be broken down into a variety of chemicals which are used as fuels. This conversion can be done in two ways. Firstly, for thermo-chemical process**,** when plant matter is heated, it breaks down into various gases, liquids, and solids. These products can be used for further processed and refined into useful fuels such as methane and alcohol. Biomass gasifies capture methane which are released from the plants and burn it in a gas turbine to produce electricity. Another approach is to take these fuels and run them through fuel cells, converting the hydrogen-rich fuels into electricity and water, with few or no emissions. Secondary, for biochemical process, bacteria, yeasts, and enzymes also break down carbohydrates. Fermentation, the process used to changes biomass liquids into alcohol, a combustible fuel which is mixed with gasoline to make gasohol. Also, when bacteria break down biomass, methane and carbon dioxide are produced. This methane can be captured, in sewage treatment plants and landfills, for example, and burned for heat and power. Thirdly, for chemical process, biomass oils, like soybean and canola oil, can be chemically converted into a liquid fuel by transesterification process such as diesel fuel and gasoline additives. Cooking oil from restaurants, for example, has been used as a source to make "biodiesel" for trucks. In addition, a better way to produce biodiesel is to use algae as a source of oils [11]

2.2 Cellulose

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units. Cellulose is the structural component of the primary cell wall of green plants, many forms of algae and the oomycetes. Some species of bacteria secrete it to form bio-films. Cellulose is the most common organic compound on Earth. About 33% of all plant matter is cellulose (the cellulose content of cotton fiber is 90%, that of wood is 40–50% and that of dried hemp is approximately 45%).

For industrial use, cellulose today is mainly obtained from wood pulp and cotton. Cellulose is mainly used to produce paperboard and paper; to a smaller extent it is converted into a wide variety of derivative products such as cellophane and rayon. Converting cellulose from energy crops into bio-fuels such as cellulosic ethanol is under investigation as an alternative fuel source. Some animals, particularly ruminants and termites, can digest cellulose with the help of symbiotic micro-organisms that live in their guts. Humans can digest cellulose to some extent, however it mainly acts as a hydrophilic bulking agent for feces and is often referred to as "dietary fiber". The major combustible component of non-food energy crops is cellulose, with lignin second. Non-food energy crops are more efficient than edible energy crops (which have a large starch component), but still compete with food crops for agricultural land and water resources. Typical non-food energy crops include industrial hemp (though outlawed in some countries), switchgrass, Miscanthus, Salix (willow), and Populus (poplar) species. Some bacteria can convert cellulose into ethanol which can then be used as a fuel; see cellulosic ethanol.

Cellulose has no taste, is odorless, is hydrophilic with the contact angle of 20–30, is insoluble in water and most organic solvents, is chiral and is biodegradable. It can be broken down chemically into its glucose units by treating it with concentrated acids at high temperature. Cellulose is derived from D-glucose units, which condense through β(1→4)-glycosidic bonds. This linkage motif contrasts with that for α(1→4)-glycosidic bonds present in starch, glycogen, and other carbohydrates. Cellulose is a straight chain polymer: unlike starch, no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod-like conformation, aided by the equatorial conformation of the glucose residues. The multiple hydroxyl groups on the glucose from one chain form hydrogen bonds with oxygen atoms on the same or on a neighbor chain, holding the chains firmly together side-by-side and forming microfibrils with high tensile strength. This strength is important in cell walls, where the microfibrils are meshed into a carbohydrate matrix, conferring rigidity to plant cells. Compared to starch, cellulose is also much more crystalline. Whereas starch undergoes a crystalline to amorphous transition when heated beyond 60–70 °C in water (as in cooking), cellulose requires a temperature of 320 °C and pressure of 25 MPa to become amorphous in water. Several different crystalline structures of cellulose are known, corresponding to the location of hydrogen bonds between and within strands. Natural cellulose is cellulose I, with structures I_α and I_β. Cellulose produced by bacteria and algae is enriched in I_α while cellulose of higher plants consists mainly of I_β. Cellulose in regenerated cellulose fibers is cellulose II. The conversion of cellulose I to cellulose II is irreversible, suggesting that cellulose I is metastable and cellulose II is stable. With various chemical treatments it is possible to produce the structures cellulose III and cellulose IV.

Many properties of cellulose depend on its chain length or degree of polymerization, the number of glucose units that make up one polymer molecule. Cellulose from wood pulp has typical chain lengths between 300 and 1700 units; cotton and other plant fibers as well as bacterial cellulose have chain lengths ranging from 800 to 10,000 units. Molecules with very small chain length resulting from the breakdown of cellulose are known as cellodextrins; in contrast to long-chain cellulose, cellodextrins are typically soluble in water and organic solvents. Plant-derived cellulose is usually found in a mixture with hemicellulose, lignin, pectin and other substances, while microbial cellulose is quite pure, has a much higher water content, and consists of long chains. Cellulose is soluble in cupriethylenediamine (CED), cadmiumethylenediamine (Cadoxen), N-methylmorpholine N-oxide and lithium chloride / dimethylformamide. This is used in the production of regenerated celluloses (such as viscose and cellophane) from dissolving pulp [12]

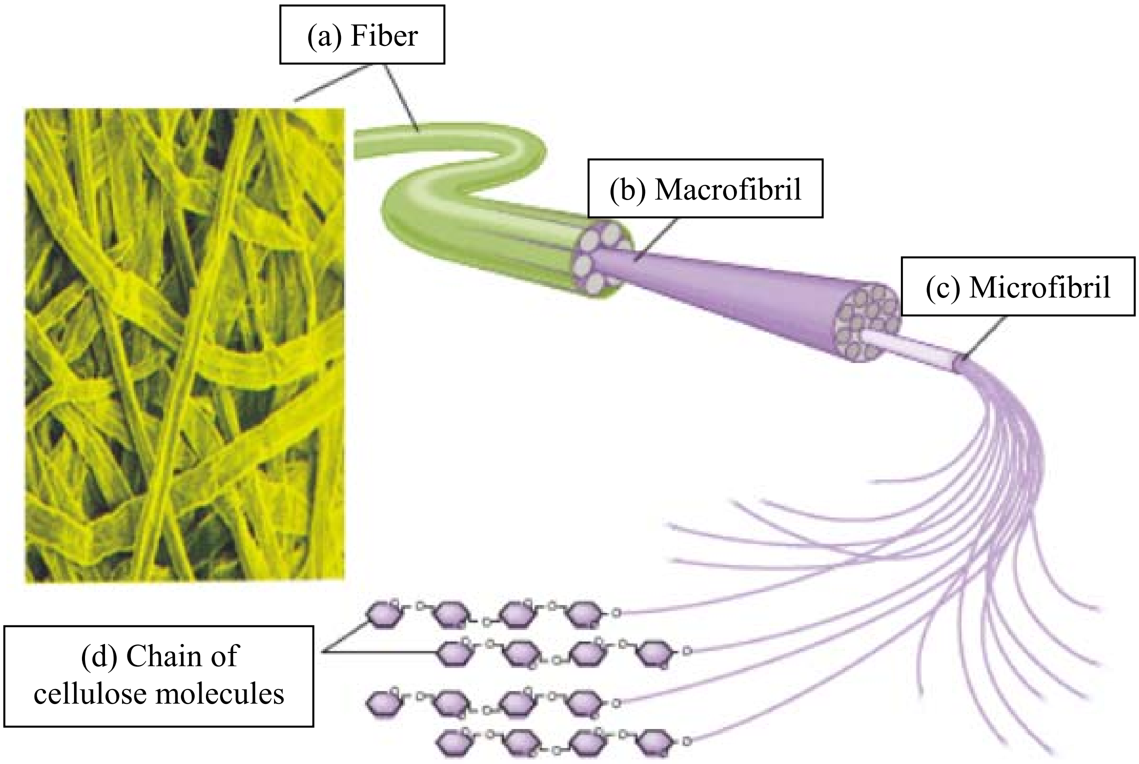


Figure 2.2 Structure of cellulose

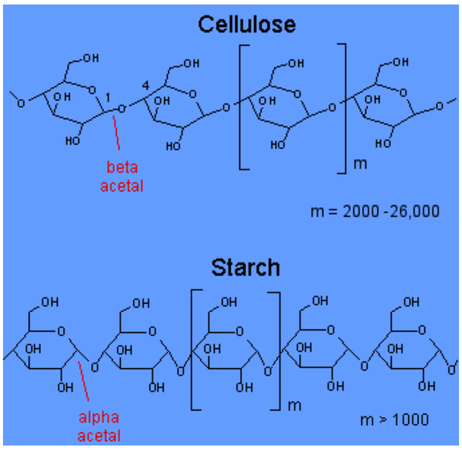


Figure 2.3 Different of chemical structure of cellulose and starch [12]

2.3 Hemicellulose

A hemicellulose (Also known as Polyose) is any of several heteropolymers (matrix polysaccharides), such as arabinoxylans, present along with cellulose in almost all plant cell walls. While cellulose is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base as well as myriad hemicellulase enzymes. Hemicelluloses include xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan. These polysaccharides contain many different sugar monomers. In contrast, cellulose contains only anhydrous glucose. For instance, besides glucose, sugar monomers in hemicellulose can include xylose, mannose, galactose, rhamnose, and arabinose. Hemicelluloses contain most of the D-pentose sugars, and occasionally small amounts of L-sugars as well. Xylose is in most cases the sugar monomer present in the largest amount, although in softwoods mannose can be the most abundant sugar. Not only regular sugars can be found in hemicellulose, but also their acidified form, for instance glucuronic acid and galacturonic acid can be present. Unlike cellulose, hemicellulose (also a polysaccharide) consists of shorter chains – 500–3,000 sugar units as opposed to 7,000–15,000 glucose molecules per polymer seen in cellulose. In addition, hemicellulose is a branched polymer, while cellulose is unbranched. Hemicelluloses are embedded in the cell walls of plants, sometimes in chains that form a 'ground' - they bind with pectin to cellulose to form a network of cross-linked fibers [13]

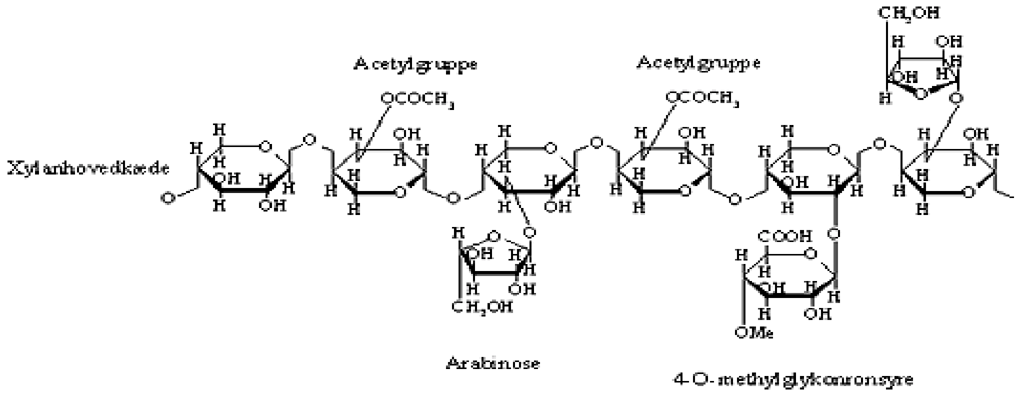


Figure 2.4 Chemical structure of hemicelluloses [13]

2.4 Lignin

Lignin or lignen is a complex chemical compound most commonly derived from wood, and an integral part of the secondary cell walls of plants and some algae. The term was introduced in 1819 by de Candolle and is derived from the Latin word lignum, meaning wood. It is one of the most abundant organic polymers on Earth, exceeded only by cellulose, employing 30% of non-fossilorganic carbon, and constituting from a quarter to a third of the dry mass of wood. As a biopolymer, lignin is unusual because of its heterogeneity and lack of a defined primary structure. Its most commonly noted function is the support through strengthening of wood (xylem cells) in trees. Global production of lignin is around 1.1 million metric tons per year and is used in a wide range of low volume, niche applications where the form but not the quality is important. Lignin fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components, especially in xylemtracheids, vessel elements and sclereid cells. It is covalently linked to hemicellulose and, therefore, crosslinks different plant polysaccharides, conferring mechanical strength to the cell wall and by extension the plant as a whole. It is particularly abundant in compression wood but scarce in tension woods, which are types of reaction wood.

Lignin plays a crucial part in conducting water in plant stems. The polysaccharide components of plant cell walls are highly hydrophilic and thus permeable to water, whereas lignin is more hydrophobic. The cross-linking of polysaccharides by lignin is an obstacle for water absorption to the cell wall. Thus, lignin makes it possible for the plant's vascular tissue to conduct water efficiently. Lignin is present in all vascular plants, but not in bryophytes, supporting the idea that the original function of lignin was restricted to water transport. However, it is present in red algae, which seems to suggest that the common ancestor of plants and red algae also synthesised lignin. This would suggest that its original function was structural; it plays this role in the red alga Calliarthron, where it supports joints between calcified segments. Another possibility is that the lignin in red algae and in plants are result of convergent evolution, and not of a common origin. Lignin is a cross-linked ceramic macromolecule with molecular masses in excess of 10,000 units. It is relatively hydrophobic and aromatic in nature. The degree of polymerisation in nature is difficult to measure, since it is fragmented during extraction and the molecule consists of various types of substructures that appear to repeat in a haphazard manner. Different types of lignin have been described depending on the means of isolation.

There are three monolignolmonomers, methoxylated to various degrees: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These lignols are incorporated into lignin in the form of the phenylpropanoids p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), respectively. Gymnosperms have a lignin that consists almost entirely of G with small quantities of H. That of dicotyledonousangiosperms is more often than not a mixture of G and S (with very little H), and monocotyledonous lignin is a mixture of all three. Many grasses have mostly G, while some palms have mainly S. All lignins contain small amounts of incomplete or modified monolignols, and other monomers are prominent in non-woody plants. Thioglycolysis is an analytical technique for lignin quantitation. Lignin structure can also be studied by computational simulation [14]

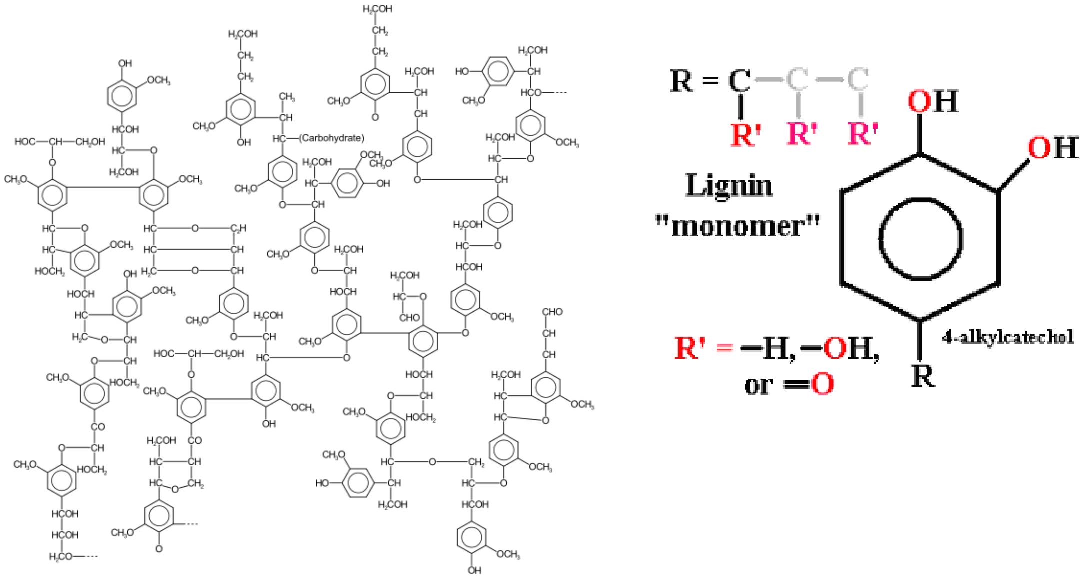


Figure 2.5 Chemical structure of lignin [14]

2.5 Calcium carbonate ($CaCO_3$)

Calcium carbonate is a chemical compound with the formula $CaCO_3$. It is a common substance found in rocks in all parts of the world, and is the main component of shells of marine organisms, snails, coal balls, pearls, and eggshells. Calcium carbonate is the active ingredient in agricultural lime, and is usually the principal cause of hard water. It is commonly used medicinally as a calcium supplement or as an antacid, but excessive consumption can be hazardous.

The main use of calcium carbonate is in the construction industry, either as a building material or limestone aggregate for road-building or as an ingredient of cement or as the starting material for the preparation of builder's lime by burning in a kiln. However, due to weathering mainly caused by acid rain, calcium carbonate (in limestone form) is no longer used for building purposes on its own, and only as a raw/primary substance for building materials. Calcium carbonate is also used in the purification of iron from iron ore in a blast furnace. The carbonate is calcined in situ to give calcium oxide, which forms a slag with various impurities present, and separates from the purified iron. In the oil industry, calcium carbonate is added to drilling fluids as a formation-bridging and filter ake-sealing agent; it is also a weighting material which increases the density of drilling fluids to control the down-hole pressure. Calcium carbonate is added to swimming pools, as a pH corrector for maintaining alkalinity and offsetting the acidic properties of the disinfectant agent. Calcium carbonate has traditionally been a major component of blackboard chalk. However, modern manufactured chalk is mostly gypsum, hydrated calcium sulfate $CaSO_4 \cdot 2H_2O$. Calcium carbonate is a main source for growing Seacrete, or Biorock. Precipitated calcium carbonate (PCC), pre-dispersed in slurry form, is a common filler material for latex gloves with the aim of achieving maximum saving in material and production costs.

Fine ground calcium carbonate (GCC) is an essential ingredient in the microporous film used in babies' diapers and some building films as the pores are nucleated around the calcium carbonate particles during the manufacture of the film by biaxial stretching. GCC or PCC is used as filler in paper because they are cheaper than wood fiber. Printing and writing paper can contain 10–20% calcium carbonate. In North America, calcium carbonate has begun to replace kaolin in the production of glossy paper. Europe has been practicing this as alkaline papermaking or acid-free papermaking for some decades. PCC has a very fine and controlled particle size, on the order of 2 micrometres in diameter, useful in coatings for paper.

Calcium carbonate is widely used as an extender in paints, in particular matte emulsion paint where typically 30% by weight of the paint is either chalk or marble. It is popular filler in plastics also. Some typical examples include around 15 to 20% loading of chalk in unplasticized polyvinyl chloride (uPVC) drain pipe, 5 to 15% loading of stearate coated chalk or marble in uPVC window profile. PVC cables can use calcium carbonate at loadings of up to 70 phr (parts per hundred parts of resin) to improve mechanical properties (tensile strength and elongation) and electrical properties (volume resistivity). Polypropylene compounds are often filled with calcium carbonate to increase rigidity, a requirement that becomes important at high use temperatures. Here the percentage is often 20–40%. It routinely used as filler in thermosetting resins (sheet and bulk molding compounds) also and has also been mixed with ABS, and other ingredients, to form some types of compression molded "clay" poker chips. Precipitated calcium carbonate, made by dropping calcium oxide into water, is used by itself or with additives as a white paint, known as whitewashing. Calcium carbonate is added to a wide range of trade and does it yourself adhesives, sealants, and decorating fillers. Ceramic tile adhesives typically contain 70 to 80% limestone. Decorating crack fillers contain similar levels of marble or dolomite. It is also mixed with putty in setting stained glass windows, and as a resist to prevent glass from sticking to kiln shelves when firing glazes and paints at high temperature. In ceramics/glazing applications, calcium carbonate is known as whiting, and is a common ingredient for many glazes in its white powdered form. When a glaze contain this material is fired in a kiln, the whiting acts as a flux material in the glaze. Ground calcium carbonate is an abrasive (both as scouring powder and as an ingredient of household scouring creams), in particular in its calcite form, which has the relatively low hardness level of 3 on the Mohs scale of mineral hardness, and will therefore not scratch glass and most other ceramics, enamel, bronze, iron, and steel, and have a moderate effect on softer metals like aluminium and copper. A paste made from calcium carbonate and deionized water can be used to clean tarnish on silver.

Calcium carbonate is widely used medicinally as an inexpensive dietary calcium supplement or gastric antacid. It may be used as a phosphate binder for the treatment of hyperphosphatemia (primarily in patients with chronic renal failure). It is also used in the pharmaceutical industry as inert filler for tablets and other pharmaceuticals. Calcium carbonate is known among IBS sufferers to help reduce diarrhea. Some individual reports being symptom-free since starting supplementation. The process in which calcium carbonate reduces diarrhea is by binding water in the bowel, which creates a stool that is firmer and better formed. Calcium carbonate supplements are often combined with magnesium in various proportions. This should be taken into account as magnesium is known to cause diarrhea. Calcium carbonate is used in the production of toothpaste and has seen a resurgence as a food preservative and color retainer, when used in or with products such as organic apples or food [15]

Figure 2.6 Powder of $CaCO_3$ [15]

2.6 Glucose

Glucose also known as D-glucose, dextrose, or grape sugar) is a simple monosaccharide found in plants. It is one of the three dietary monosaccharides, along with fructose and galactose that are absorbed directly into the bloodstream during digestion. An important carbohydrate in biology, cells use it as the primary source of energy and a metabolic intermediate. Glucose is one of the main products of photosynthesis and fuels for cellular respiration. Glucose exists in several different molecular structures, but all of these structures can be divided into two families of mirror-images (stereoisomers). Only one set of these isomers exists in nature, those derived from the "right-handed form" of glucose, denoted D-glucose. D-glucose is sometimes referred to as dextrose, although the use of this name is strongly discouraged. The term dextrose is derived from dextrorotatory glucose. This name is therefore confusing when applied to the enantiomer, which rotates light in the opposite direction. Starch and cellulose are polymers derived from the dehydration of D-glucose. The other stereoisomer, called L-glucose, is hardly ever found in nature.

The reason that glucose, and not another monosaccharide such as fructose, is so widely used in organisms is not clearly understood. One reason might be that glucose has a lower tendency, relative to other hexose sugars, to react non-specifically with the amino groups of proteins. This reaction (glycation) reduces or destroys the function of many enzymes. The low rate of glycation is due to glucose's preference for the less reactive cyclic isomer. Nevertheless, many of the long-term complications of diabetes (e.g., blindness, renal failure, and peripheral neuropathy) are probably due to the glycation of proteins or lipids. In contrast, enzyme-regulated addition of glucose to proteins by glycosylation is often essential to their function. Another reason as to why glucose is the most common sugar is that it is the most conformationally stable among other possibilities

Glucose is a common medical analyze measured in blood samples. Eating or fasting prior to taking a blood sample has an effect on the result. A high fasting glucose blood sugar level may be a sign of prediabetes or diabetes mellitus. Glucose is a ubiquitous fuel in biology. It is used as an energy source in most organisms, from bacteria to humans. Use of glucose may be by either aerobic respiration, anaerobic respiration, or fermentation. Glucose is the human body's key source of energy, through aerobic respiration, providing approximately 3.75 kilocalories (16 kilojoules) of food energy per gram. Breakdown of carbohydrates (e.g. starch) yields mono- and disaccharides, most of which is glucose. Through glycolysis and later in the reactions of the citric acid cycle (TCAC), glucose is oxidized to eventually form CO_2 and water, yielding energy sources, mostly in the form of ATP. The insulin reaction and other mechanisms, regulate the concentration of glucose in the blood.

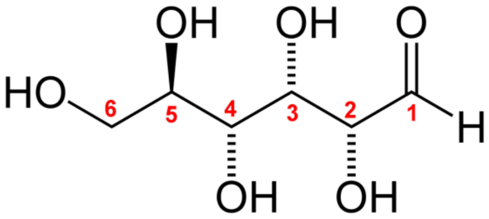


Figure 2.7 Open-chain structure of glucose [16]

Glucose is a monosaccharide with formula $C_6H_{12}O_6$ or H-(C=O)-$(CHOH)_5$-H, whose five hydroxyl (OH) groups are arranged in a specific way along its six-carbon backbone. In its fleeting open-chain form, the glucose molecule has an open (as opposed to cyclic) and unbranched backbone of six carbon atoms, C-1 through C-6; where C-1 is part of an aldehyde group H(C=O)-, and each of the other five carbons bears one hydroxyl group -OH. The remaining bonds of the backbone carbons are satisfied by hydrogen atoms -H. Therefore glucose is a hexose and an aldose, or an aldohexose. Each of the four carbons C-2 through C-5 is a stereocenter, meaning that its four bonds connect to four different substitutents. (Carbon C-2, for example, connects to -(C=O)-H, -OH, -H, and -$(CHOH)_4H$.) In D-glucose, these four parts must be in a specific three-dimensional arrangement. Namely, when the molecule is drawn in the Fischer projection, the hydroxyls on C-2, C-4, and C-5 must be on the right side, while that on C-3 must be on the left side. The positions of those four hydroxyls are exactly reversed in the Fischer diagram of L-glucose. D- and L-glucose are two of the 16 possible aldohexoses; the other 14 are allose, altrose, mannose, gulose, idose, galactose, and talose, each with two enantiomers, "D-" and "L-" [16]

2.7 Hydroxymethylfurfural

Hydroxymethylfurfural (HMF), also 5-(Hydroxymethyl)furfural, is an organic compound derived from dehydration of certain sugars. This yellow low-melting solid is highly water-soluble. The molecule consists of a furan ring, containing both aldehyde and alcohol functional groups. HMF has been identified in a wide variety of heat-processed foods including milk, fruit juices, spirits, honey, etc. HMF, which is derived from cellulose without use of fermentation, is a potential "carbon-neutral" feedstock for fuels and chemicals. Related to the production of furfural, HMF is produced from sugars. It arises via the dehydration of fructose. Treatment of fructose with acids followed by liquid-liquid extraction into organic solvents such as methyl isobutyl ketone. The conversion is affected by various additives such as DMSO, 2-butanol, and Poly vinyl pyrrolidone, which minimize the formation of side product. Ionic liquids facilitate the conversion of fructose to HMF. Chromous chloride catalyzes the direct conversion of both fructose (yielding 90 %+) and glucose (yielding 70 %+) into an HMF. Subsequently cellulose has been directly converted into HMF (yielding 55 % at 96 % purity). The chromium chloride catalyzes the conversion of glucose into fructose. A variety of methods have been developed to convert cellulosic biomass to HMF.

HMF is practically not present in fresh food, but it is naturally generated in sugar-containing food during heat-treatments like drying or cooking. Along with many other flavor- and colour-related substances, HMF is formed in the Maillard reaction as well as during caramelization. In these foods it is also slowly generated during storage. Acid conditions favour generation of HMF. HMF can be found in low amounts in honey, fruit-juices and UHT-milk. Here as well as in vinegars, jams, alcoholic products or biscuits HMF can be used as an indicator for excess heat-treatment. For instance, fresh honey only has low amounts of HMF—less than 15 mg/kg—depending on pH-value and temperature and age, and the codex alimentarius standard require that honey have less than 40 mg/kg HMF to guarantee that the honey has not undergone heating during processing, except for tropical honeys which must be below 80 mg/kg. Higher quantities of HMF are found naturally in coffee and dried fruit. Several types of roasted coffee contained between 300 – 2900 mg/kg HMF. Dried plums were found to contain up to 2200 mg/kg HMF. In dark beer 13.3 mg/kg were found, bakery-products contained between 4.1 – 151 mg/kg HMF. HMF can form in high-fructose corn syrup (HFCS), levels around 20 mg/kg HMF were found, increasing during storage or heating. This is a problem for American beekeepers because they use HFCS as a source of sugar when there are not enough nectar sources to feed honeybees, and HMF is toxic to them. Adding bases such as soda ash or potash to neutralize the HFCS slows down the formation of HMF. Depending on production-technology and storage, levels in food vary considerably. To evaluate the contribution of a food to HMF intake, its consumption-pattern has to be considered. Coffee is the food that has a very high relevance in terms of levels of HMF and quantities consumed. HMF is a natural component in heated food but usually present in low concentrations. The daily intake of HMF may underlie high variations due to individual consumption-patterns. It has been estimated that in a western diet, in the order of magnitude of 5 – 10 mg of HMF are ingested per day from food. In former times, HMF was used in food for flavoring purposes, but in Europe this practice now is suspended. HMF is also found in cigarette smoke [17]

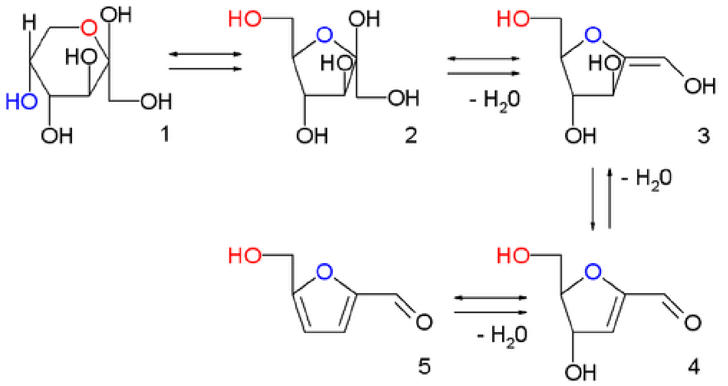


Figure 2.8 The series of chemical equilibria: 1. Fructopyranose, 2. Fructofuranose, 3, 4.two intermediate stages of dehydration (not isolated), and finally 5. HMF [17]

2.8 Hydrothermal treatment process

A phase diagram of water is shown in Figure 2.9 indicating a critical point of water at 374 ºC and 22.06 MPa [18] With an increase in the temperature and pressure along the liquid-vapor saturation line, the density of the liquid phase gradually decreases; on the other hand, the density of the vapor phase gradually increases. The point at which the density of both phases become identical (ρc = 322 kg/m3) is defined as the critical point. At this point, the phase boundary between two phases disappears and the water acts as the single fluid [19] Above the critical point is the supercritical water. The subcritical water, on the other hand, exists at the pressure and temperature lower than the critical values [20]

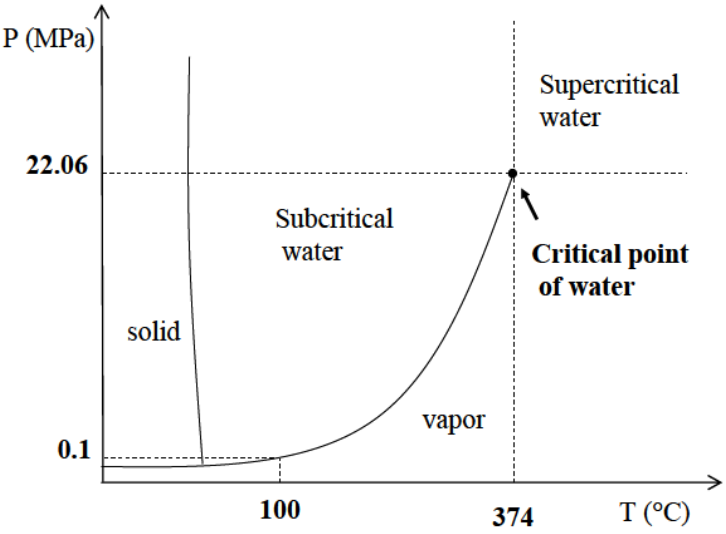


Figure 2.9 Phase diagram of water [18]

The subcritical and supercritical water has been applied for many chemical reactions and synthesis as the reaction medium, especially in the field of biomass utilization. This is due to an advantage of a wide range of properties, which are obtained only by changing the temperature and pressure. The dielectric constant (ε) and ion product of water (*Kw*) as a function of temperature at a constant pressure (25 MPa) are shown in Figure 2.10. In the subcritical region, the ion product increases up to three orders of magnitude higher than that in the ambient condition [21] The ionic-type reactions, therefore, are being catalyzed by the H+ and/or OH- ions from the water dissociation without any addition of acid/base catalysts [22] The reaction under subcritical condition, therefore, is the environmentally-friendly system. The ionic reactions include the hydrothermal pretreatment of lignocellulosic biomass [23] In this reaction, the cellulose, hemicellulose, polysaccharide, and protein are hydrolyzed to yield their monosaccharides and smaller compounds (e.g., glucose, xylose, amino acids, and organic acids), which are utilized further as the bio-chemicals and bio-ethanol [24] As approaching the critical point, the ion product and dielectric constant decrease dramatically [25] The water turns into the nonpolar-like solvent with the high solubility of the organic compounds and gases. The ionic reaction, thus, is demoted and the radical reaction is enhanced instead, indicating that the reaction pathway can be controlled by manipulating the water conditions.

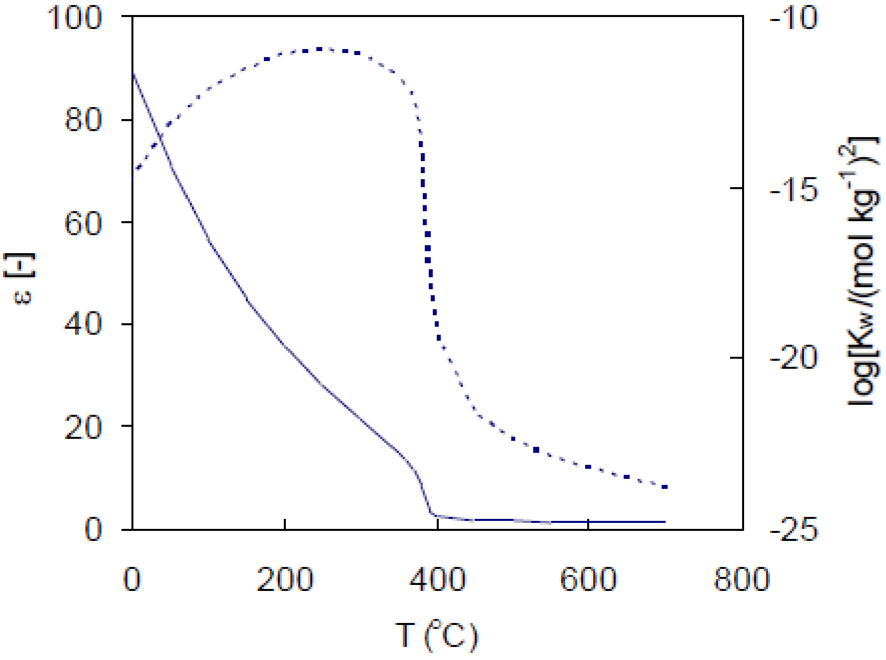


Figure 2.10 Dielectric constant (ε) and ion product of water (Kw) as a function of temperature at 25 MPa [19]

2.9 The reaction rate constant

In the chemical reaction considered in the following paragraphs, we take as the basis of calculation a species A, which is one of the reactants that is disappearing as a result of the reaction. The limiting reactant is usually chosen as our basis for calculation. The rate of disappearance of A, r_A, depends on temperature and composition. For many reaction it can be written as the product of a *reaction rate constant k* and a function of the concentrations (activities) of the various species involved in the reaction: The rate law gives the relationship between reaction rate and concentration as shown in equation (2.2)

$$-r_A = [k_A\ (T)]\ [\text{fn } C_A, C_B, \ldots] \qquad (2.2)$$

The algebraic equation that relates $-r_A$ to the species concentrations is called the kinetic expression or rate law. The specific rate of reaction, $k_{A,}$ like the reaction rate $-r_A$, is always referred to a particular species in the reactions and normally should be subscripted with respect to that species. However, for reactions in which the stoichiometric coefficient is 1 for species involved in the reaction.

The reaction rate constant $k$is not truly a constant, but is merely independent of the concentrations of the species involved in the reaction. The quantity k is also referred to as the specific reaction rate (constant). It is almost always strongly dependent on temperature. In gas- phase reaction, it depends on the catalyst and many be a function of total , pressure , and in addition can depend on other parameter s, such as ionic strength and choice of solvent. These other variables normally exhibit much less effect on the specific reaction rate than dose temperature, so for the purposes of the material presented here it will be assumed that k_A depends only on temperature. This assumption is valid in most laboratory and industrial reactions and seems to work quite well.

It was the great Swedish chemist Arrhenius who first suggested that the temperature dependence of the specific reaction rate k_A, could be correlated by an equation of the type.

$$k_A = Ae^{(E/RT)} \tag{2.3}$$

Where A = preexponential factor or frequency factor

E= activation energy, J/mol or cal/mol

R= gas constant = 8.314 J/mol•K = 1.987 cal/mol•K

T= absolute temperature, K

Equation (2.3), known as the *Arrhenius equation*, has been verifield empirically to give the temperature behavior of most reaction rate constants within experimental accuracy over fairly large temperature ranges (Foglor, 1999)

CHAPTER III

LITERATURE REVIEW

3.1 Hydrothermal treatment of pulp and paper sludge

3.1.1 Production of D-glucose from pseudo paper sludge with hydrothermal treatment

Torii, *et al*. (2010) studied to convert cellulose of pulp and paper sludge to glucose, raw material was pseudo paper sludge which composed of pure cellulose powder and inorganic powder of $CaCO_3$, talc $(Mg_3(Si_4O_{10})(OH)_2)$, kaolin $(Al_2(Si_2O_5)(OH)_4)$ by hydrothermal treatment. Samples were prepared in a laboratory. Conditions were fixed temperature at 250 °C and varied reaction time 2-20 min and varied ratio kinds of inorganic additives. The Maximum yield of glucose was 23 % in reaction time 12 min. Identified liquid products with high-performance liquid chromatography (HPLC) and find concentration of each dissolved inorganic ion (Ca, Mg and Al) was identified by inductively coupled plasma (ICP) spectroscopy [5]

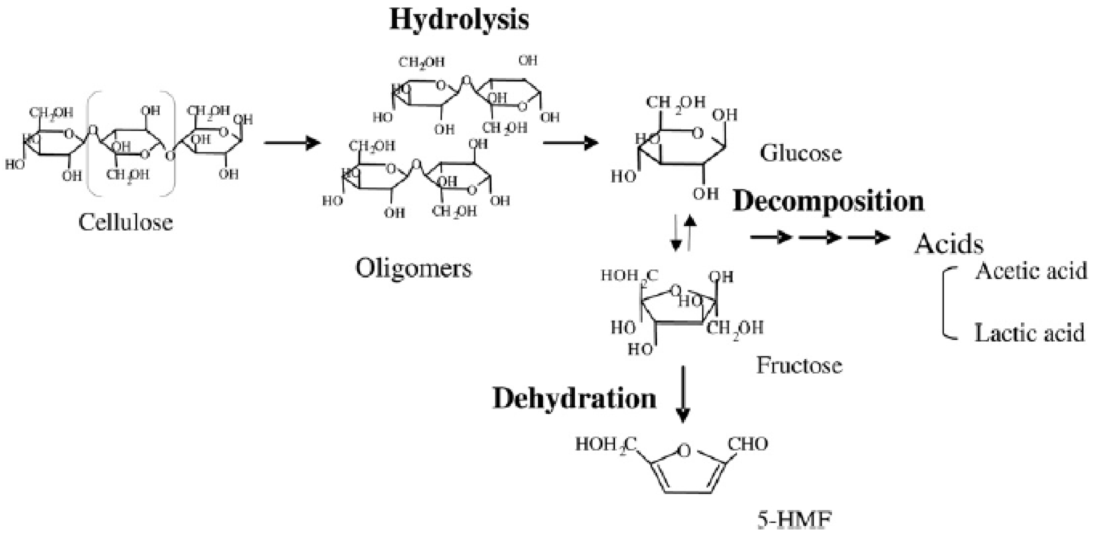


Figure 3.1 Simplified hydrothermal reaction pathway of cellulose [5]

3.1.2 Bio-crude production from secondary pulp/paper-mill sludge and waste newspaper via co-liquefaction in hot-compressed water

Zhang, *et al*. (2011) studied to investigate the mixed raw material between secondary pulp and paper sludge and waste newspaper and used HCO_2H, FeS, or KOH at 5 wt% of the total solids as catalyst. Condition varied ratio of mixed raw material and temperature from 250-380 º C. In without-catalyst experiments, the most yield of heavy oil (HO) was 28.0 wt% at 350 º C. And in catalyst-used condition, HCO_2H, FeS, or KOH was found to improve the HO yield at 300 º C, the most effective catalyst was HCO_2H, which increased the HO yield from 24.9 to 34.4 wt%. In addition, Ratio of mixed raw material effect with the yield of HO also [4]

3.1.3 Energy recovery from secondary pulp/paper-mill sludge and sewage sludge with supercritical water treatment

Zhang, *et al*. (2010) studied to treated the secondary pulp/paper-mill sludge (SPP) and sewage sludge under supercritical water in a range of temperatures from 400 ºC-550 ºC and varied reaction time in a range from 20–120 minutes for energy products. At low temperature and short reaction time produced the formation of heavy oil (HO) products. For the formation of synthetic gases, H_2, CO_2, CO, CH_4, and other light hydrocarbon, reaction time was ineffective but temperature was dramatic effective. The maximum yield of gas was produced 37.7 wt% of the SPP (on dry basis) at 500 ºC. H_2 was the maximum gas product [26]

3.1.4 Conversion of secondary pulp/paper sludge powder to liquid oil products for energy recovery by direct liquefaction in hot-compressed water

Xu and Lancaster (2008) demonstrated that secondary pulp/paper sludge powder (smaller than 20 mesh) was treated by direct liquefaction process under hot-compressed water condition and K_2CO_3, $Ca(OH)_2$ and $Ba(OH)_2$ were used as catalyst. The experiment of 0.1 M K_2CO_3 improved the conversion of solid, but suppressed the formation of both heavy oil and water-soluble oil. The experiments of $Ca(OH)_2$ and $Ba(OH)_2$ did not convert organic solid, but it catalyzed the formation of water-soluble oil and generated higher yields of total oil products [27]

3.2 Hydrolysis of cellulose

3.2.1 Cellulose hydrolysis in subcritical and supercritical water

Sasaki et al. (1998) proposed a new process to degrade cellulose rapidly under supercritical water (SCW) for glucose, fructose and oligomers (cellobiose, cellotriose, cellotetraose, etc.). Cellulose degradation experiments were operated with a flow type reactor in the range of temperature from 290 to 400°C and fixed pressure at 25 MPa and found that the glucose or oligomer conversion rate was much faster than the hydrolysis rate of cellulose. Therefore, even if the hydrolysis products, such as glucose or oligomers, are generated, their further decomposition rapidly takes place and thus high yields of hydrolysis products cannot be produced [10]

3.2.2 A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass

Akhtar, *et al*. (2011) described about hydrothermal liquefaction, which is a technique for produced clean biofuel from biomass with the water solvent at medium to high temperature (250–550 ºC) and pressure (5–25 MPa). Hydrothermal decomposition of biomass produced the various formation, which depending on operating parameters (final liquefaction temperature, residence times, rate of biomass heating, size of biomass particles, type of solvent and hydrogen donor solvents) [9]

3.3 Glucose decomposition

3.2.1 Kinetics of Non-catalyzed Decomposition of Glucose in High-temperature Liquid Water

Jing and LU (2008) studied the decomposition kinetics of glucose in high-temperature liquid water (HTLW), condition varied 180 to 220 º C under a pressure of 10 MPa. Main Products from process were 5-hydroxymethylfurfural (5-HMF) and levulinic acid (LA) [28]

3.2.2 Degradation kinetics of monosaccharides in subcritical water

Khajavis*et al*. (2005) studied decomposition kinetics of the monosaccharides, there were the aldohexose (glucose, galactose and mannose) and ketohexose (fructose and sorbose). A tubular reactor was used in continuous process under subcritical water. Conditions varied temperature in a range of 180–260 °C and fixed pressure at 10 MPa. The main product was 5-HMF, which was produced from every types of sample [29]

3.2.3 Glucose decomposition kinetics in water at 25 MPa in the temperature range of 448-673 K

Matsumura et al. (2006) studied the decomposition kinetics of glucose under supercritical water in the temperature ranging from 448 to 673 K and fixed pressure at 25 MPa in a continuous reactor. In the model, the reaction is assumed to be of the first order to calculate the reaction rate coefficient, but in this study, reaction order was also calculated from the experimental data and found that reaction order decreased from unity at a high temperature. This result was considered that reaction field changes from ionic to radicalic with increasing temperature from 448 to 673 K, change in reaction mechanism is referred [30]

3.2.4 Glucose and fructose decomposition in subcritical and supercritical water: detailed reaction pathway, mechanisms, and kinetics

Kabyemela et al. (1999) studied the products of glucose decomposition from short residence time condition to explain the reaction pathways and kinetics of glucose and fructose decomposition were determined under subcritcal and supercritical water. The conditions were varied in a range of temperature from 300-400 °C and pressure from 25-40 MPa for extremely short residence times between 0.02 and 2 seconds. The products of glucose decomposition were fructose, a isomerization product was 1,6-anhydroglucose, a dehydration product, erythrose and glyceraldehyde, products of C-C bond cleavage. The differential equations resulting from the proposed pathways were fit to experimental results to determine the kinetic rate constants [31]

3.4 Hydrothermal upgrading catalyst

3.3.1 Hydrothermal upgrading of wood biomass: Influence of the addition of K_2CO_3 and cellulose/lignin ratio

Bhaskar*et al*. (2008) studied to treat two different kinds of wood biomass, cherry (hardwood) and cypress (softwood) with K_2CO_3 as catalyst. Main compositions of raw material are lignin, cellulose and hemicelluloses. This experiments varied concentration of K_2CO_3 in a range 0 – 1 M, and fixed temperature at 280 º C for 15 min of reaction time. The result, K_2CO_3 0.5 M condition was the optimal concentration to improve % yield of product and % conversion of raw material [32]

3.3.2 5-Hydroxymethylfurfural production from sugars and cellulose in acid- and base-catalyzed conditions under hot compressed water

Daorattanachai et al. (2012) studied the conversion of glucose, fructose, and cellulose to 5-hydroxymethylfurfural (HMF) under hot compressed water condition. The effect of acidic (H_3PO_4) and alkaline (NaOH) catalysts was investigated by combining experimental and theoretical studies. The experimental results showed that formation of HMF from fructose is more active than that from glucose and cellulose. The effect of catalysts on reaction mechanism and energy profile of glucose transformation were explained from density functional calculations [33]

CHAPTER IV

EXPERIMENTAL

This chapter describes the experimental procedure in this research. This chapter is separated into four sections; raw materials and chemical, reactor and equipments, experiment conditions and analyze.

4.1 Raw material and chemical

4.1.1 Raw material

Biomass sample is secondary pulp/paper sludge supplied from Norske Skog Thailand Co,Ltd. For better control of initial sludge concentration, the sludge is subject to filtration and drying in an oven at 105 ºC overnight so as to completely remove the contained water. For use in each experiment, the dried solid will be ground by a household blender (Moulinex) into fine powder and screened. The content of cellulose in feedstock will be determined following the procedure recommended by The Technical Association of Pulp and Paper Industry (TAPPI).

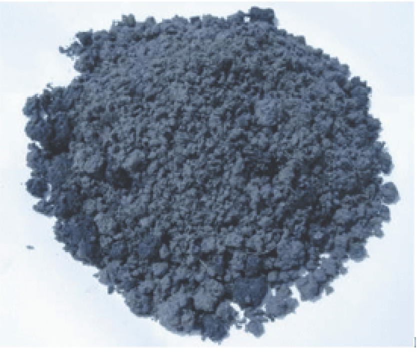


Figure 4.1 Pulp and paper sludge

Table 4.1 Compositions of Pulp and Secondary pulp and paper sludge (Over 840, 595-840 and Lower 595 μm) by TAPPI

	Pulp	Sludge (μm)		
		840	595-840	595
Cellulose	0.48	0.40	0.33	0.20
Hemicellulose	0.23	0.23	0.25	0.27
Lignin	0.17	0.18	0.20	0.19
$CaCO_3$	0.07	0.17	0.21	0.32
		S1	S1	S3

4.1.2 Chemicals

The glucose standards were obtained from Wako Chemical Co. (Osaka). The 5-hydroxymethylfurfural was obtained from Sigma–Aldrich Japan (Tokyo). Inorganic, calcium carbonate ($CaCO_3$) was obtained from Sigma–Aldrich.

4.2 Reactors and equipments

4.2.1 Tubular reactor

Reactions were carried out in type-316 stainless steel tube bomb reactors made from 1inch o.d. tubing (Swagelok Co., 1/2-inch) that had an inner volume of 100 cm3 (Figure 4.2), heated up by an electric furnace and its temperature was recorded every 1 minute.

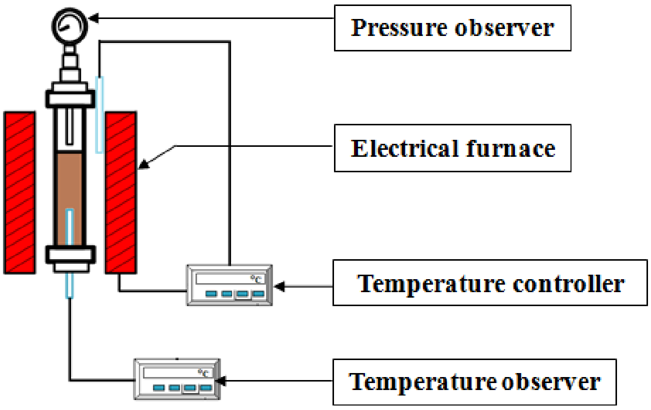


Figure 4.2 Tubular bomb reactor

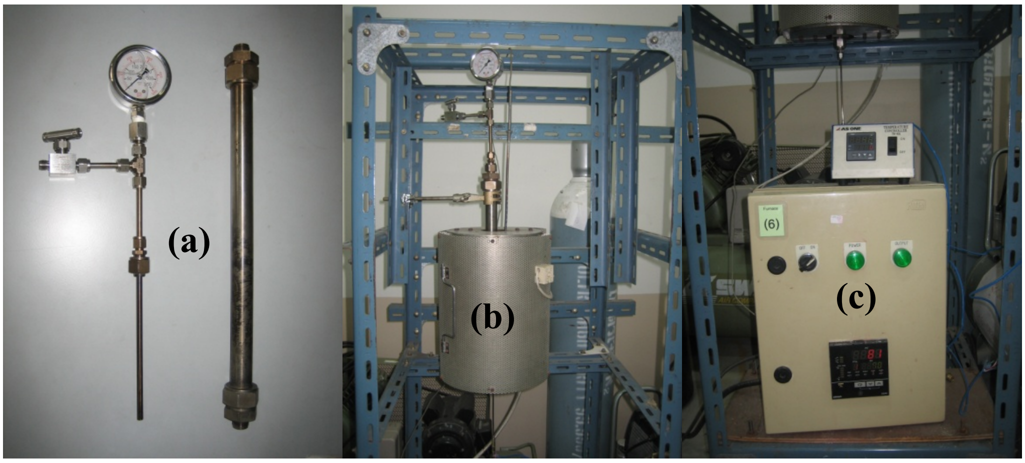


Figure 4.3 Reactors and equipments (a) Tubular reactor with pressure gauge, (b) Electric furnace and (c) Temperature controller and observer

4.2.2 Vacuum suction flask set

Products from hydrothermal process were separated into solid residue and liquid products. Figure 4.4 shows a vacuum suction flask, of which including flask, and vacuum pump for separating the solid products from the liquid products.

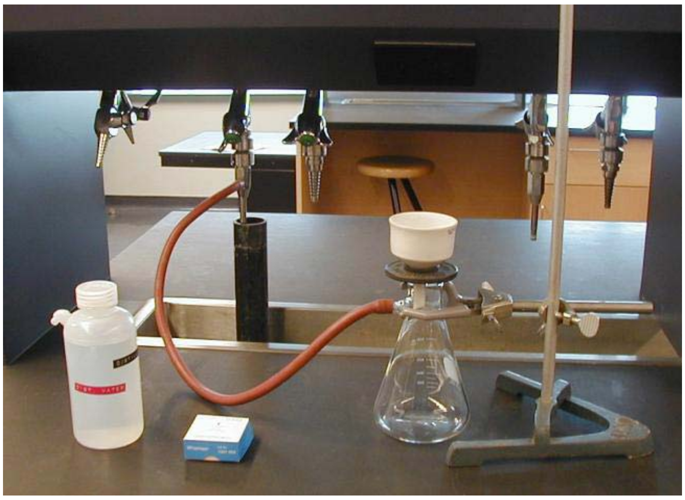


Figure 4.4 Vacuum suction flask set for separation of solid from liquid samples

4.2.3 Cellulose acetate syringe filter for filtration

The solid products were the particles suspended in the liquid products or precipitated under bottom of storage bottles. The former was obtained by filtering the liquid product through cellulose acetate membranes (0.45 µm pore size) as shown in Figure 4.5.

Figure 4.5 Cellulose acetate syringe filter 0.45 µm pore size

4.2.4 A hot air oven for drying

The solids residue after filtration was dried in a hot air oven (as shown in Figure 4.6) at 105°C until constant weight. After a drying step, the solids residue was cooled down to room temperature and collected in a desiccator for preventing them from moisture.

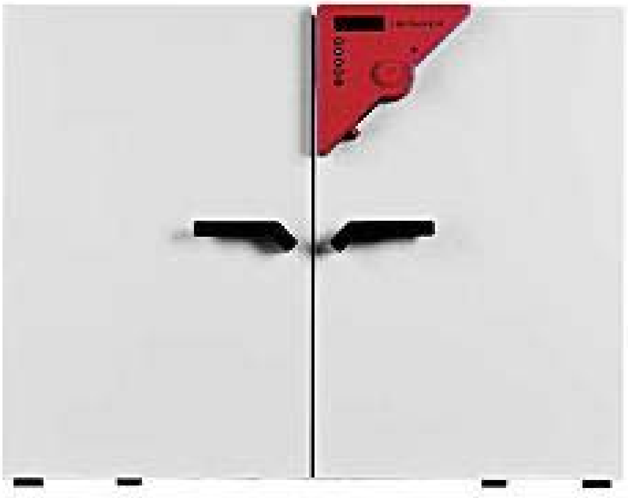


Figure 4.6 The hot air oven for dry solids residue

4.3 Experimental conditions

4.3.1 The effect of reaction temperature in a range of 200 – 260 °C

At first, in this study, the effects of reaction temperature on a hydrothermal treatment of pure pulp and SPP have been investigated. By varies in a range of 200 – 260 °C to find out the optimal temperature of this process. Table 4.2 shows the condition for studied on the effect of reaction temperature.

Table 4.2 Reaction temperature conditions for the hydrothermal treatment

Hydrothermal treatment	
Temperature (º C)	200, 220, 240, 260
Particles size of SPP (µm)	Over 841, 595-841, lower 595
Reaction time (min)	0

4.3.2 The effect of holding time

By varies the holding time 0, 10, 20 30 and 40 minutes. The holding time could be identified for glucose yields optimization. Table 4.3 shows the holding time condition.

Table 4.3 Holding time conditions for the hydrothermal treatment

Hydrothermal treatment	
Temperature (º C)	200, 220, 240, 260
Particles size of SPP (µm)	Over 841, 595-841, lower 595
Reaction time (min)	0, 10, 20, 30, 40

4.3.3 The effect of classified secondary pulp and paper sludge size

Four size of pure pulp and secondary pulp and paper sludge as received, P, S1, S2 and S3 from screening section. The compositions of pure pulp and secondary pulp and paper sludge are different in cellulose, hemicelluloses, lignin and $CaCO_3$. However amount of cellulose content decreased with decreasing particles sizes, $CaCO_3$ increased. The optimal condition of particle size was observed in the same time with react temperature and holding time effects.

4.3.4 The effect of calcium carbonate ($CaCO_3$) adding

SPP S2 is added with pure $CaCO_3$, varied amount of $CaCO_3$ in ranging from 0-0.6 gram for the hydrothermal treatment. When we know the optimal temperature and particles size therefore they were used in this condition for studied the effect of $CaCO_3$ on the hydrothermal treatment. Table 4.4 shows the $CaCO_3$ adding conditions.

Table 4.4 $CaCO_3$ adding conditions for the hydrothermal treatment

Hydrothermal treatment	
Temperature (° C)	220
Particles size of SPP (µm)	595-841
Reaction time (min)	0, 10, 20, 30, 40
Pure $CaCO_3$ Adding (g)	0, 0.3, 0.6

4.3.5 The effect of adding catalyst on hydrothermal treatment: 0, 0.25, 0.5, 1 %wt of CH_3COOH

In this study, at first, the content of lignin in palm kernel shell residues were varied by varying the reaction time in the elimination of lignin step and then the content of lignin in treated palm kernel shell residues were determined by the USDA's method. Table 4.4.4 illustrates the effect of lignin content conditions.

Table 4.5 CH_3COOH-adding conditions for the hydrothermal treatment

Hydrothermal treatment	
Temperature (º C)	220
Particles size of SPP (µm)	595-841
Reaction time (min)	0, 10, 20, 30, 40
Catalyst CH_3COOH (% wt)	0, 0.25, 0.5, 1

4.4 Analyze

4.4.1 High performance liquid Chromatography analysis (HPLC)

Identification and quantification of organic compounds and liquid reaction products in the aqueous phase were performed with high-performance liquid chromatography (HPLC). Columns preveil carbonyl 250x4.6 mm with reflextive index (RI) detector and 69 % acetonitrile: 31 % H_2O was use as mobile phases were needed to detect the saccharides. 5-HMF was measure with a fluorescent detector and an Octadecyl Silane (ODS) C18 column. Sample size was 20 μl. The amount of glucose and -5HMF were determined from calibration curves, obtained by analyzing standard solution with known amount.

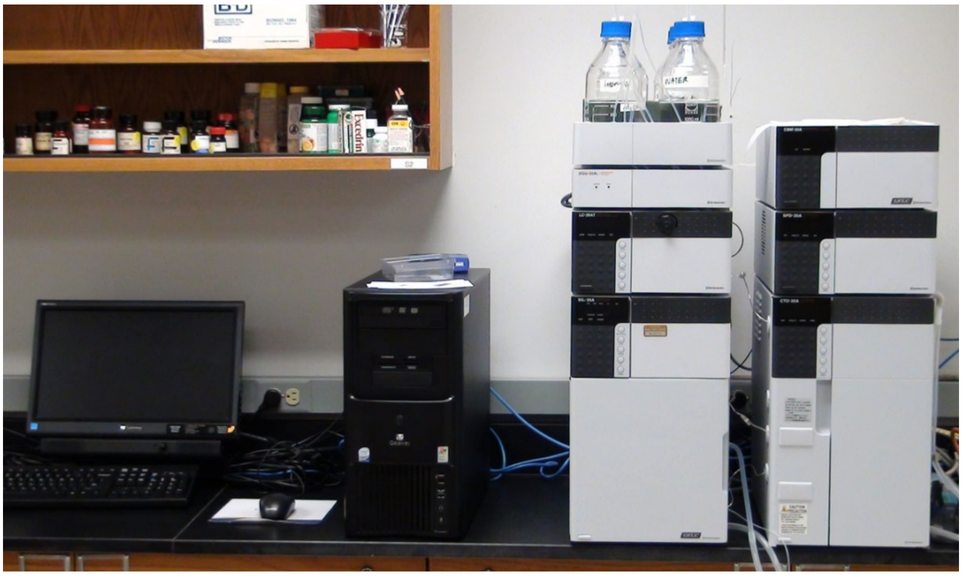


Figure 4.7 High performance liquid chromatography analyzer (HPLC)

4.4.2 Total organic carbon analysis (TOC)

The liquid products were also analyzed by a total organic carbon (TOC) analyzer (Shimadzu TOC-V CHP) to quantify the amounts of organic carbon and In-organic carbon in the liquid products. Standards were standard total carbon (STD TC) and standard inorganic carbon (STD IC). Potassium hydrogen phthalate (KHP) which was dried at 105°C for 1 h. was dissolved with ultra pure water to obtain STD TC (10-1000 ppm). A mixture of sodium bicarbonate which was calcined at 280°C for 1 hr and sodium carbonate which was desiccated for 2 h at 1.60 mole ratio, was dissolved to obtain STD IC (10-1000 ppm). A 2 Molar of Hydrochloric acid and 25 %v/v of phosphoric acid were used for non-purgeable organic carbon analysis. An air zero gas was used to decompose organic carbon to CO_2 gas for detecting. The following conditions were used for the analysis: carrier gas flow rate and pressure were 150 ml/min and 200 kPa, respectively; the oven temperature 686-700°C.

Figure 4.8 Total organic carbon (TOC) analyzer (Shimadzu TOC-V CHP)

4.4.3 Inductively coupled plasma spectroscopy (ICP)

Concentration of inorganic material (Ca) was determined with inductively coupled plasma (ICP) spectroscopy.

Figure 4.9 Inductively coupled plasma spectroscopy (ICP)

4.4.4 Scanning electron microscope (SEM)

Scanning electron microscope (SEM) was used to visually observe CMS particles by placing them onto conductive carbon tape. Morphologies and shapes of the CMS particles, therefore, were characterized by Scanning Electron Microscope (*SEM, JEOL: JSM-5410LV, Japan*) as shown in Figure 4.10.

Figure 4.10 Scanning electron microscope (*SEM, JEOL: JSM-5410LV, Japan*)

4.4.5 TAPPI standard test method

The raw materials were analyzed by TAPPI method for preliminary composition of cellulose, hemicellulose, lignin and calcium carbonate. The solid residues after hydrothermal treatment were analyzed by TAPPPI method for measuring cellulose and hemicelluloses remaining in residue and these values used for determining carbon balance. The product yields and conversion of cellulose were calculated from following equation

$$\text{Yields}\,(\%) = 100\left(\frac{\text{Carbon wt. of glucose or 5 - HMF in liquid product}}{\text{Carbon wt. of Holocellulose in feed stock}}\right) \qquad (1)$$

$$\text{Conversion}\,(\%) = 100\left(\frac{\text{Carbon wt. of cellulose in feedstock - in solids residue}}{\text{Carbon wt. of cellulose in feedstock}}\right) \qquad (2)$$

4.4.6 Experiment procedure.

Figure 4.11 gives an overview of the product analyses used in this study

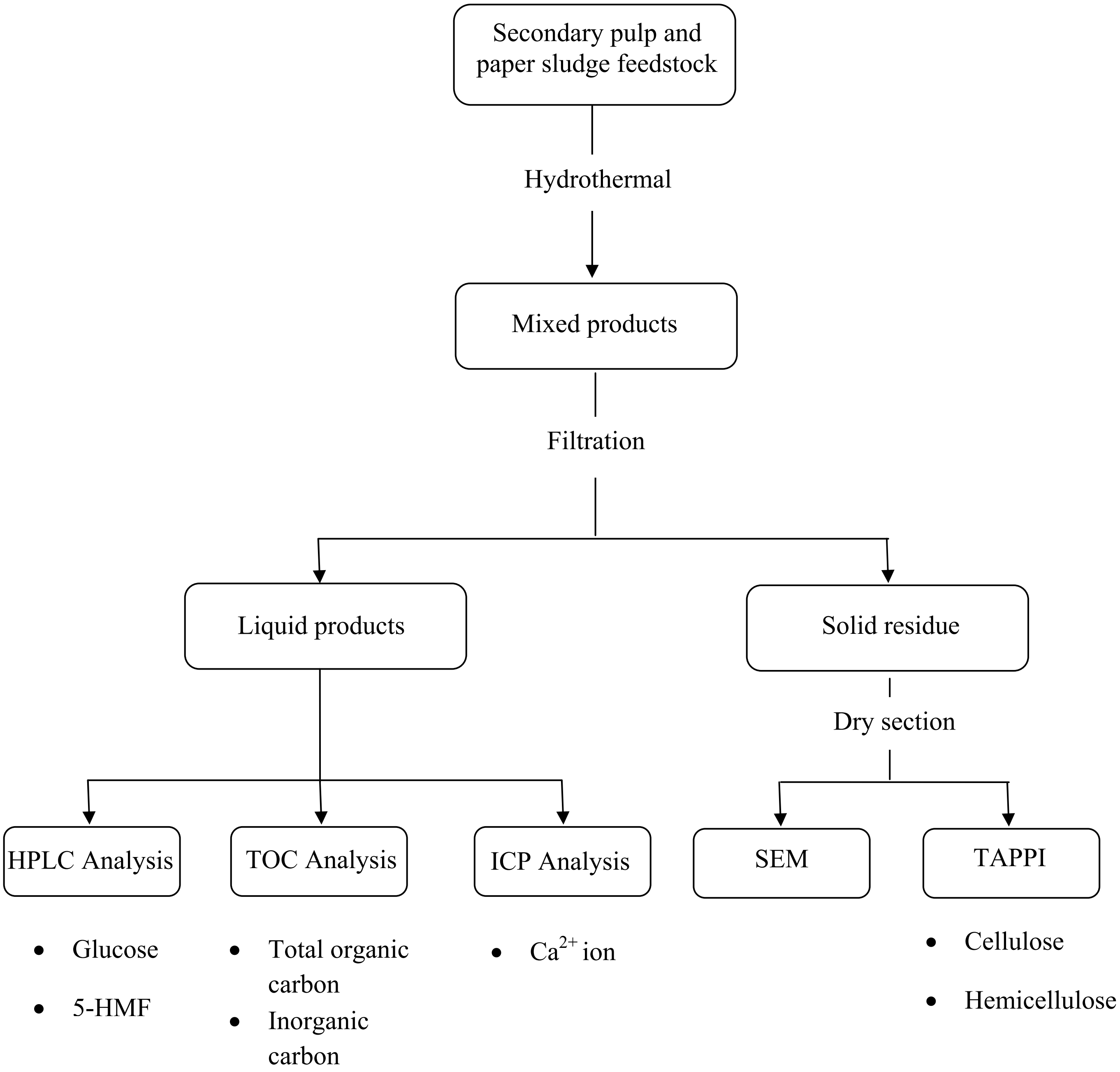


Figure 4.11 Schematics of an overview of product characterizations

CHAPTER V

RESULTS AND DISCUSSIONS

Effects of reaction temperature, holding time, particle size, calcium carbonate ($CaCO_3$) and catalyst (CH_3COOH), as well as characterizations of typical liquid products are discussed below.

5.1 Composition of Secondary pulp and paper sludge (SPP)

Secondary pulp and paper sludge (SPP) is the residue produced in the biological treatment process of wastewaters from the pulp/ and paper industry, mainly consisting of fibers, fines and fillers ($CaCO_3$).

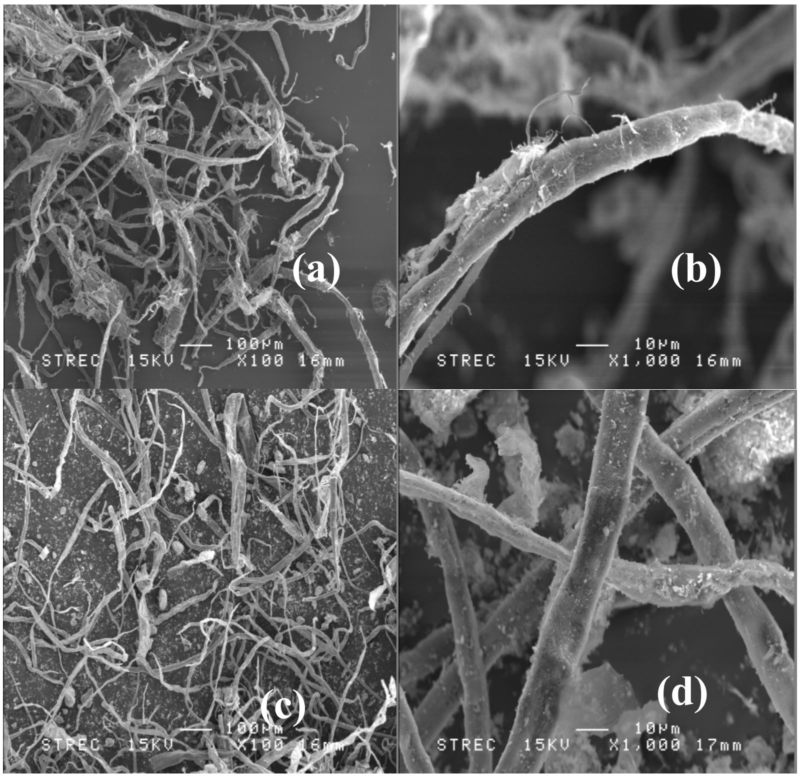


Figure 5.1 Images of pure pulp and Secondary pulp/paper sludge (by Scan electron microscope, SEM)

(a) Pulp x 100, (b) Pulp x 1,000, (c) Sludge x 100, (d) Sludge x 1,000

Table 5.1 Compositions of pure pulp and secondary pulp and paper sludge after screening (lower 595, 595 - 841, over 841 μm) by TAPPI

	Pulp	Sludge (μm)		
		840	595-840	595
Cellulose	0.48	0.40	0.33	0.20
Hemicellulose	0.23	0.23	0.25	0.27
Lignin	0.17	0.18	0.20	0.19
$CaCO_3$	0.07	0.17	0.21	0.32
	P	S1	S1	S3

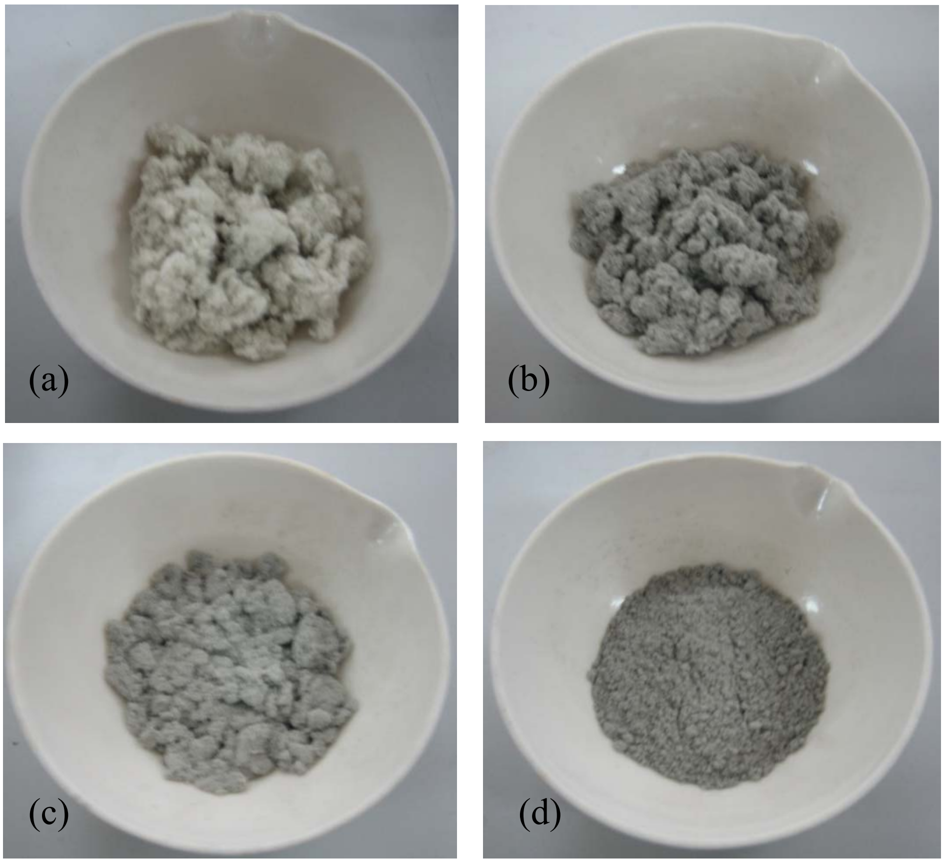


Figure 5.2 Pulpand Secondary pulp and paper sludge after screen (lower 595, 595 - 841, over 841 μm)

(a) Pulp P, (b) SPP S1,(c) SPP S2, (d) SPP S3

From Figure 5.1, pure pulp looks similar to secondary pulp and paper (SPP) but SPP has some small particles of calcium carbonate ($CaCO_3$). From Table 5.1 shows the components of the pure pulp and the secondary pulp and paper sludge powder (dry weight basis) and figure 5.2 show solids samples pure pulp (P), secondary pulp and paper sludge (SPP) S1, S2 and S3 after screening, respectively. The compositions were determined by the United States Department of Agriculture method (TAPPI's method). There are pure pulp (P), SPP sizes over 840 μm (S1), SPP sizes 595-840 μm (S2), SPP sizes lower 595 μm (S3) which has mainly cellulose reactant content 0.48, 0.40, 0.33 and 0.20 respectively.

5.2 The effect of reaction temperature

5.2.1 Temperature history

At first, all sizes of pulp and paper sludge were treated by hydrothermal treatment method under conditions of temperature from 200 to 260 °C. Figure 5.1 show the temperature history inside tubular reactor.

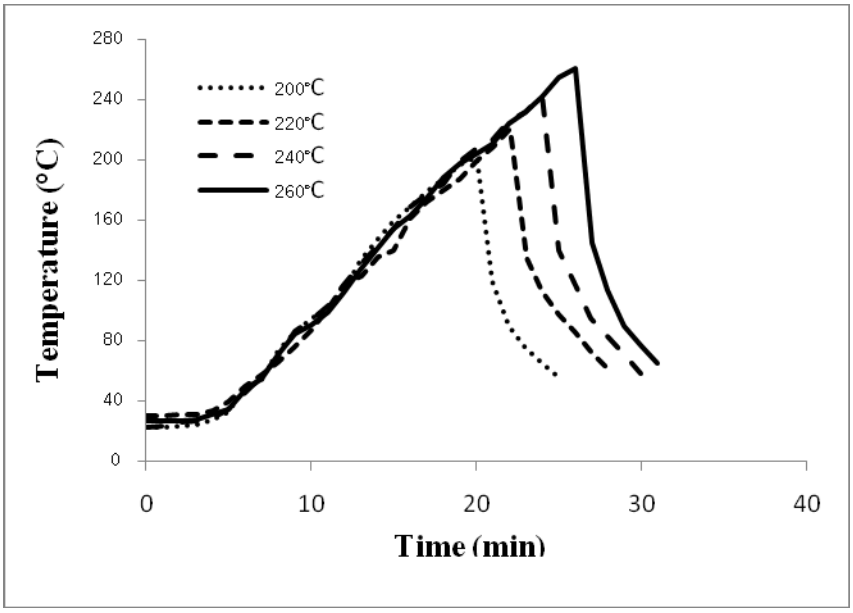


Figure 5.3 Temperature history in different target temperature

From Figure 5.4 show samples pure pulp, SPP S1, SPP S2 and SPP S3 respectively before hydrothermal treatment. And Figure 5.5 show samples after hydrothermal treatment. In each experiment, solid sample and liquid sample were separated by filtration. Base on visualization, the higher the operating temperature, obtained darker the color of the liquid product. Appearance of the liquid products were shown in Figure 5.6

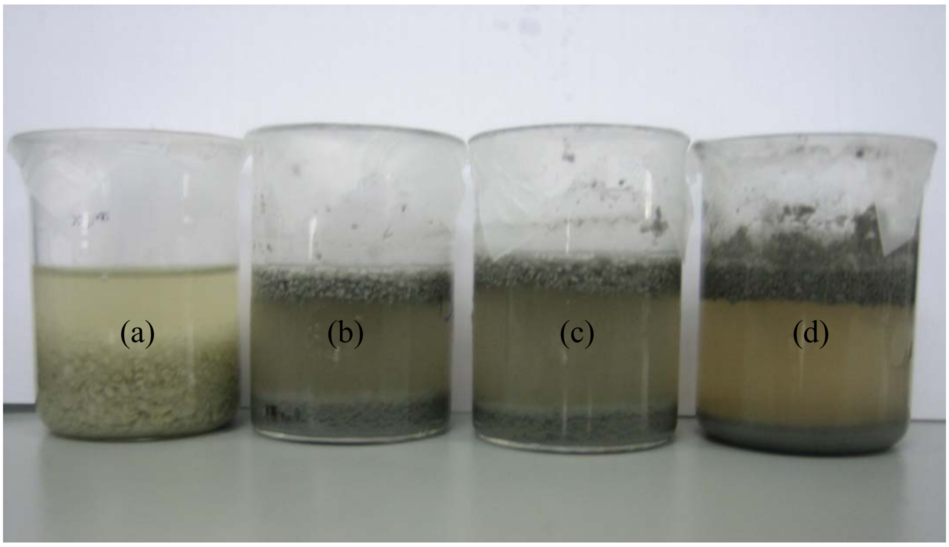


Figure 5.4 Feed stock before hydrothermal treatment at different particles size
(a) Pure pulp, (b) Pulp and paper sludge size over 841 μm,
(c) Pulp and paper sludge sizes 595-841 μm, (d) Pulp and paper sludge size under 595 μm

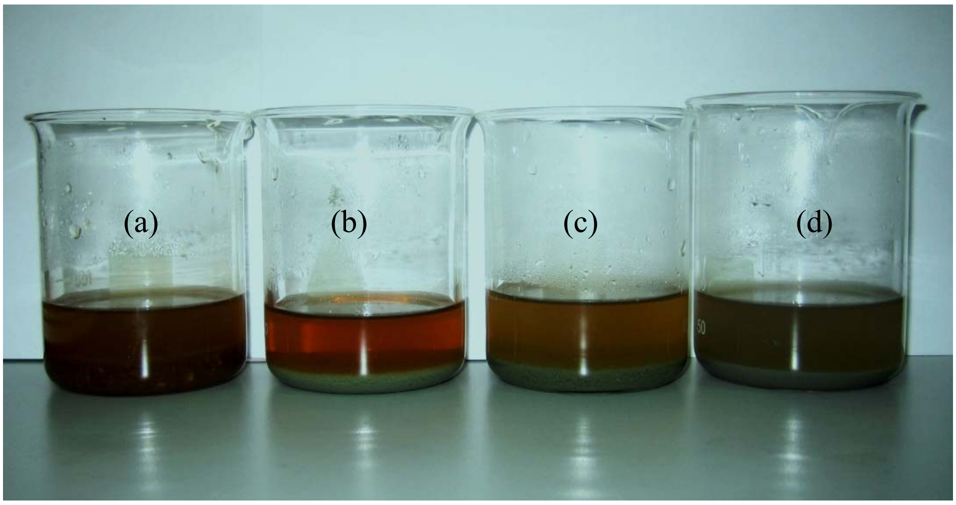


Figure 5.5 Mixed samples after hydrothermal treatment at different particles size
(a) Pure pulp, (b) Pulp and paper sludge size over 841 μm,
(c) Pulp and paper sludge sizes 595-841 μm, (d) Pulp and paper sludge size under 595 μm

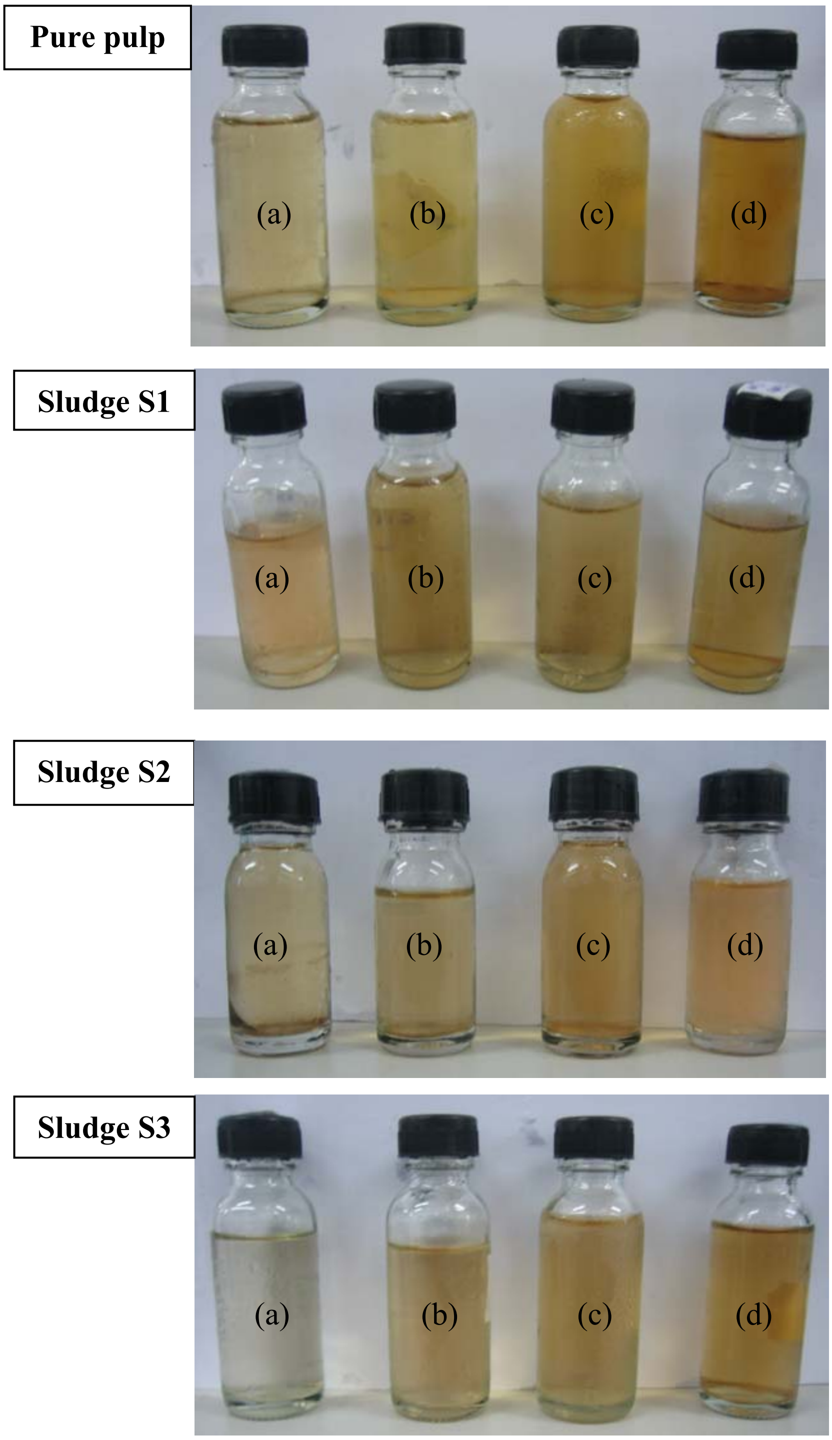
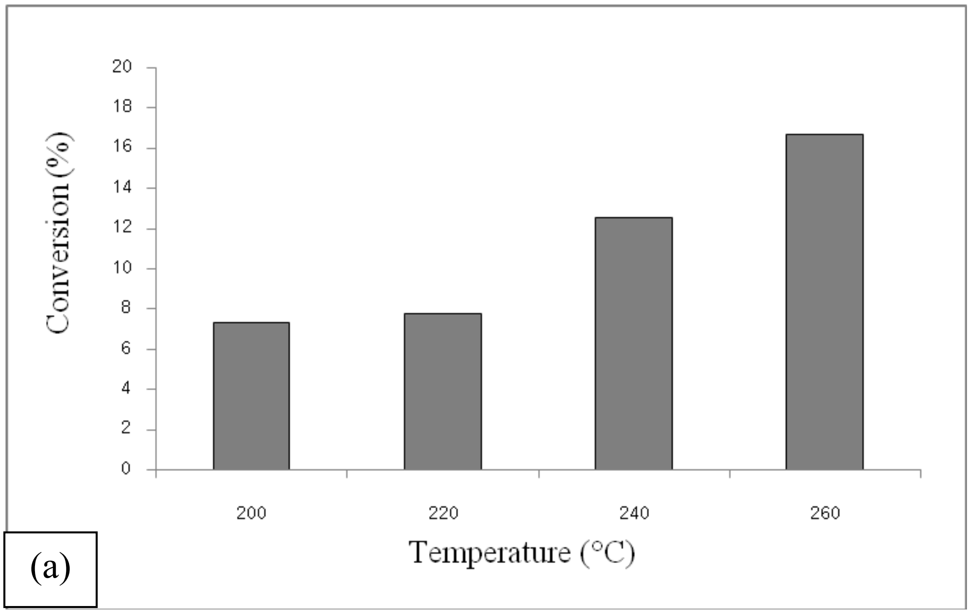


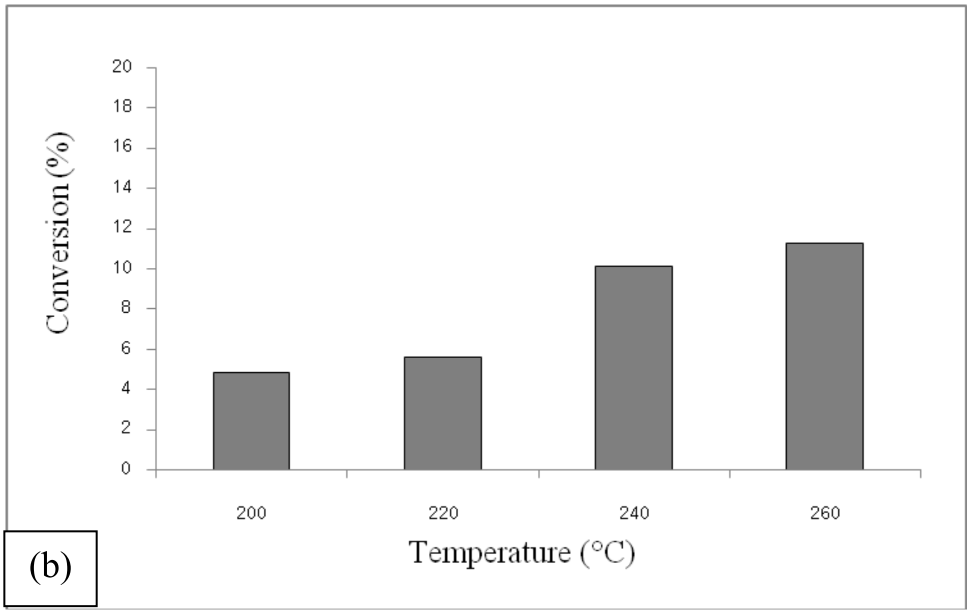
Figure 5.6 Color of liquid products after hydrothermal treatment in different reaction temperature

(a) 200 °C, (b) 220 °C, (c) 240 °C, (d) 260 °C

5.2.2 Effect of reaction temperature on conversion of cellulose

In this study, solid sample was sampled for examination on hydrolysis. The liquid extract obtained from solid sample was analyzed by TOC analysis. Figure 5.7 shows the percentage of cellulose conversion with reaction temperature in each particles size.





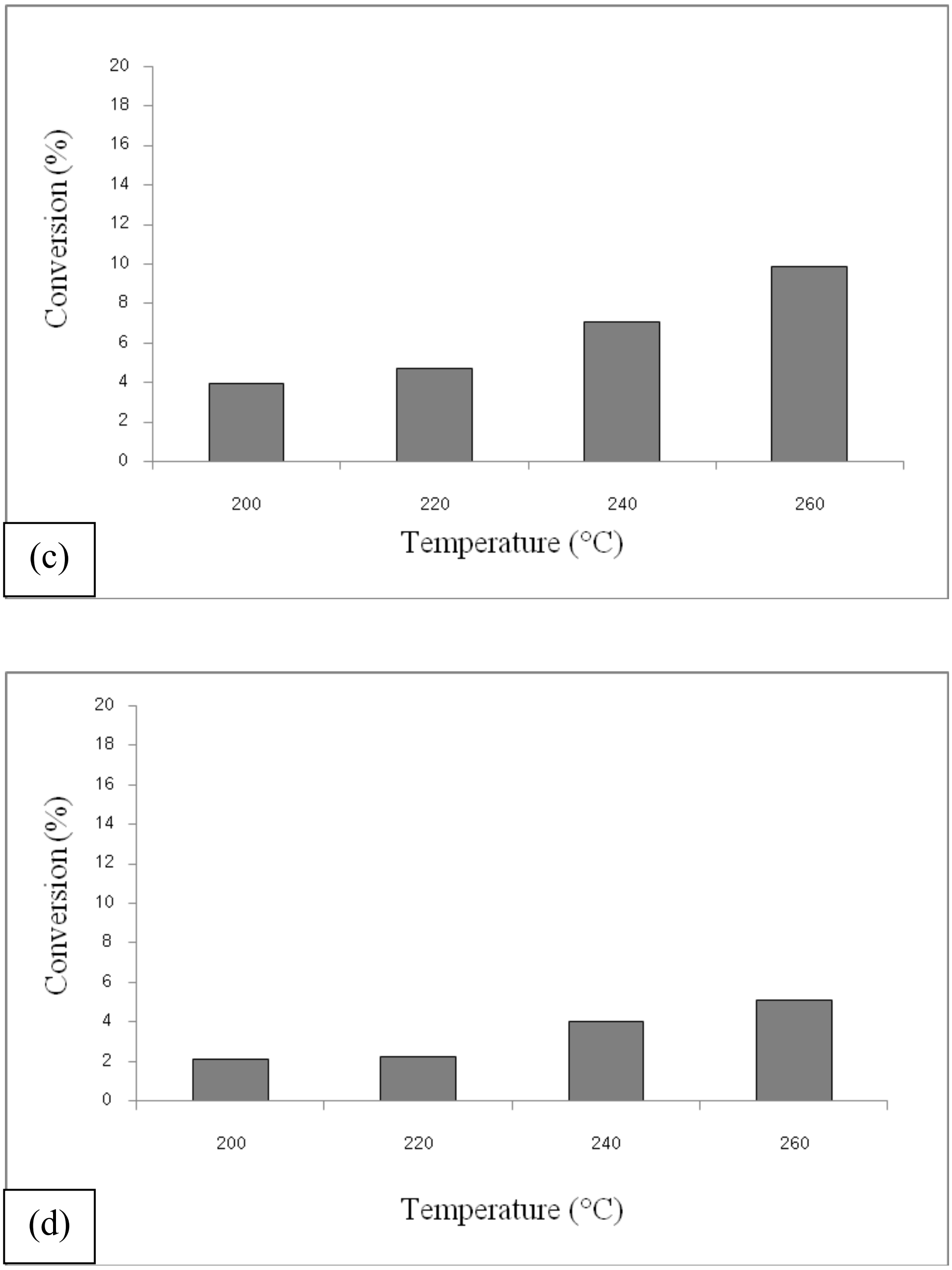
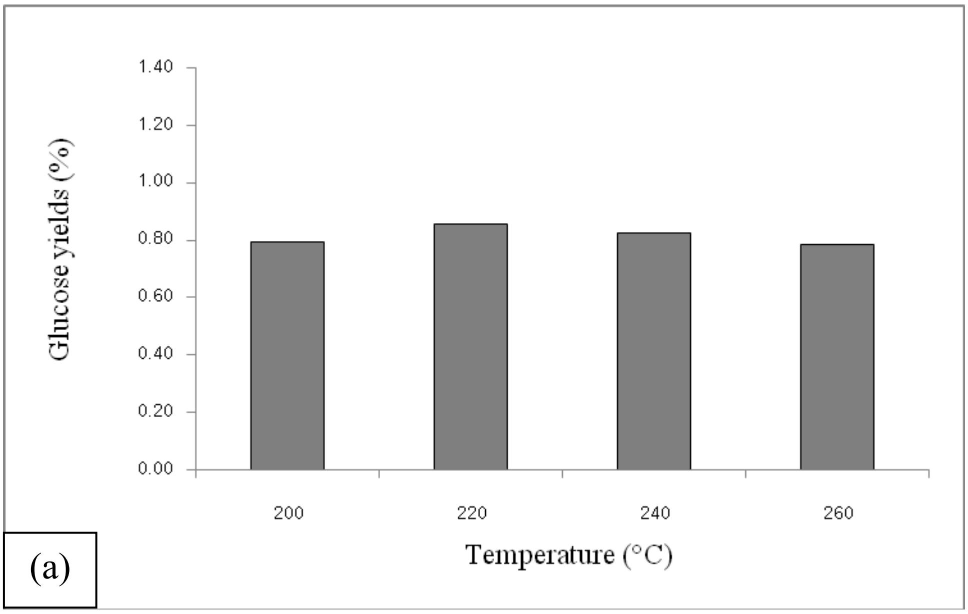


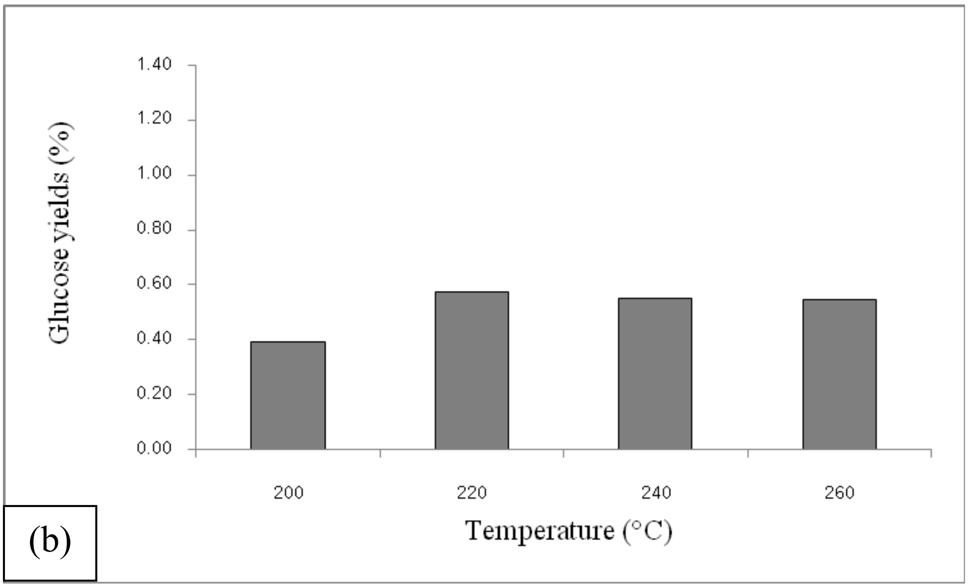
Figure 5.7 Cellulose conversion from raw material with time on varied with different temperature in the range of 200-260°C
(a) Pulp P, (b) SPP over 841 μm S1,
(c) PP 595 - 841 μm S2, (d) SPP lower 595 μm S3

The effect of reaction temperature hydrothermal treatment in temperature on the conversion of cellulose is shown in Figure 5.7 which presents results obtained from the hydrothermal operation at various temperatures ranging from 200 to 260°C (subcritical water) for a same heating rate of 10 °C/min without catalyst in each size where the amount of cellulose was all fixed. At all conditions, the conversion of cellulose increase with increasing reaction temperature. The conversion of cellulose was in a range 4-18 %. It was found that an increase in the treating temperature resulted in a gradual increase in conversion of cellulose. These results suggest that the increase in the temperature improves hydrolysis of cellulose.

5.2.3 Effect of reaction temperature on glucose products

The liquid extract obtained from solid sample was analyzed by HPLC analysis for glucose production. Figure 5.8 shows the glucose yield with reaction temperature.





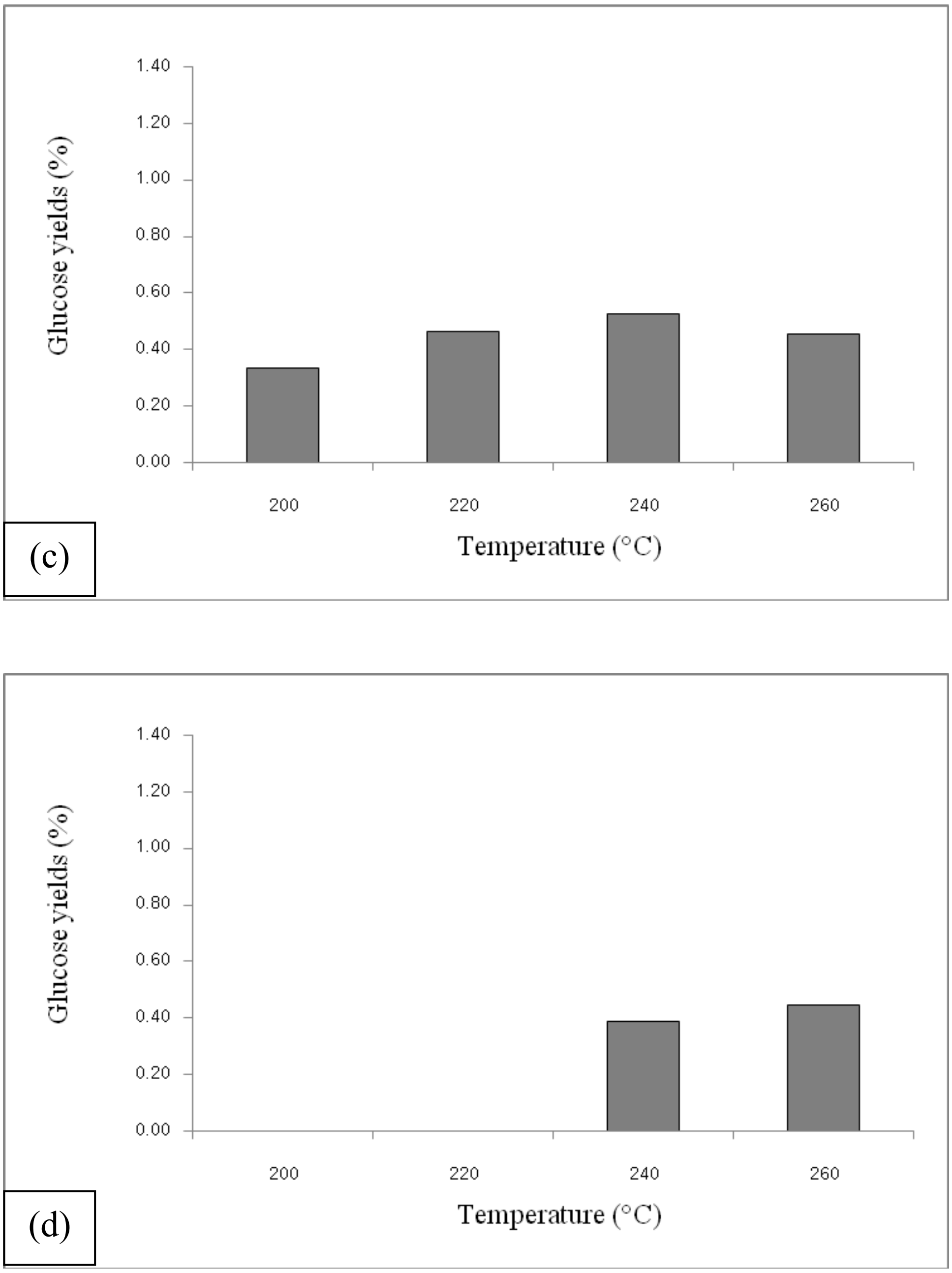
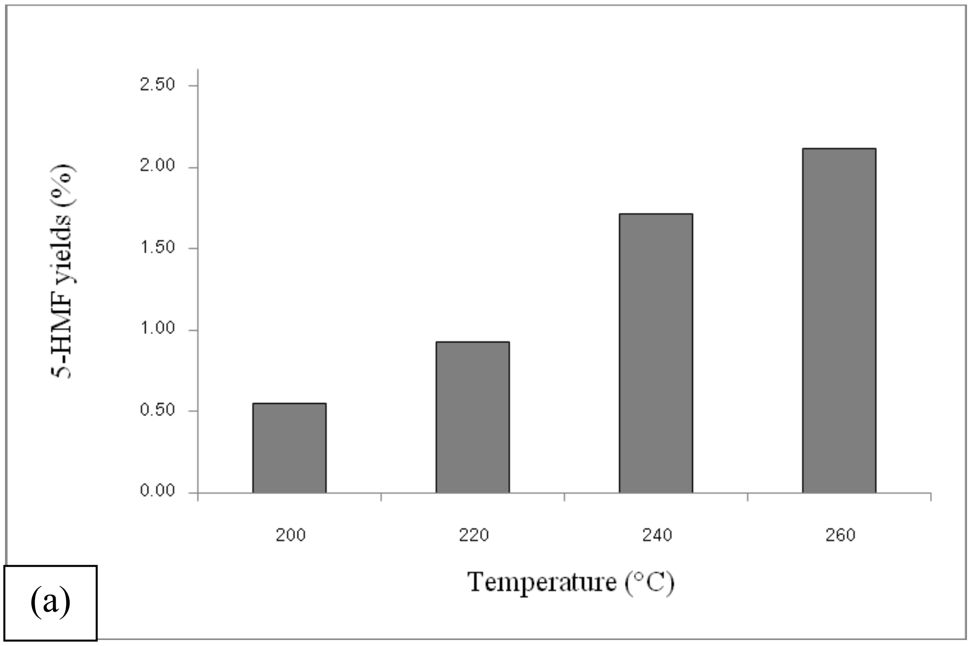


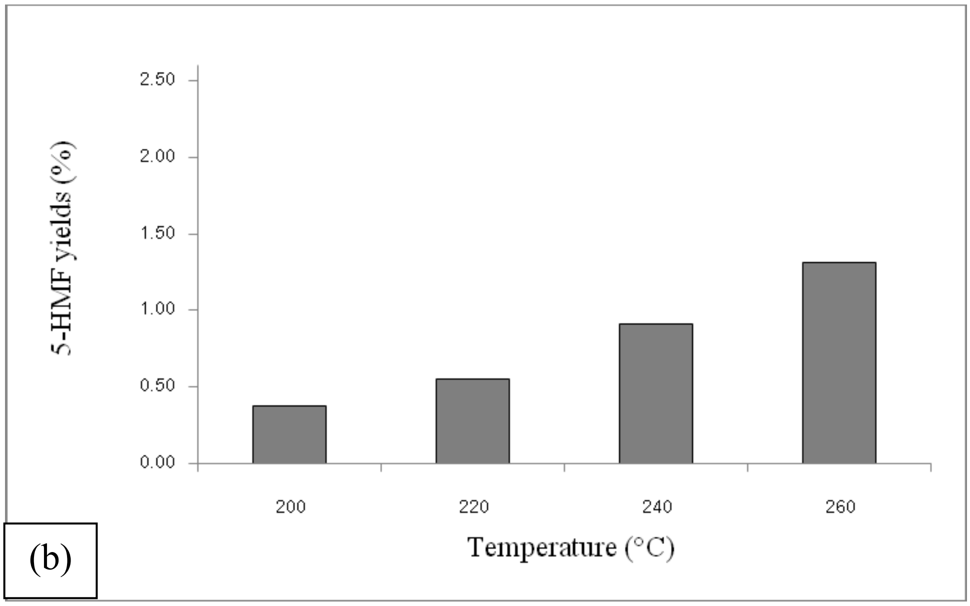
Figure 5.8 Yield of glucose produced from samples with time on varied with different temperature in the range of 200 – 260 °C
(a) Pulp P, (b) SPP over 841 µm S1,
(c) PP 595 - 841 µm S2, (d) SPP lower 595 µm S3

To obtain the highest product yield, it is necessary to optimize the reaction conditions by varying the reaction temperature. The reaction was implemented at various temperatures (200–260 °C) in without catalyst. For particles sizes P and S1, at 200 and 220 °C, glucose yield increased with reaction temperature but at temperature higher than 220 °C, glucose yield gave the opposite results. The yield of glucose was very low at about 0.4–0.8 %wt. The maximum yields of pure pulp and SPP S1 were 0.85 and 0.57 % respectively. For S2 the highest glucose yield was at 240 °C and in a range 04-06 %wt. On the other hand, S3 has highest $CaCO_3$ content, the glucose yield was close to 0% at 200-220 °C and increase at 240-260 °C in a range 0.4-05 %. For SPP, the maximum yields for glucose was 0.6 % in 20 min at 220 °C from S1.

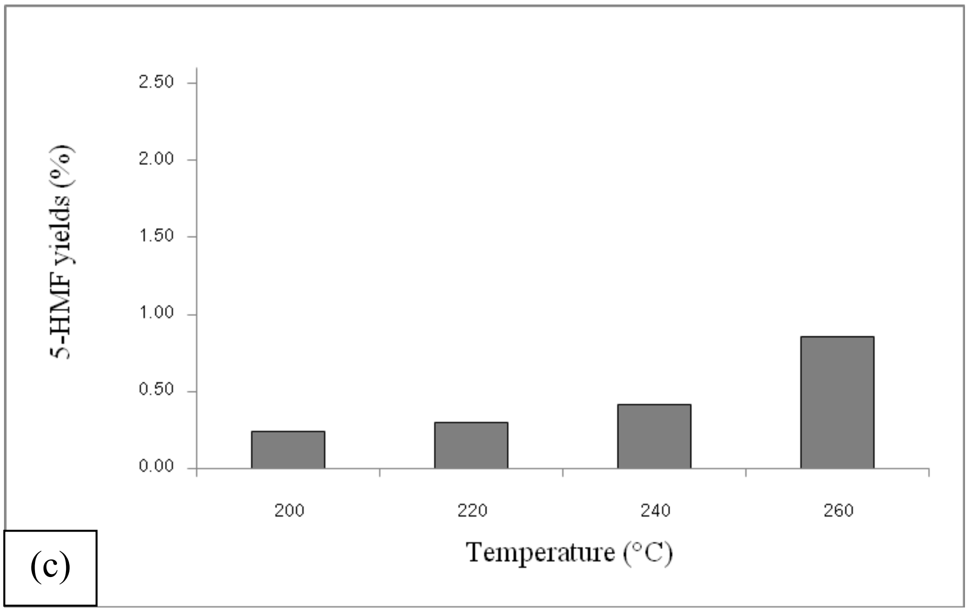
5.2.4 Effect of reaction temperature on decomposition products 5-HMF



(a)



(b)



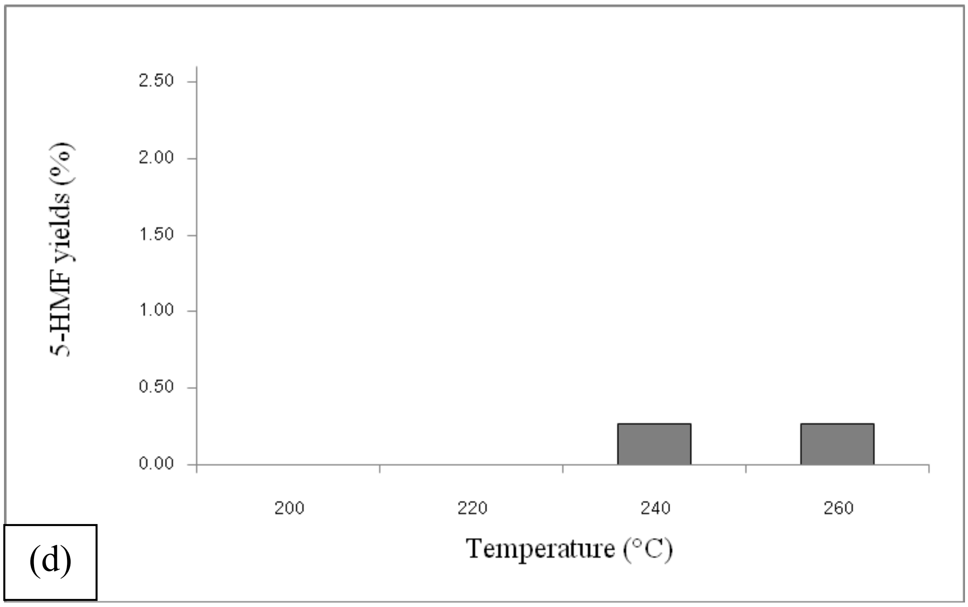


Figure 5.9 Yields of 5-HMF produced from samples with time on varied with different temperature in the range of 200 – 260 °C
(a) Pulp P, (b) SPP over 841 µm S1,
(c) PP 595 - 841 µm S2, (d) SPP lower 595 µm S3

Sakaki et al. [10] studied cellulose hydrolysis in subcritical and supercritical water and found that the decomposition product of glucose are fructose, 5-HMF and etc. In this study, 5-HMF yields increased dramatically with reaction temperature in every size of raw material. These results suggest that cellulose hydrolysis produces glucose and glucose decompose to 5-HMF.

5.2.5 Comparison glucose and 5–HMF yields

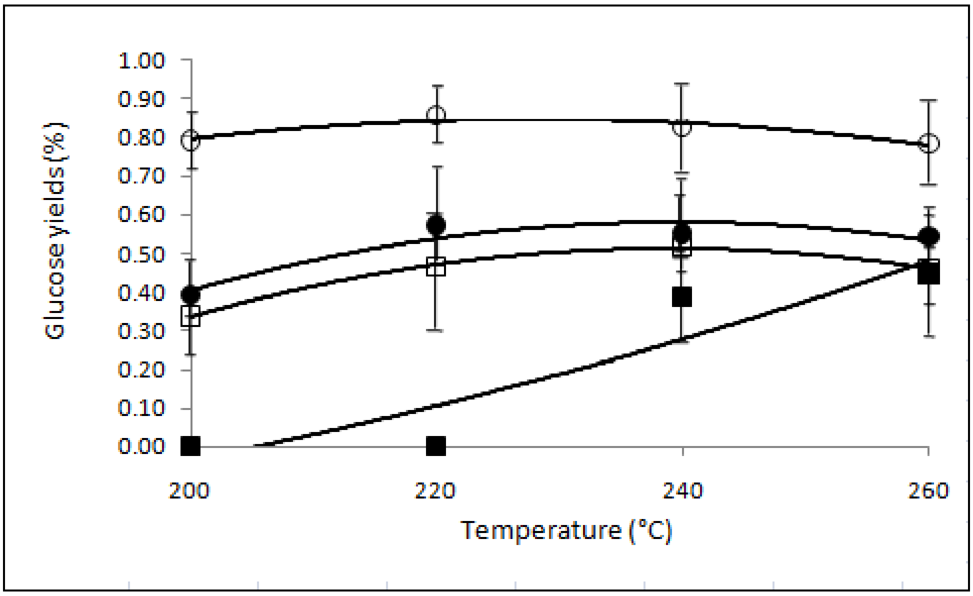


Figure 5.10 Effects of temperature on the glucose yields in the liquid product of Secondary pulp and paper sludge hydrothermal treated in different temperature: ○ Pulp,● over 841 µm,☐ SPP 595 - 841 µm, ■ SPP lower 595 µm

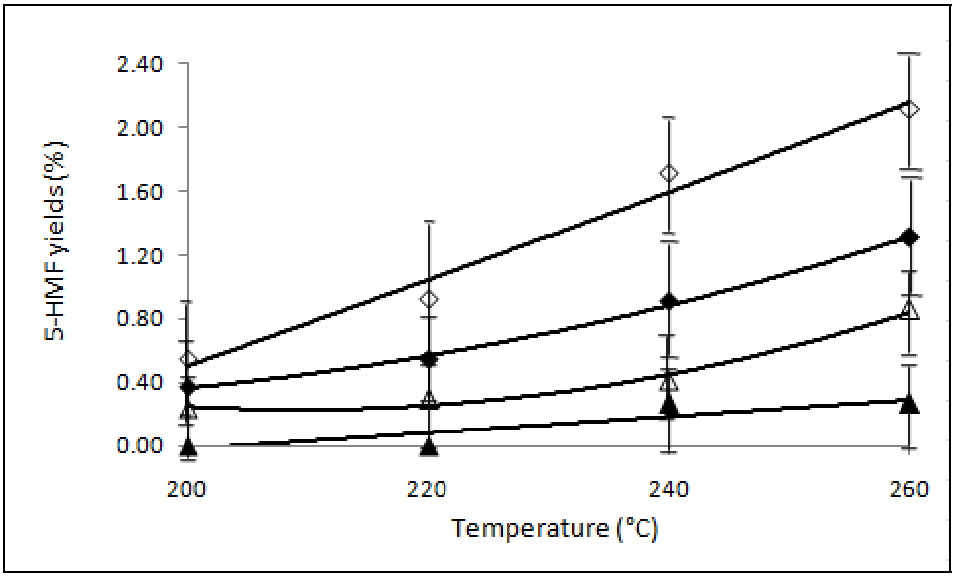


Figure 5.11 Effects of temperature on the glucose yields in the liquid product of Secondary pulp and paper sludge hydrothermal treated in different temperature: ◇ Pulp,♦ SPP over 841 µm, △ SPP 595 - 841 µm, ▲SPP lower 595 µm

Effect of reaction temperature in a range of 200-260 °C on production yields of glucose and 5-HMF is shown in Figure 5.10-5.11. It was found that an increase in the treating temperature resulted in a gradual decrease in glucose yield. However, Figure 5.9 shows that the production yield of 5-HMF became higher with the increased temperature. Regarding to characteristics of each classified secondary pulp and paper sludge, similar tendency was observed. These results would be ascribed to the competitive rate of conversion of cellulose to saccharides against decomposition of saccharides. Sasaki et al [10] revealed the glucose decomposition rate, at a high reaction temperature, the glucose or oligomer conversion rate is much faster than the hydrolysis rate of cellulose. Thus, the hydrolysis products, such as glucose or oligomers are formed, their further decomposition rapidly takes place to 5-HMF or other decomposition products and thus a high yield of hydrolysis products or glucose cannot be obtained. In this study, the reaction temperature range of 200-220 °C, amount of glucose converted from cellulose was comparatively faster than its decomposition, leading to the increasing yield of glucose. In addition, there is also possibility that glucose would be transformed to 5-HMF.

5.3 The effect of holding time

5.3.1 Temperature history

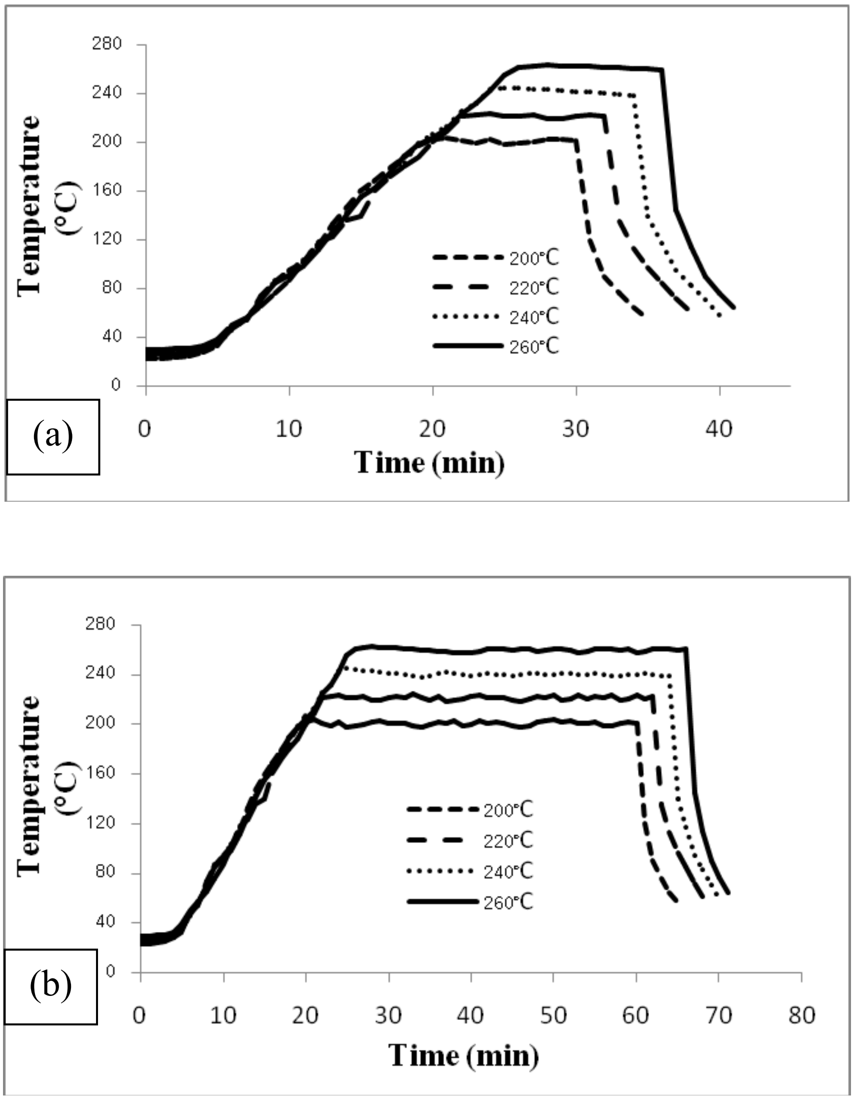


Figure 5.12 Temperature history in different target temperature with holding times (a) 10 minutes and (b) 40 minutes

Every sizes of pulp and paper sludge were treated by hydrothermal treatment method under conditions of temperature from 200 to 260 °C and holding time in a range of 0 – 40 minutes. Figure 5.12 shows the temperature history inside tubular reactor at 10 and 40 minutes of holding time.

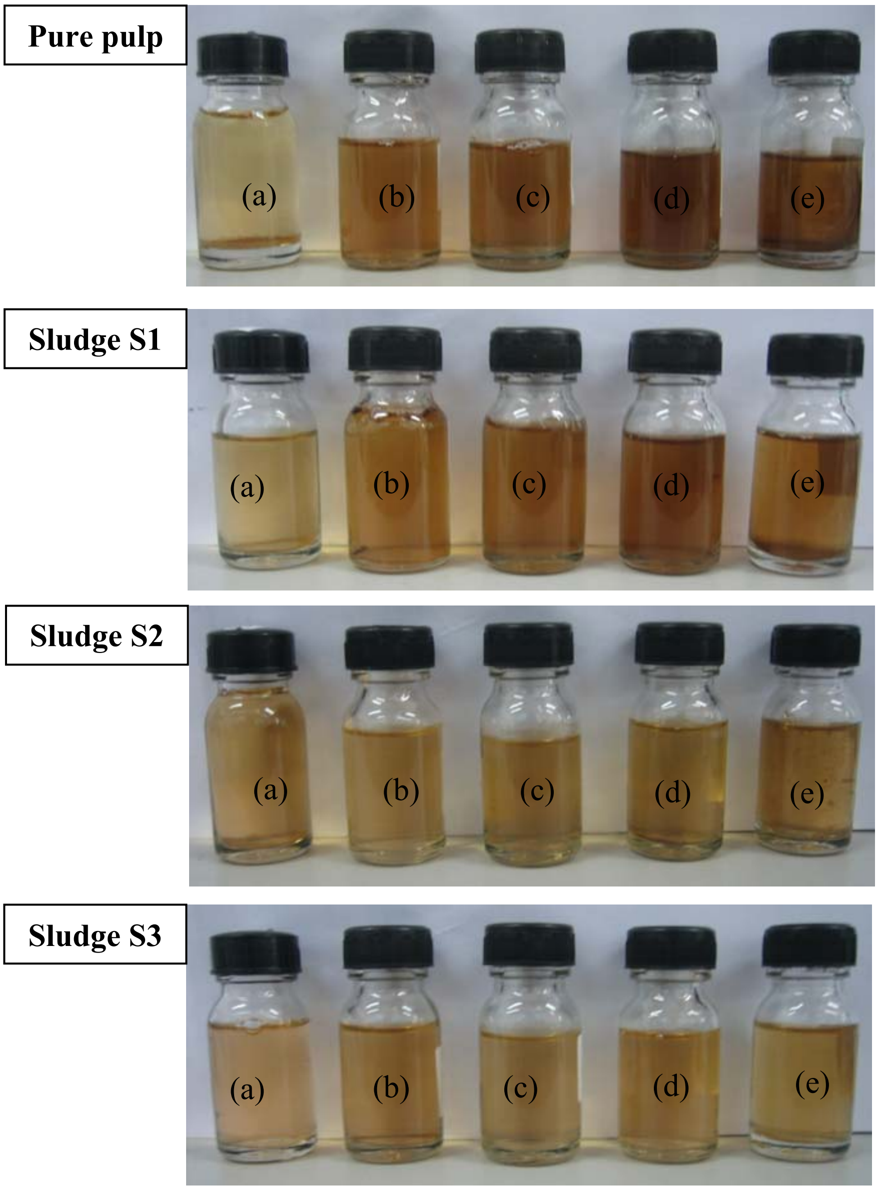


Figure 5.13 Liquid products after hydrothermal treatment at temperature 220 °C and different holding time

(a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min and (e) 40 min

The appearances of the liquid products were shown in Figure 5.13. Liquid products were separated from solids by filtration. Base on visualization, the higher the holding time, obtained darker color of the liquid product, but the smaller size of raw material pale down the color of liquid products.

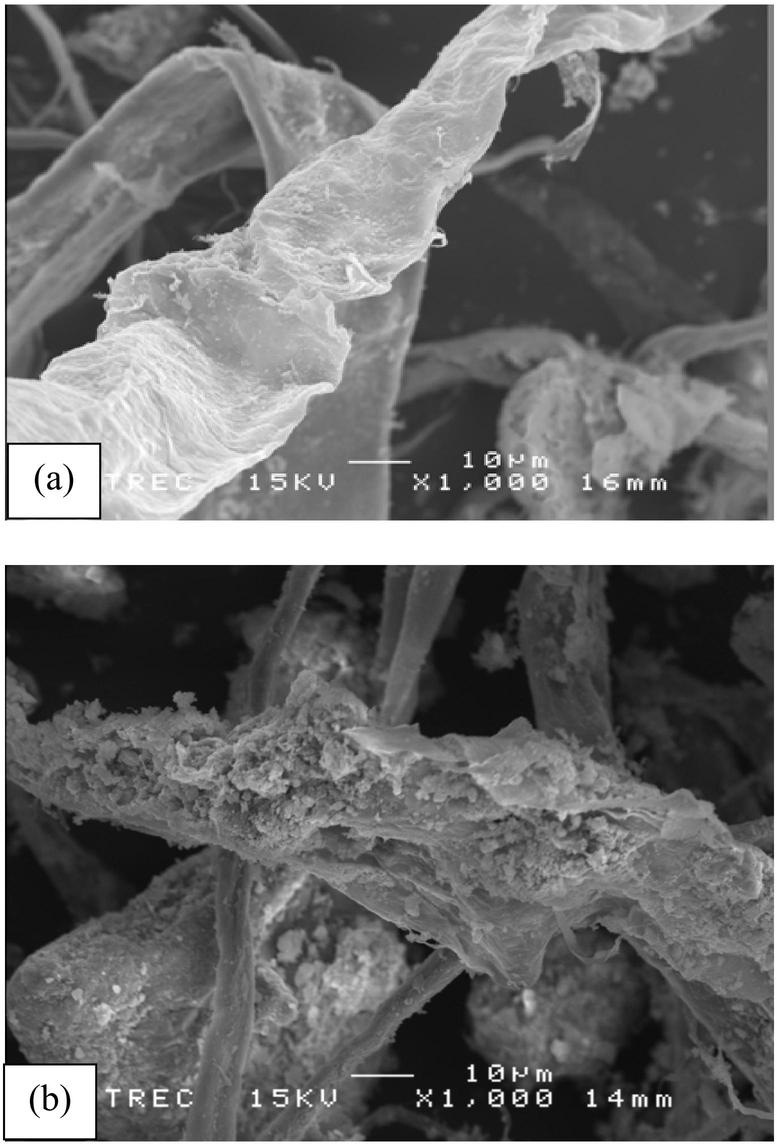


Figure 5.14 SEM images of fiber (a) before and (b) after hydrothermal treatment at 220 ºC and 40 minutes of holding time

Figure 5.14 shows SEM images of fiber in solid fractions before and after hydrothermal treatment process. The results show that the structure of fiber in secondary pulp and paper sludge after hydrothermal treatment was destroy with the temperature and holding time increasing.

5.3.2 Effect of holding time on cellulose conversion

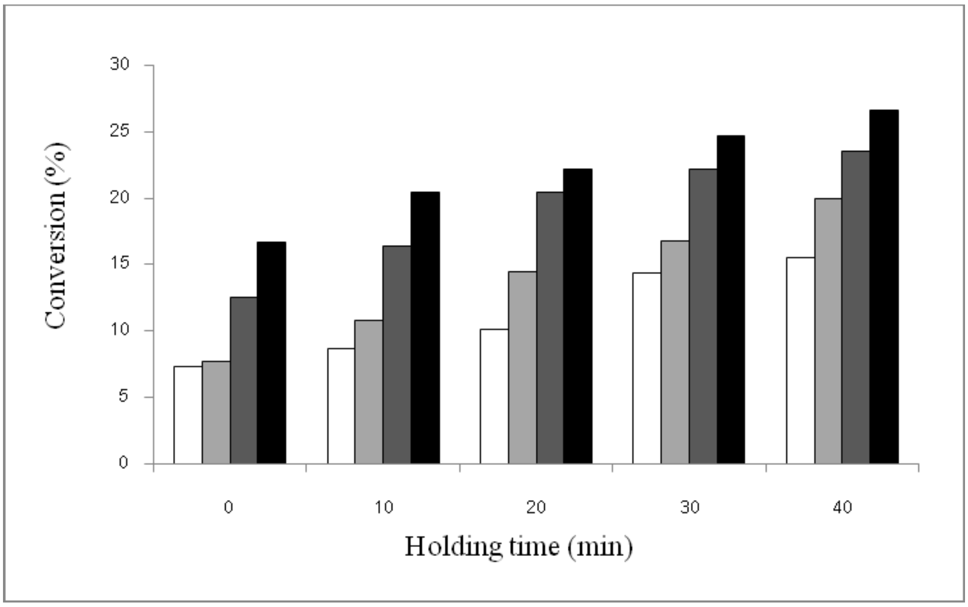


Figure 5.15 Conversion of cellulose in pure pulp at holding time of 0-40 min:
□ 200°C, ▒220°C,▓240°C, ■ 260°C

Figure 5.15 shows the cellulose conversion of pure pulp which was treated by hydrothermal treatment method under conditions of temperature from 200 to 260 °C, holding time 0-40 minutes and heating rate of 10 °C /min without catalyst. An increased holding time was resulted a greater cellulose conversion. The conversion of cellulose was in a range 7.33-26.6 %. The maximum cellulose conversion was 26.6 % at 260 °C and 40 minutes of holding time.

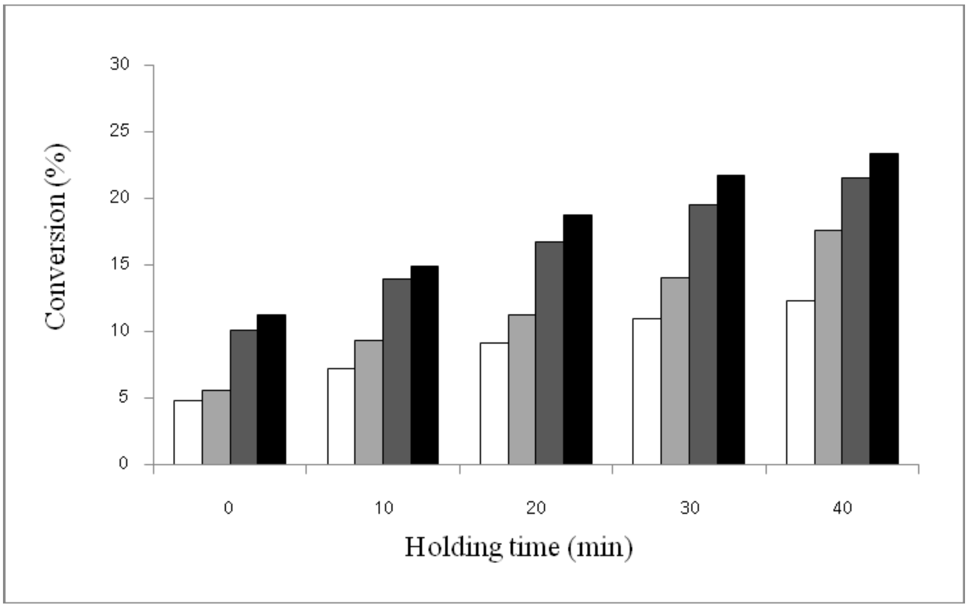


Figure 5.16 Conversion of cellulose in SPP S1 at holding time of 0-40 min:
☐ 200°C, ▨220°C,▩240°C, ■ 260°C

Figure 5.16 shows the cellulose conversion of Secondary pulp and paper sludge S1 which was treated by hydrothermal treatment method under conditions of temperature from 200 to 260 °C, holding time 0-40 minutes and heating rate of 10 °C /min without catalyst. An increased holding time was resulted a greater cellulose conversion. The conversion of cellulose was in a range 4.8-23.36 %. The maximum cellulose conversion was 23.36 % at 260 °C and 40 minutes of holding time.

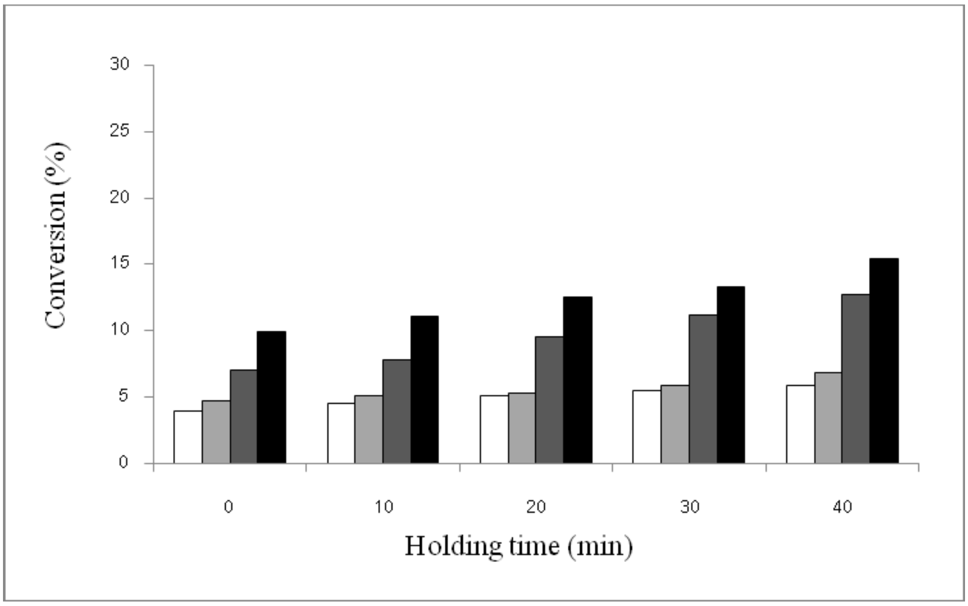


Figure 5.17 Conversion of cellulose in SPP S2 at holding time of 0-40 min:
☐ 200°C, ▒220°C,▓240°C, ■ 260°C

Figure 5.17 shows the cellulose conversion of Secondary pulp and paper sludge S2 which was treated by hydrothermal treatment method under conditions of temperature from 200 to 260 °C, holding time 0-40 minutes and heating rate of 10 °C /min without catalyst. An increased holding time was resulted a greater cellulose conversion. The conversion of cellulose was in a range 3.95-15.46 %. The maximum cellulose conversion was 15.46 % at 260 °C and 40 minutes of holding time

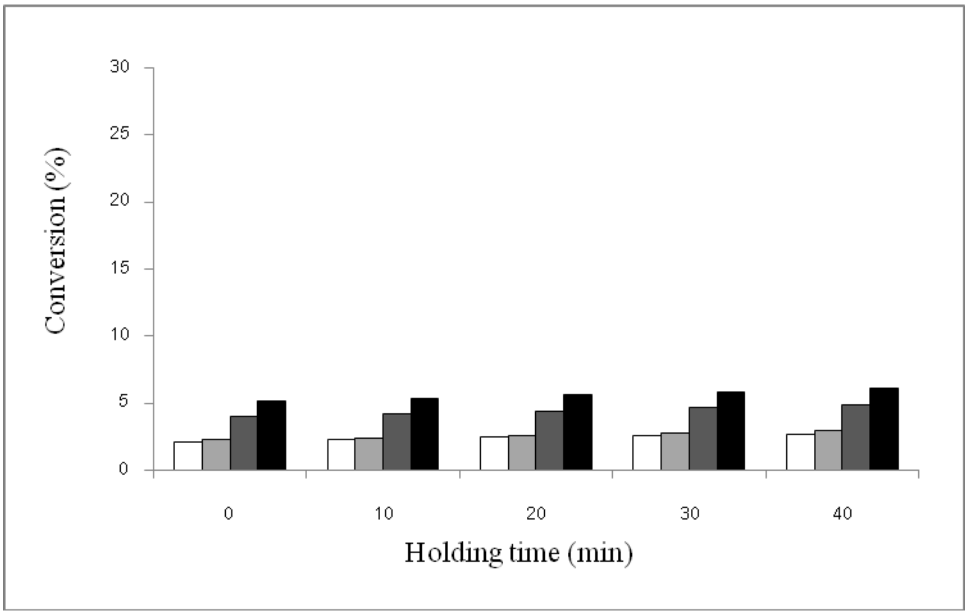


Figure 5.18 Conversion of cellulose in SPP S3 at holding time of 0-40 min:
□ 200°C, ▨220°C,▨240°C, ■ 260°C

Figure 5.18 shows the cellulose conversion of Secondary pulp and paper sludge S3 which was treated by hydrothermal treatment method under conditions of temperature from 200 to 260 °C, holding time 0-40 minutes and heating rate of 10 °C /min without catalyst. An increased holding time was resulted a greater cellulose conversion, but not clearly. The conversion of cellulose was in a range 2.11-6.08 %. The maximum cellulose conversion was 6.08 % at 260 °C and 40 minutes of holding time

From Figure 5.14-5.18 the trends of the cellulose conversion with holding time also suggest hydrolysis reaction of cellulose as the holding time prolonged as similarly proposed above for the effect of reaction temperature.

5.3.3 Effect of holding time on glucose yield

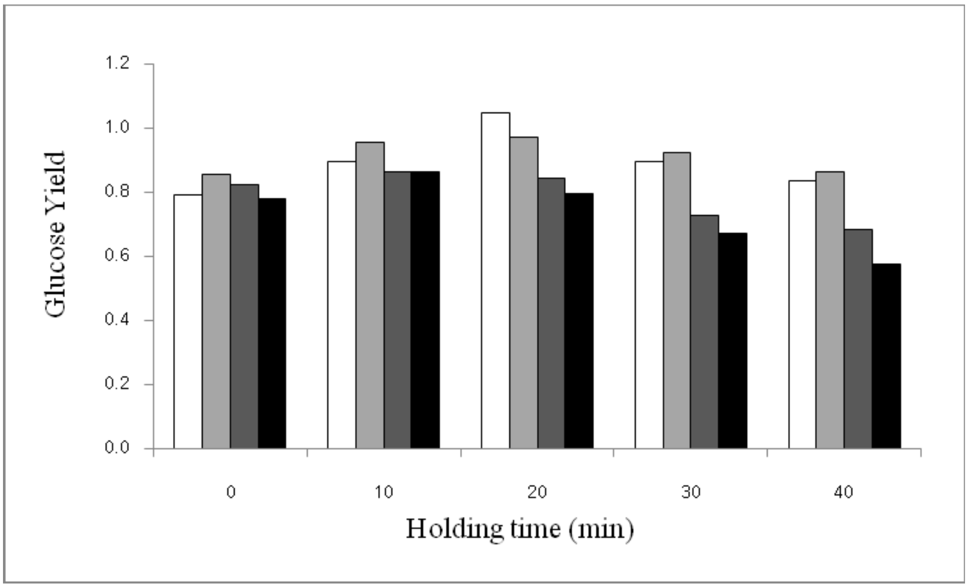


Figure 5.19 Effects holding time on the glucose in the liquid product of pure pulp hydrothermal treated in different temperature.

□ 200°C, ▨220°C,▩240°C, ■ 260°C

Figure 5.19 shows the yields of hydrolysis product (glucose), in hydrothermal treatment of the pure pulp at temperatures of 200 to 260 °C, for various lengths of holding time 0–40 minutes without catalyst. The glucose yield increased with holding time but at temperature higher than 220 °C, glucose yield gave the opposite results. The glucose yield of pure pulp was about 0.58–1.05%wt. The maximum yield was 1.05 at 200°C and 20 minutes of holding time.

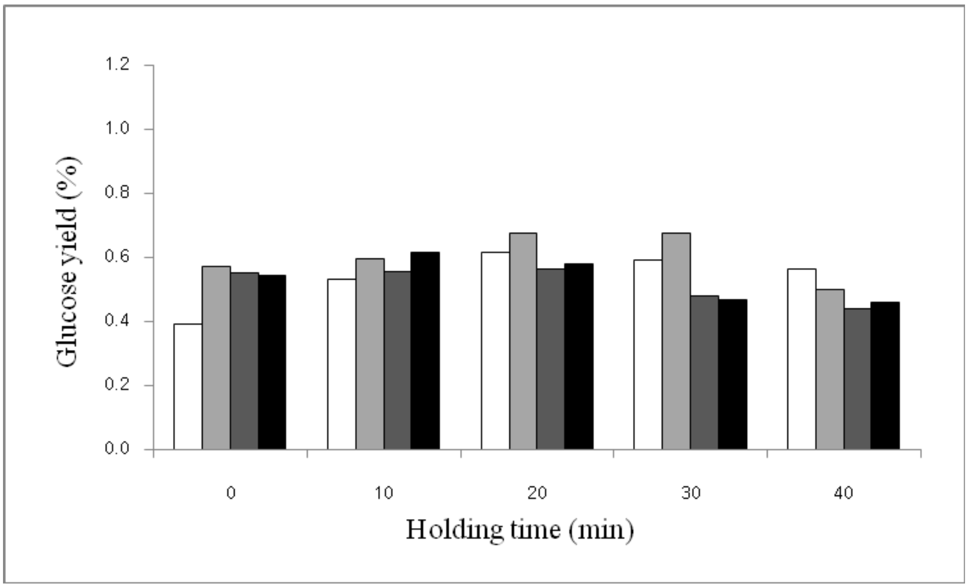


Figure 5.20 Effects holding time on the glucose in the liquid product of SPP S1 hydrothermal treated in different temperature

□ 200°C, ▨220°C,▩240°C, ■ 260°C

Figure 5.20 shows the yields of hydrolysis product (glucose), in hydrothermal treatment of the SPP S1 at temperatures of 200 to 260 °C, for various lengths of holding time 0–40 minutes without catalyst. The glucose yield trend of SPP S1 followed the similar trend as pure pulp but lower than. The glucose yield of SPP S1 was about 0.39–0.68 %wt. The maximum yield was 0.68 at 220°C and 20-30 minutes of holding time.

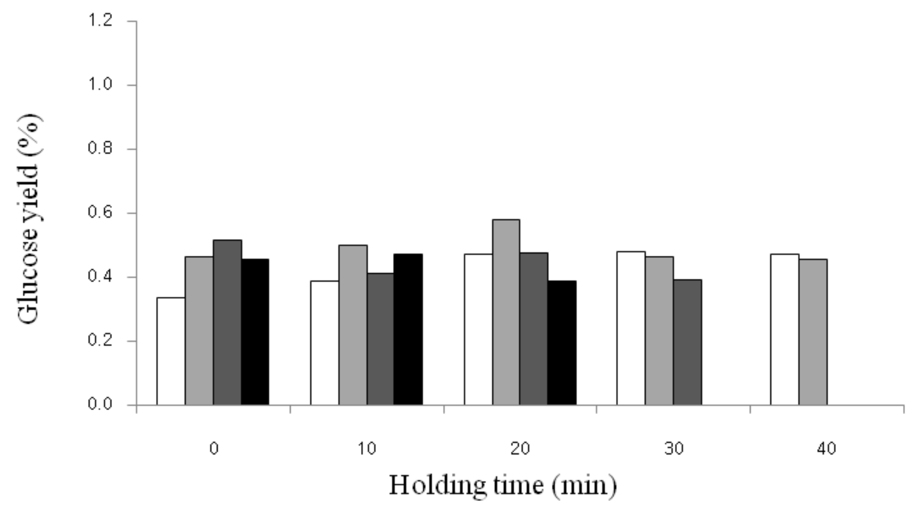


Figure 5.21 Effects holding time on the glucose in the liquid product of SPP S2 hydrothermal treated in different temperature

□ 200°C, ▨220°C,▩240°C, ■ 260°C

Figure 5.21 shows the yields of hydrolysis product (glucose), in hydrothermal treatment of the SPP S2 at temperatures of 200 to 260 °C, for various lengths of holding time 0–40 minutes without catalyst. The glucose yield trend of SPP S2 followed the similar trend as pure pulp and SPP S1 but lower than. And at 260 °C glucose yield was closed to 0 % in 30-40 minutes. The glucose yield of SPP S1 was about 0–0.58 %wt. The maximum yield was 0.58 at 220°C and 20 minutes of holding time.

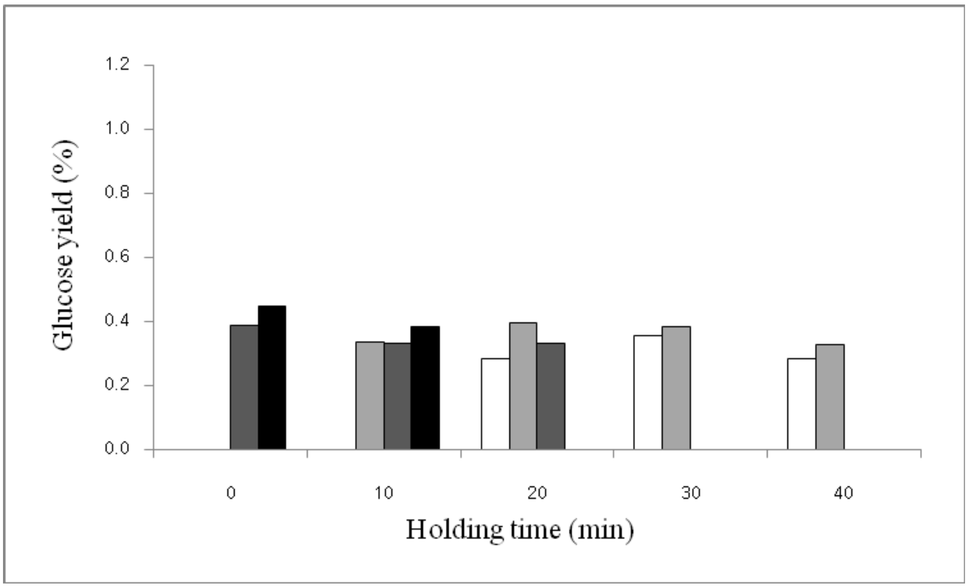


Figure 5.22 Effects holding time on the glucose in the liquid product of SPP S3 hydrothermal treated in different temperature

□ 200°C, ▨220°C,▨240°C, ■ 260°C

Figure 5.22 shows the yields of hydrolysis product (glucose), in hydrothermal treatment of the SPP S3 at temperatures of 200 to 260 °C, for various lengths of holding time 0–40 minutes without catalyst. The glucose yield trend of SPP S3 closed to 0 % at low temperature (200-220) and short time of holding (0-10 minutes) but after 10 minute, the glucose yield increased. And at 240- 260 °C glucose yield was maximum at 0 minute of holding, decreasd and closed to 0 % with holding time prolonged. The glucose yield of SPP S3 was about 0–0.45 %wt. The maximum yield was 0.45 at 260°C and 0 minutes of holding time.

5.3.4 Effect of holding time on decomposition product 5-HMF

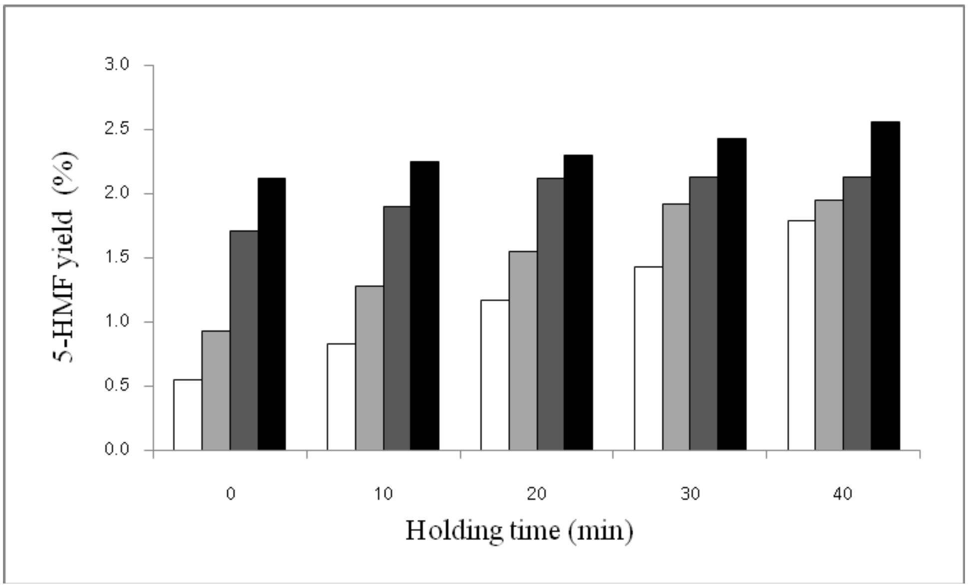


Figure 5.23 Effects holding time on the 5-HMF in the liquid product of pure pulp hydrothermal treated in different temperature
□ 200°C, ▒ 220°C, ▓ 240°C, ■ 260°C

Figure 5.23 shows the yields of decomposition product (5-HMF), in hydrothermal treatment of the pure pulp at temperatures of 200 to 260 °C, for various lengths of holding time 0–40 minutes without catalyst. An increased holding time was resulted a greater amount of 5-HMF yield. The 5-HMF yield was in a range 0.55-2.56 %. The maximum 5-HMF yield was 2.56 % from 260 °C and 40 minutes of holding time.

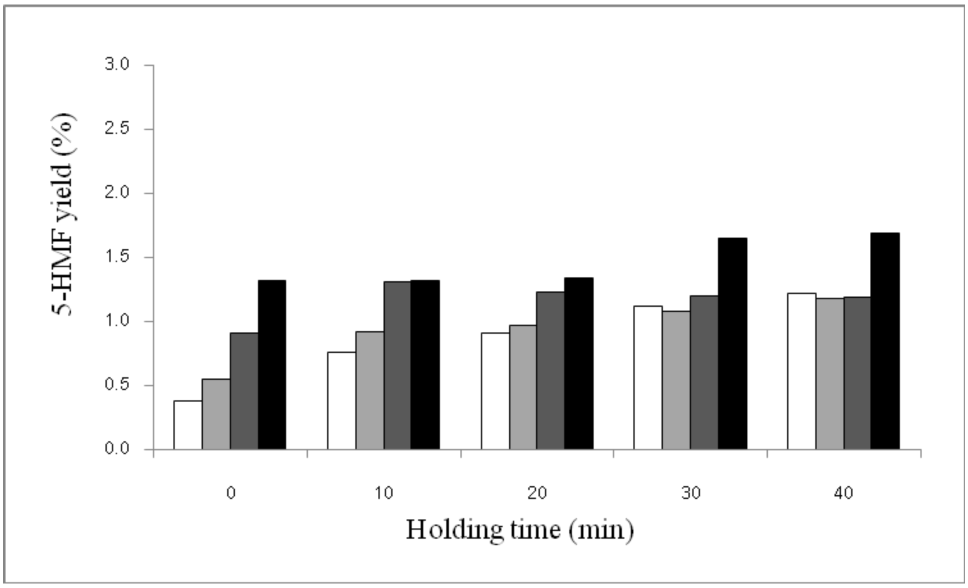


Figure 5.24 Effects holding time on the 5-HMF in the liquid product of SPP S1 hydrothermal treated in different temperature

□ 200°C, ▨220°C,▨240°C, ■ 260°C

Figure 5.24 shows the yields of decomposition product (5-HMF), in hydrothermal treatment of the SPP S1 at temperatures of 200 to 260 °C, for various lengths of holding time 0–40 minutes without catalyst. The 5-HMF yield trend of SPP S1 followed the similar trend as pure pulp but lower than. The -5-HMF yield of SPP S1 was about 0.38–1.69 %wt. The maximum yield was 1.69 from 260°C and 40 minutes of holding time.

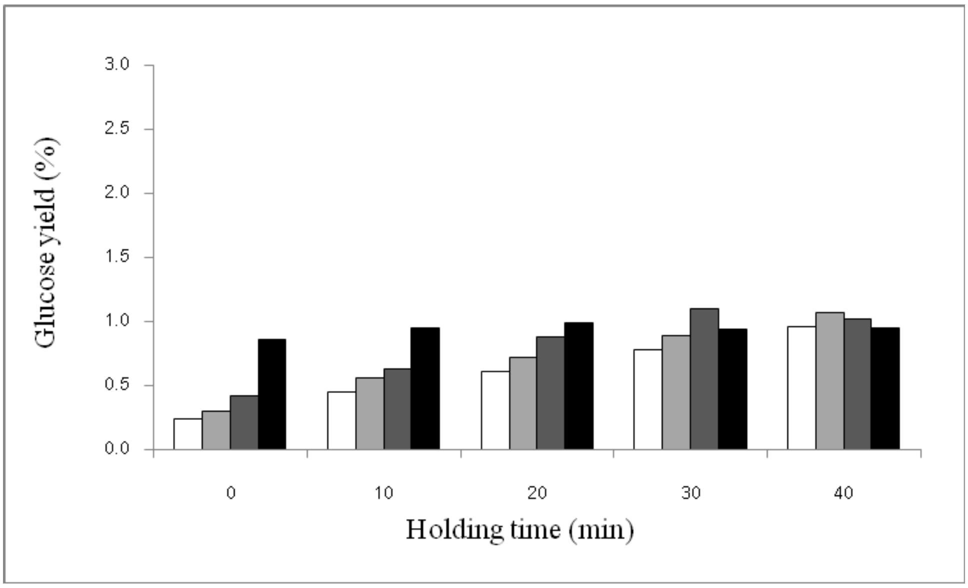


Figure 5.25 Effects holding time on the 5-HMF in the liquid product of SPP S2 hydrothermal treated in different temperature

□ 200°C, ▨220°C,▩240°C, ■ 260°C

Figure 5.25 shows the yields of decomposition product (5-HMF), in hydrothermal treatment of the SPP S2 at temperatures of 200 to 260 °C, for various lengths of holding time 0–40 minutes without catalyst. The 5-HMF yield trend of SPP S2 followed the similar trend as pure pulp and SPP S1 but lower than. The 5-HMF yield of SPP S2 was about 0.24–1.10 %wt. The maximum yield was 1.10 from 240°C and 30 minutes of holding time.

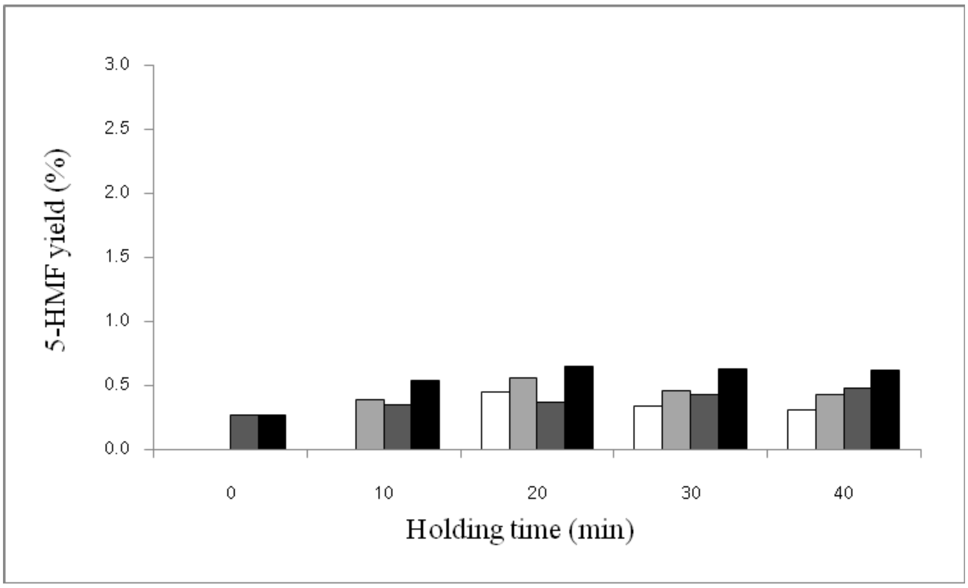


Figure 5.26 Effects holding time on the 5-HMF in the liquid product of SPP S3 hydrothermal treated in different temperature

□200°C, ▨220°C, ▩240°C, ■ 260°C

Figure 5.26 shows the yields of decomposition product (5-HMF), in hydrothermal treatment of the pure pulp at temperatures of 200 to 260 °C, for various lengths of holding time 0–40 minutes without The 5-HMF yield of SPP S2 at low temperature (200-220°C) closed to zero and the 5-HMF yield trend followed the similar trend as pure pulp, SPP S1 and SPP S2 but lower than. The 5-HMF yield of SPP S3 was about 0–0.65 %wt. The maximum yield was 0.65 at 260°C and 20 minutes of holding time.

Figure 5.15-5.18 show the hydrolysis of cellulose was studied as a function of time under subcritical water conditions at 200, 220, 240 and 260 °C, respectively. The trends of the cellulose conversion with holding time also suggest hydrolysis reaction of cellulose as the holding time prolonged. Figure 5.19-5.22 shows the product yields of glucose from hydrolysis of cellulose at reaction temperature of 220 °C for 0–40 min. In 0- 20 min, the glucose yield increased with increasing holding time but in 20-40 min, gave the opposite results. Figure 5.23-5.26 show the decomposed product 5-HMF from glucose and an increased holding time was obtained a greater 5-HMF yield in all conditions. These results suggest that the increase in the holding time not improve only the formation of glucose but also at the same time decomposition rate. At 20-40, the glucose production decrease with increasing holding time. Sasaki et al. [10] revealed that the glucose decomposition rate is much faster than the hydrolysis rate of cellulose under subcritical and supercritical conditions. And Jing and Lu (2008) [28] as well as Khajavi et al. (2005) [29] reported that glucose would be decomposed by thermal treatment in a temperature range of 180-220 °C and 180-260 °C respectively. Thus, the hydrolysis products are formed and decomposed rapidly and thus a high yield of hydrolysis products cannot be obtained.

According to the results in figure 5.19-5.22, glucose was the first hydrolyzed product from cellulose in secondary pulp and paper sludge and then decomposed to 5-HMF or others formations. The amount of glucose from hydrolysis was more than decomposition products of glucose at initial time of reaction. Then, when higher amount of glucose was produced, the 5-HMF yield increased in the same time. The glucose decomposition rate is faster than the hydrolysis of cellulose. Moreover, at 20-40 min glucose production decreased because glucose converted to 5-HMF or others products. The reaction pathways were shown in Figure 5.27.

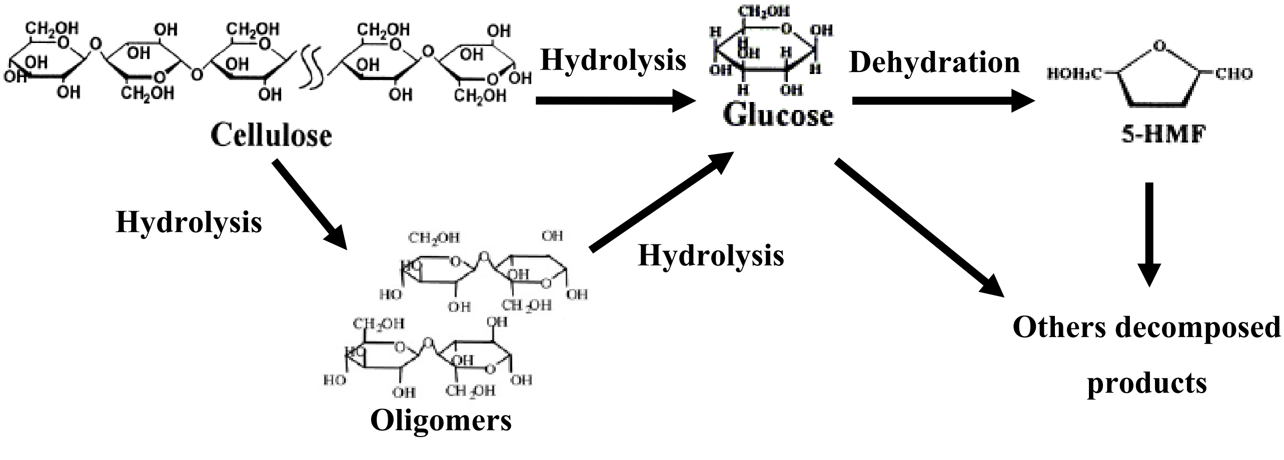


Figure 5.27 Reaction pathway

5.4 The effect of classified secondary pulp and paper sludge

From Table 5.1, four sizes of pure pulp and secondary pulp and paper sludge as received, P, S1, S2 and S3 from screening section. The compositions of pure pulp and secondary pulp and paper sludge are different in cellulose, hemicelluloses, lignin and $CaCO_3$. However amount of cellulose content decreased with decreasing size of raw material, $CaCO_3$ increased.

The appearances of the liquid products were shown in Figure 5.28. Liquid products were separated from solids by filtration. Base on visualization, the higher the holding time, obtained darker the color of the liquid product but the smaller sizeof raw material pale the color of liquid products down.

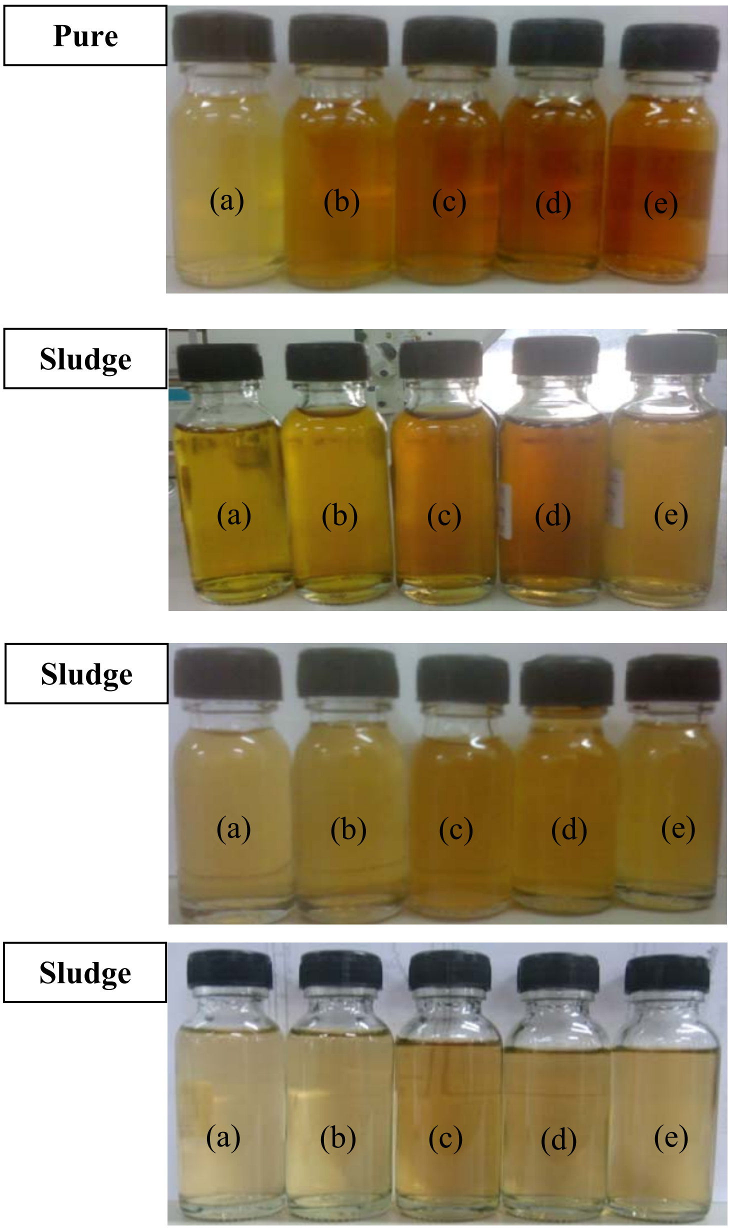


Figure 5.28 Visual comparisons of liquid products after hydrothermal treatment at 260 °C: (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min and (e) 40 min

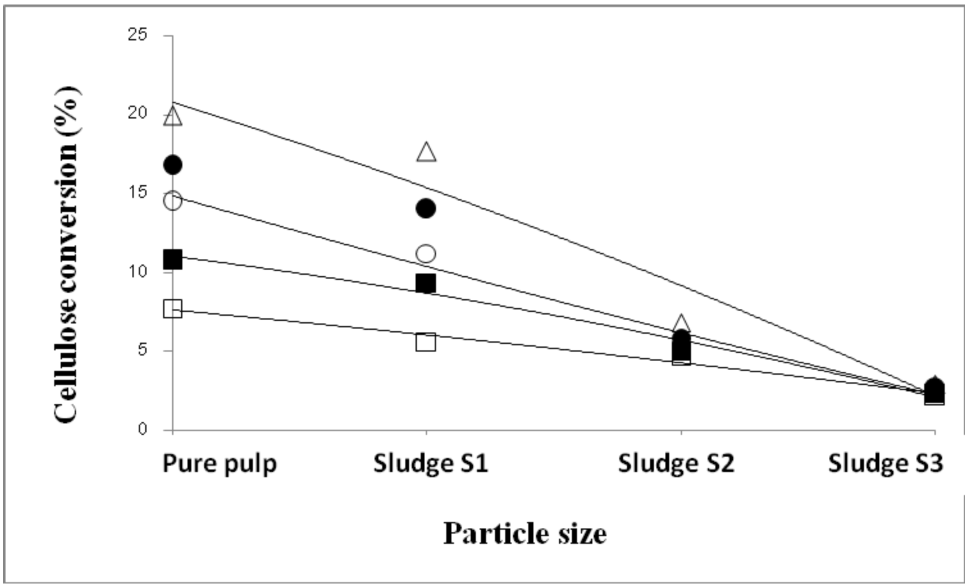


Figure 5.29 Comparison of the cellulose conversion on different holding time: □ 0 min, ■ 10 min, ○ 20 min, ● 30 min, △40 min

Figure 5.29 shows the conversion of cellulose in hydrothermal treatment of the pure pulp, SPP S1, S2 and S3 at temperatures of 220 °C, for various lengths of holding time 0–40 minutes without catalyst. The pure pulp obtained the highest cellulose conversion. For SPP, The trend of cellulose conversion decreased with decreasing size of raw material. This result suggested that composition of samples effect on hydrolysis reaction. Carrier et al. reported that lignin would be hydrolyzed in the same time with cellulose in hydrothermal treatment process [34]. Furthermore, Torii et al. resulted that the hydrolysis products decrease with increasing $CaCO_3$ [5]

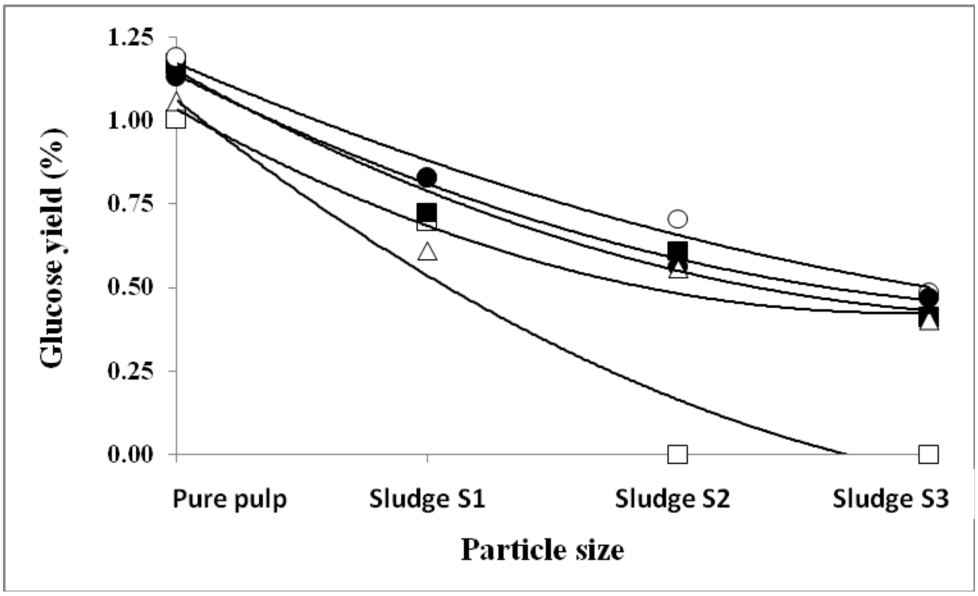


Figure 5.30 Comparison of the glucose yields on different holding time:
□ 0 min, ■ 10 min,○ 20 min, ● 30 min, △40 min

Figure 5.30 shows the yields of glucose product from hydrothermal treatment of the pure pulp at temperatures of 200 to 260 °C, for various lengths of holding time 0–40 minutes without catalyst. The glucose yield trend followed the similar trend as conversion. This result suggested that glucose yield decreased because of cellulose conversion. The lowest glucose yields are from SPP S3. These results followed the similar trend as results Torii et al. Torii et al. revealed that glucose yield closed to zero when $CaCO_3$ was added [5]

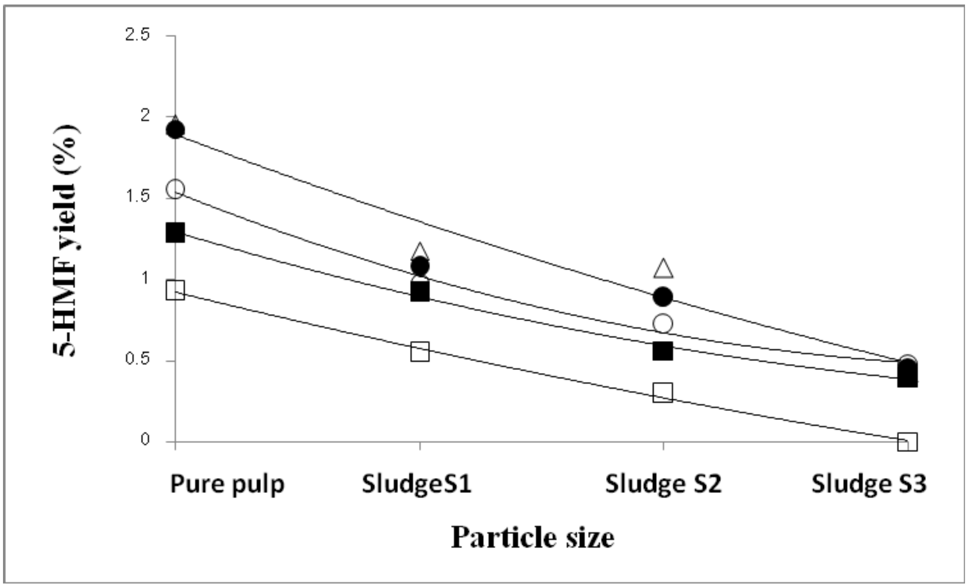


Figure 5.31 Comparison of the 5-HMF yields on different holding time:
□ 0 min, ■ 10 min,○ 20 min, ● 30 min, △40 min

Figure 5.31 shows the yields of 5-HMF product from hydrothermal treatment of the pure pulp at temperatures of 200 to 260 °C, for various lengths of holding time 0–40 minutes without catalyst. The 5-HMF yield trend followed the similar trend as cellulose conversion and glucose yields. This result suggested that 5-HMF yield decreased because of cellulose conversion also

From the information above, cellulose, hemicellulose, lignin and $CaCO_3$ would be hydrolyzed in the same time. This result suggested that the presence of lignin and $CaCO_3$ decreased cellulose conversion and cellulose hydrolysis products (glucose and 5-HMF).

5.5 The effect of calcium carbonate ($CaCO_3$)

From Table 5.1, Amount of calcium carbonate increase with decreasing size of raw material and from information above suggested that $CaCO_3$ effected on hydrolysis reaction. Torii et al. [5] purposed to convert pseudo pulp and paper to glucose, studied effect of calcium carbonate ($CaCO_3$) on glucose and 5-HMF yields and resulted that glucose yield decreased closed to zero and obtained very low 5-HMF yields with increasing calcium carbonate. In this study, from Table 5.1, compositions of pure pulp and secondary pulp and paper sludge are different in cellulose, hemicelluloses, lignin and $CaCO_3$. Thus effect was not from $CaCO_3$ only.

In this topic, the presence of $CaCO_3$ would be proposed and discussed on hydrolysis reaction, glucose yields and 5-HMF yields. The new conditions for $CaCO_3$ effect were created and shown in Table 5.2.

Table 5.2 Compositions of mixtures between secondary pulp and paper sludge S2 and $CaCO_3$

	Initial weight, g	Cellulose, g	Hemicellulose, g	Lignin, g	$CaCO_3$, g	$CaCO_3$ Adding, g	Total weight, g
S21	2.00	0.66	0.50	0.40	0.44	0.00	2.00
S22	2.00	0.66	0.50	0.40	0.44	0.30	2.30
S23	2.00	0.66	0.50	0.40	0.44	0.60	2.60

From Table 5.2, SPP S21, S22 and S23 were the mixed samples between SPP S2 and pure $CaCO_3$ in a different amount of $CaCO_3$. SPP S21, S22 and S23 were added with pure $CaCO_3$ 0 gram, 0.3 gram and 0.6 gram, respectively.

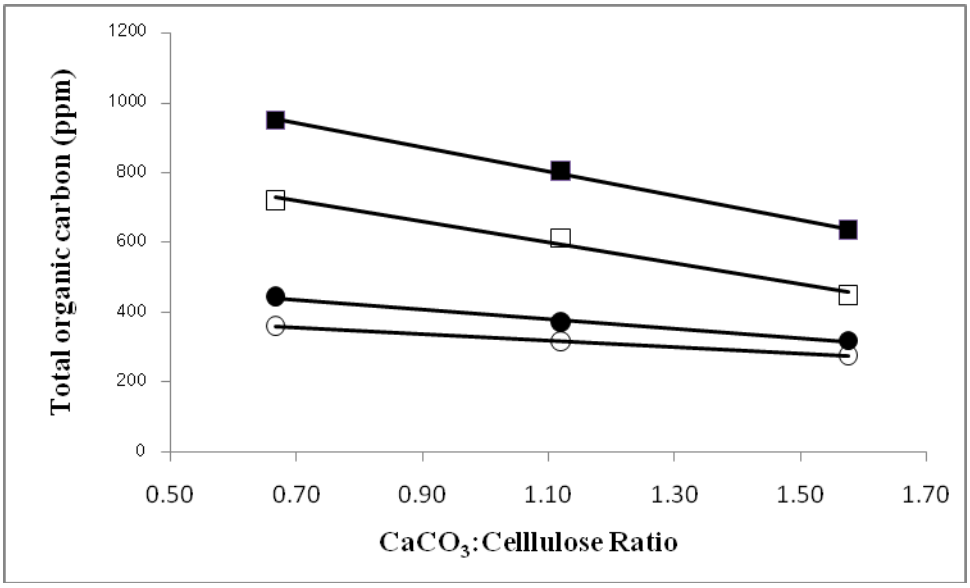


Figure 5.32 Comparison of the cellulose conversion on different $CaCO_3$/cellulose ratio: ○ 200 °C, ● 220 °C,☐ 240 °C, ■ 260 °C

Figure 5.32 show the cellulose conversion of mixed samples S21, S22 and S23 which was treated by hydrothermal treatment method under conditions of temperature from 200 to 260 °C and heating rate of 10 °C /min without catalyst. At all conditions, the conversion of cellulose increased with increasing reaction temperature. But conversion decreased with increasing $CaCO_3$: cellulose ratio. This result followed the similar trend as Torii et al. results [5].

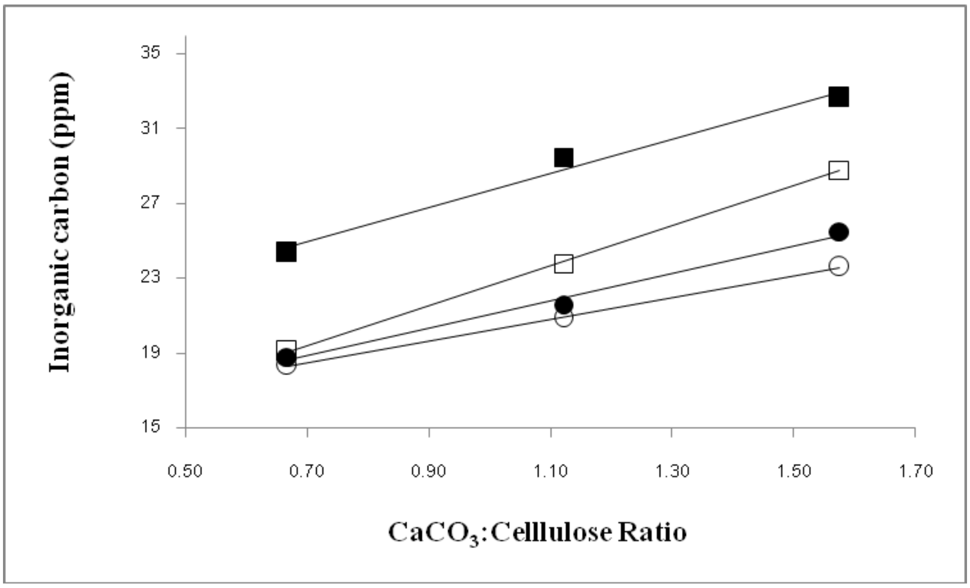


Figure 5.33 Comparison of the Inorganics carbon concentration in liquid product on different CaCO$_3$/cellulose ratio: ○200 °C, ●220 °C, □240 °C, ■260 °C

Figure 5.33 show the Inorganic carbon concentration of liquid products from SPP S21, S22 and S23 feedstock which were treated by hydrothermal treatment method under conditions of temperature from 200 to 260 °C and heating rate of 10 °C /min without catalyst and analyzed by TOC analyzer. At all conditions, Inorganic carbon concentration increased with increasing reaction temperature and CaCO$_3$: cellulose ratio. This result suggested that CaCO$_3$ would be reacted by hydrolysis reaction and gave HCO_3^- or CO_3^{2-} ion.

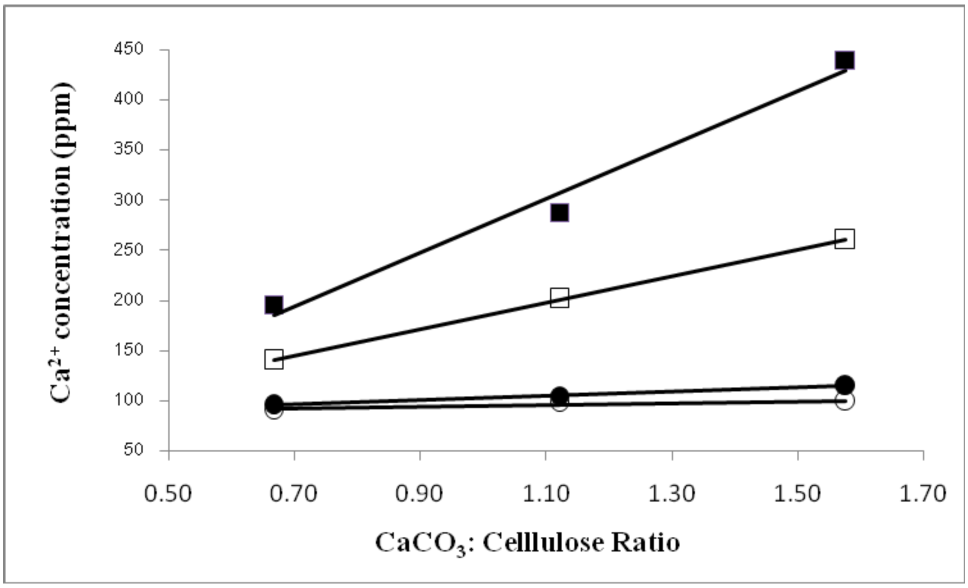


Figure 5.34 Comparison of the calcium ion concentration in liquid product on different $CaCO_3$/cellulose ratio: ○200 °C,● 220 °C,□ 240 °C, ■ 260 °C

Figure 5.34 shows the calcium ion concentration of liquid products from SPP S21, S22 and S23 feedstock which were treated by hydrothermal treatment method under conditions of temperature from 200 to 260 °C and heating rate of 10 °C /min without catalyst and analyzed by Inductively couple plasma (ICP). At conditions, calcium ion concentration increased with increasing reaction temperature and $CaCO_3$: cellulose ratio and especially at 240-260 °C, calcium ion concentration increased dramatically. This result suggested that $CaCO_3$ would be reacted by hydrolysis reaction and gave calcium ion.

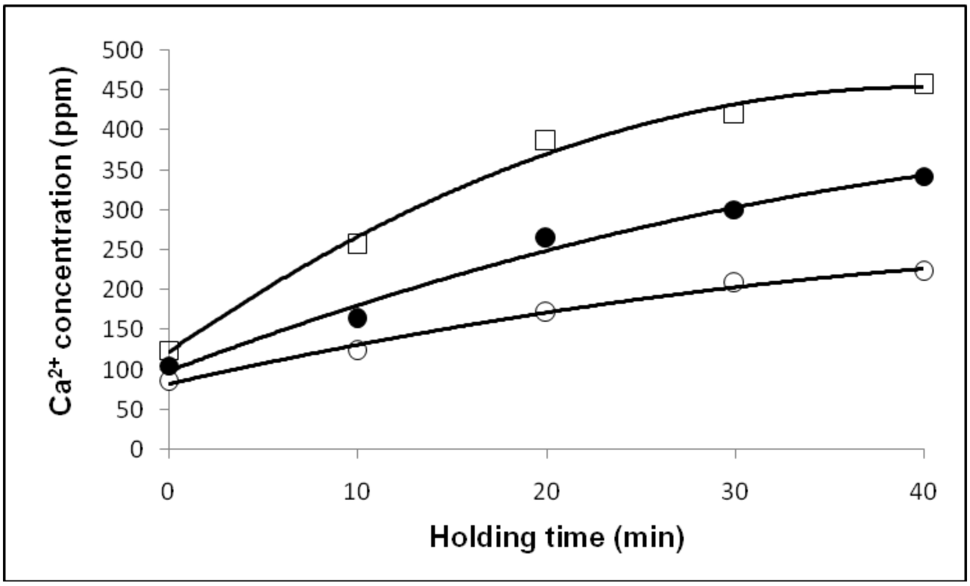


Figure 5.35 Comparison of the Ca^{2+} concentration in liquid product on different holding time: ○0 g, ● 0.3 g, □ 0.6 g of CaCO3 adding

Figure 5.35 shows the calcium ion concentration of liquid products from SPP S21, S22 and S23 feedstock which were treated by hydrothermal treatment method under conditions of temperature 220 °C, holding time 0-40 min and heating rate of 10 °C /min without catalyst and analyzed by Inductively couple plasma (ICP). At conditions, calcium ion concentration increased with amount of $CaCO_3$ Adding and holding time increasing. This result suggested that $CaCO_3$ would be reacted by hydrolysis reaction and gave calcium ion more with holding time prolong.

From the information above, the presence of calcium carbonate is also expected to provide a basic reaction environment for hydrolysis. Hydrolysis reaction has H^+ as effective ion to break glycosidic bond in cellulose chain. From equation 5.1-5.4 [35], the presence of calcium carbonate react with water and then will be obtained CO_3^{2-}, HCO_3^-, the solids and ion of calcium carbonate will react with proton ion or effective proton and then the proton decreased and effected on hydrolysis reaction of cellulose. Rate of hydrolysis reaction was decreased by calcium carbonate and make glucose yield or others decrease also.

$$2H_2O \longleftrightarrow H_3O^+ + OH^- \quad (5.1)$$

$$CaCO_3 \longleftrightarrow Ca^{2+} + CO_3^{2-} \quad (5.2)$$

$$CO_3^{2-} + H_3O^+ \longleftrightarrow HCO_3^- + H_2O \quad (5.3)$$

$$CaCO_3 + H_3O^+ \longrightarrow Ca^{2+} + HCO_3^- + H_2O \quad (5.4)$$

The presence of calcium carbonate gave lower cellulose conversion and make glucose yield or others lower also. From the results in this study, it can be concluded that removal of $CaCO_3$ from secondary pulp and paper sludge prior to hydrothermal treatment is necessary for obtaining high cellulose conversion, glucose and 5-HMF yields from secondary pulp and paper sludge.

5.6 Effect of adding acetic acid on hydrothermal pretreatment

From section 5.5 the presence of calcium carbonate gave lower cellulose conversion, glucose and 5-HMF yields, so CH_3COOH was selected for hydrothermal upgrading catalyst. New conditions were added with CH_3COOH in a different concentration 0.25, 0.5, 10 % wt respectively.

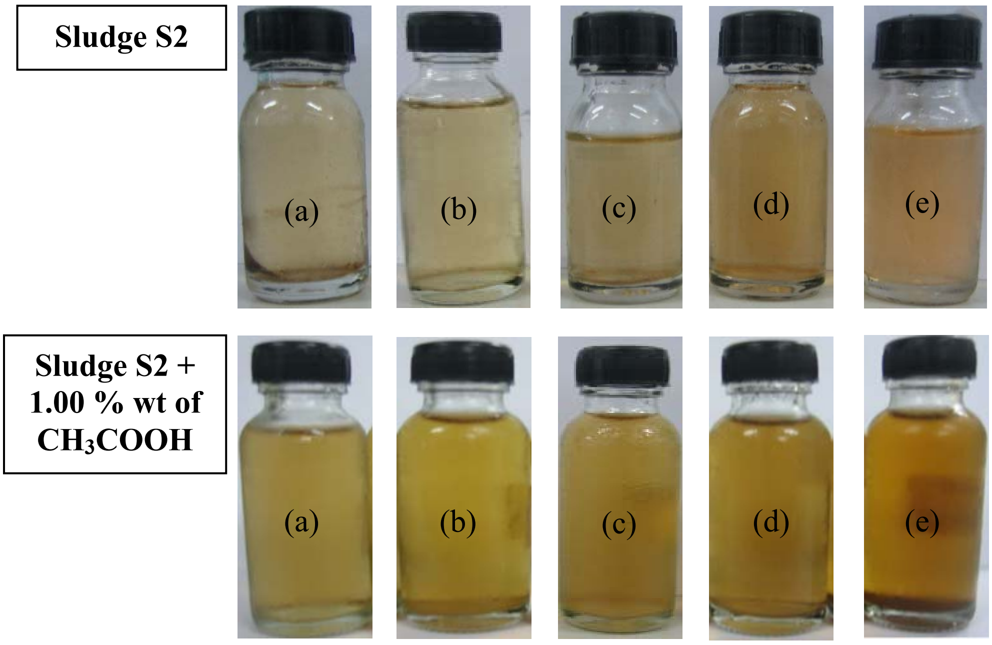


Figure 5.36 Visual comparisons of liquid products after hydrothermal treatment at 220 °C without and with CH_3COOH
(a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min and (e) 40 min

The appearances of the liquid products were shown in Figure 5.36 Liquid products were separated from solids by filtration. Base on visualization, the higher the CH_3COOH, obtained darker the color of the liquid product.

5.6.1 Effect of CH_3COOH on cellulose conversion

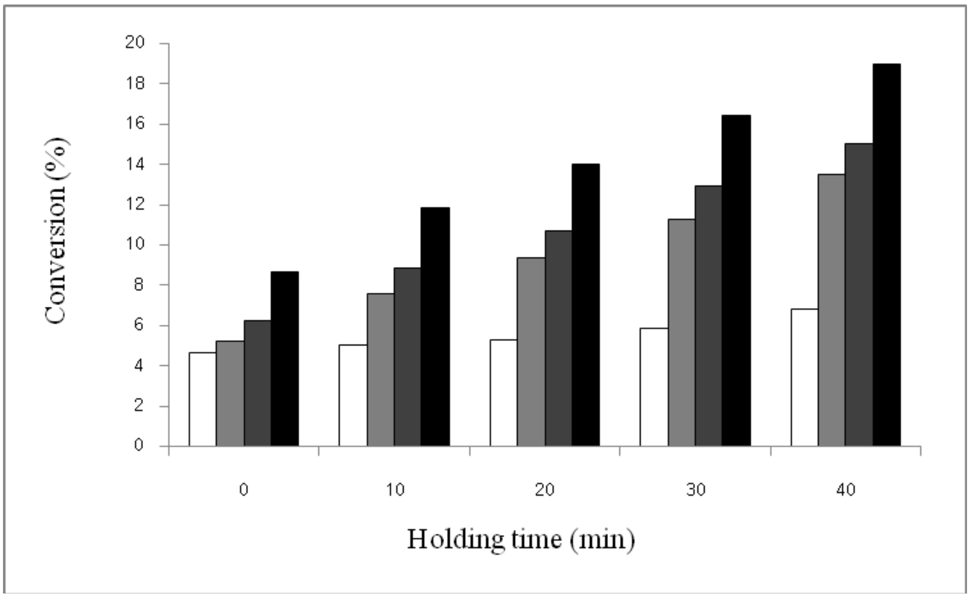


Figure 5.37 Effects holding time on the cellulose conversion in the liquid product of SPP S2 hydrothermal treated at 220 ºC in different concentration of CH_3COOH
□ 0 %wt , ▨ 0.25 %wt, ▩ 0.5 %wt, ■ 1.0%wt

Figure 5.37 shows the cellulose conversion of SPP S2 which was treated by hydrothermal treatment method under conditions of temperature from 220 °C, heating rate of 10 °C /min and holding time 0-40 minutes with 0, 0.25, 0.5, 1 % wt of CH_3COOH, respectively. Cellulose conversion monotonously increased with increasing reaction time, and increased with increasing CH_3COOH also. The conversion of cellulose was in a range 4.49-19.94 %. The maximum cellulose conversion without CH_3COOH at 220 °C was 6.85 increased to 19.94 % wt when 1.00 % wt of CH_3COOH was added. These results suggested that the increase in concentration of CH_3COOH improves the hydrolysis reaction rate.

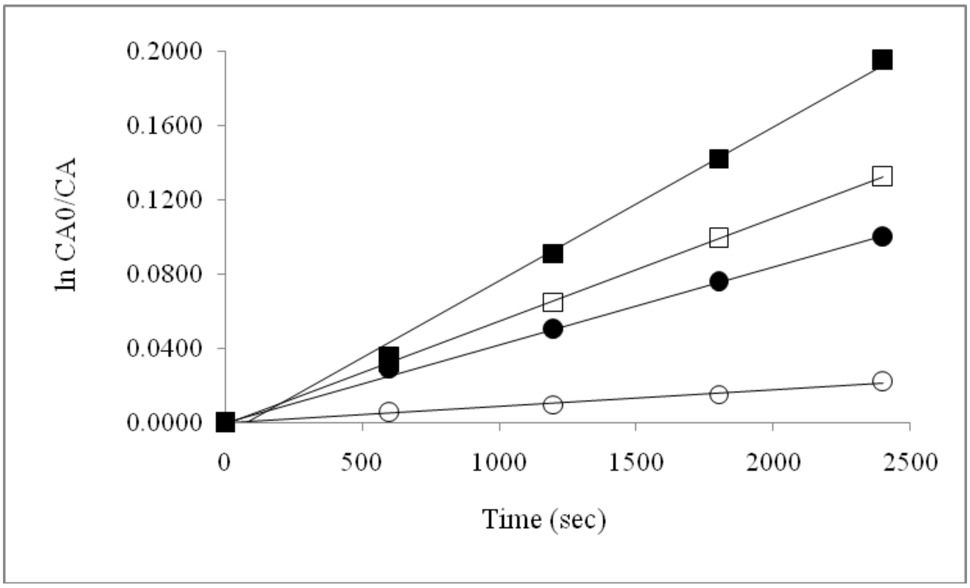


Figure 5.38 Pseudo 1st order plot

○ 0 % wt, ● 0.25 % wt, □ 0.5 % wt, ■ 1.00 % wt of CH_3COOH

From Figure 5.38 Show the plot of natural logalhm of cellulose in feedstock SPP S2 remaining againts time.

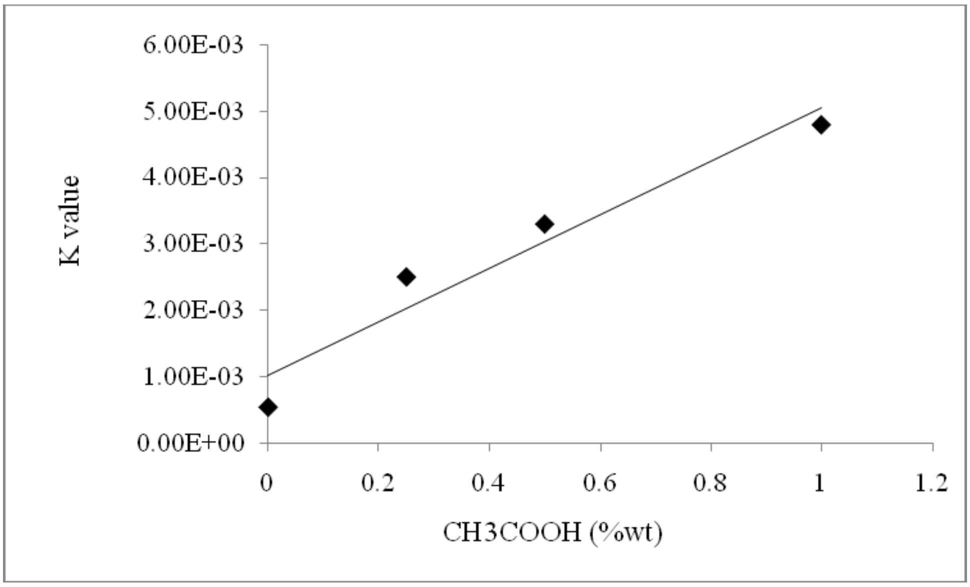


Figure 5.39 Effect of CH_3COOH on K constant

From Figure 5.39 shows the plot of rate constant k of cellulose degradation againts with catalyst (CH_3COOH) concentration. The rate constants k increased with increasing CH_3COOH concentration. This result suggested that CH_3COOH could increase the hydrolysis rate of cellulose in SPP S2 feedstock make the percentage of cellulose conversion higher.

5.6.2 Effect of CH_3COOH on glucose yield

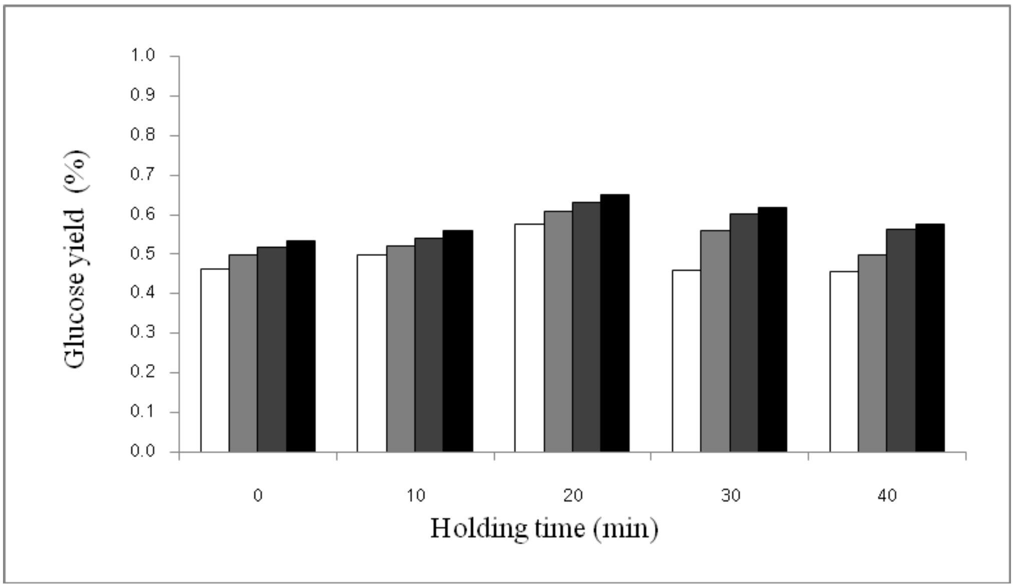


Figure 5.40 Effects holding time on the glucose yield in the liquid product of SPP S2 hydrothermal treated at 220 °C in different concentration of CH_3COOH
□ 0 %wt , ▩ 0.25 %wt, ▨ 0.5 %wt, ■ 1.0%wt

Figure 5.40 show the glucose yield of SPP S2 which was treated by hydrothermal treatment method under conditions of temperature from 220 °C, heating rate of 10 °C /min and holding time 0-40 minutes with 0, 0.25, 0.5, 1 % wt of CH_3COOH, respectively. The glucose yield increased slightly with increasing CH_3COOH. For effect of holding time, glucose yield at the beginning (0-20min) increased when holding time prolong and then decreased. These results suggested that the increase in concentration of CH_3COOH would give glucose yield higher.

5.6.3 Effect of CH_3COOH on 5-HMF yield

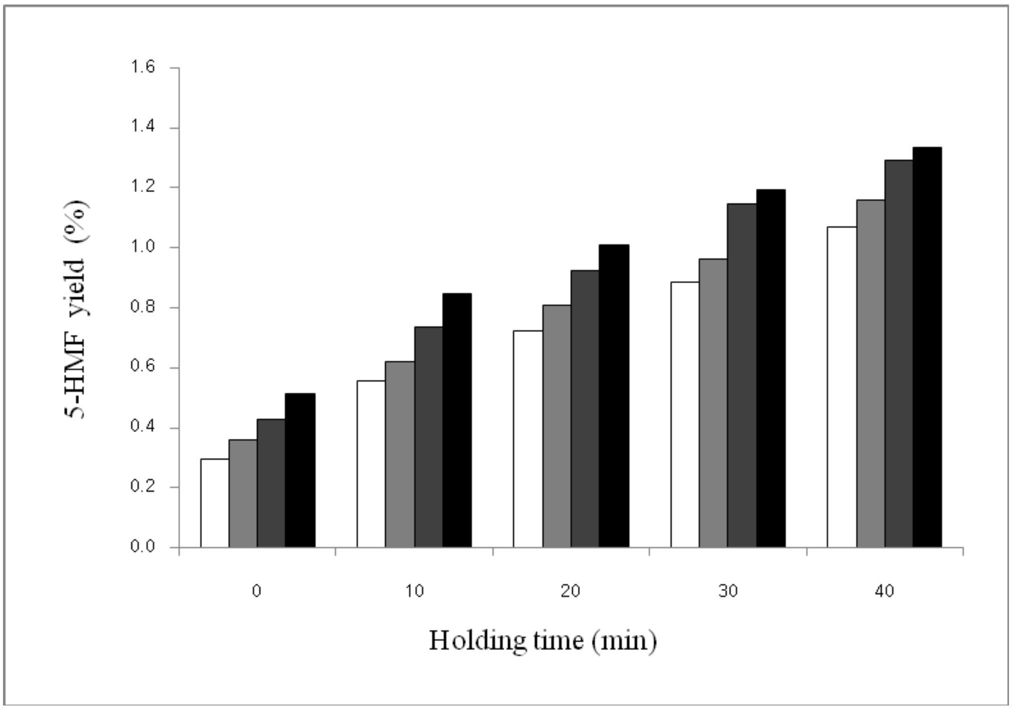


Figure 5.41 Effects holding time on the 5-HMF yield in the liquid product of SPP S2 hydrothermal treated at 220 ºC in different concentration of CH_3COOH
□ 0 %wt , ▨ 0.25 %wt, ▩ 0.5 %wt, ■ 1.0%wt

Figure 5.41 shows the 5-HMF yield of SPP S2 which was treated by hydrothermal treatment method under conditions of temperature from 220 °C, heating rate of 10 °C /min and holding time 0-40 minutes with 0, 0.25, 0.5, 1 % wt of CH_3COOH, respectively. The 5-HMF yield trend followed the similar trend as cellulose conversion. These results suggested that the increase in concentration of CH_3COOH would give 5-HMF yield higher.

From the information above CH_3COOH catalyst could upgrade hydrolysis rate of cellulose, which gave higher percentage of cellulose conversion, glucose and 5-HMF yields. These results are good agreement with Daorattanachai et al. [33] Daorattanachai et al. revealed the acid catalyst was much higher than that of without catalyst in enhancing the formation of glucose and HMF [33]. And Yin et al., who studied the pathway of alkaline hydrothermal. The pH of the reaction media was reduced to less than 7, the acidic hydrothermal pathway came into action, and the main bio-oil component gradually became HMF [36]

5.7 Reaction Kinetics

5.7.1 Arrhenius rate law

From the section 5.3, for the investigation of reaction kinetic, its has been reported that the Arrhenius rate law is applicable (Foglor, 1999) Each reaction rate constant, could be obtained from analysis of concentration change with respect to the reciprocation of temperature as shown in Figure 5.40, the rate constants G, P, S1, S2 and S3 were determined from degradation of glucose, cellulose in pure pulp, SPP S1, SPP S2 and SPP S3 respectively, and assumption of the first order reaction. These rate constants were analyzed by using a reaction which is expressed by equation 5.5

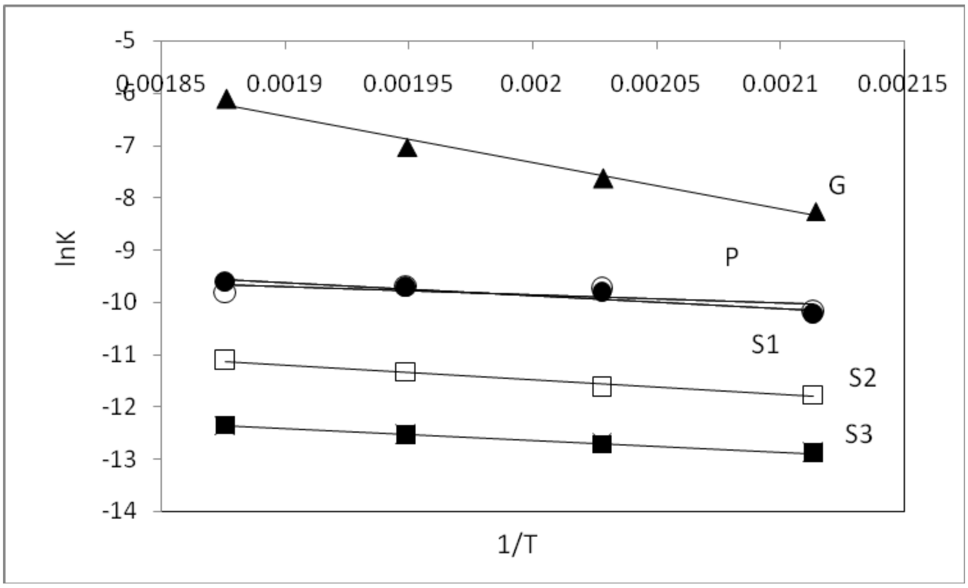


Figure 5.42 Comparison of reaction parameters obtained by assuming first order reaction for pure pulp and secondary pulp and paper

○ Pulp,●SPP S1,□ SPP S2, ■ SPP S3,▲Glucose

$$\frac{d[C]}{dt} = -k[C] \qquad (5.5)$$

Table 5.3 Parameters of reaction rate

	Preexponential factor (1/s)	Ea (KJ/mol)
K-Glucose	3.12E+04	73.48
K-pulp	1.13E-03	12.79
K-S1	6.52E-03	20.10
K-S2	3.02E-03	23.62
K-S3	2.79E-04	18.52

From Figure 5.42, K constant from P and S1 have similar values which are much higher than S2 and S3 respectively, which indicates that the pure pulp and SPP S1 is more favorable to be converted to the hydrolysis product than S2 and S3. These results suggested that the hydrolysis rate of P and S1 faster than S2 and S3. If we consider in term of activation energy (Ea), Ea of K-pulp is the lowest activation energy. It is indicated that the reaction rate of pure pulp is the highest rate. This result would be attributed to the barriers of calcium carbonate which could hinder to cellulose hydrolysis [5] Therefore, before the hydrothermal treatment section would remove the calcium carbonate and lignin from the raw material, resulting in a more effective hydrolysis of cellulose by the hydrolysis. In addition to, the glucose decomposition gave the highest K constant and Ea value. These results suggested that the reaction rate of glucose is the lowest rate.

5.7.2 *Glucose decomposition: n th order reaction*

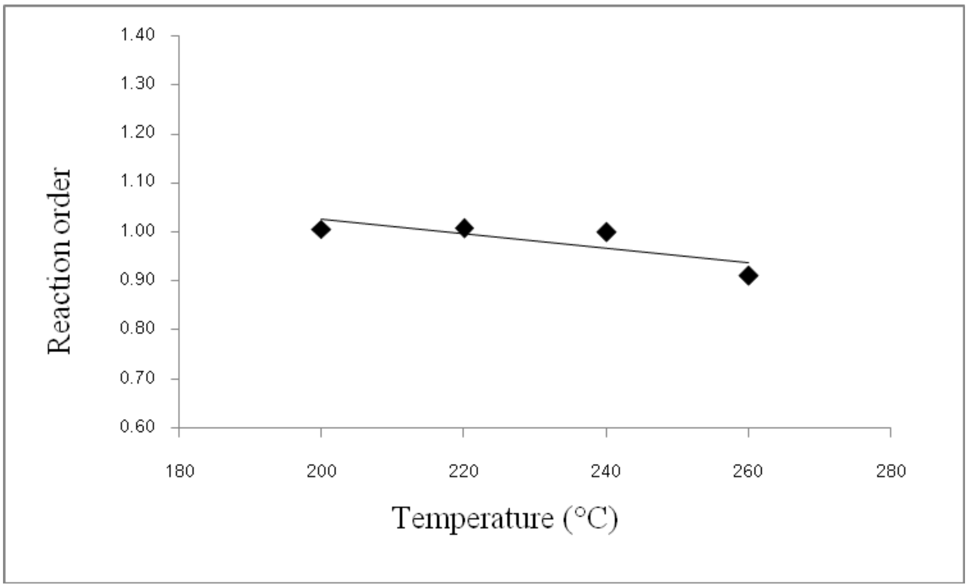


Figure 5.43 Order plot of glucose decomposition

From Figure 5.43 shows the determined order of reaction for glucose decomposition in a range of temperature at 200-260 ºC in tubular reactor. From Figure 5.42 K constant value was not straight line at high temperature (240-260 ºC). This result led the author to the further analysis using an *n* th order reaction rate equation.

$$d[C]/dt = -k[C]^n \qquad (5.6)$$

$$C_2 = [C_1^{1-n} - (1 - n)\, k\, (t2 - t1)]^{1/1-n} \qquad (5.7)$$

To determine the reaction order and reaction rate constant in the glucose decomposition from equation 5.6 and integrated the above equation for *n* not equal to unity from time t1 to t2 for the corresponding concentration *C*1 and *C*2 to obtain equation 5.7. The reaction order changed from unity to lower values as temperature increased. These results are in good agreement with Matsumura et al. [30] Matsumura et al revealed reaction order is directly affected by the reaction mechanism, and considering that reaction field changes from ionic to radicalic as temperature increases. This change in reaction order implies a change in reaction mechanism with the change of reaction temperature [30]

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

In this thesis, pure pulp and SPP were used as biomass for glucose production using hydrothermal treatment process in a batch reactor. The raw materials were treated at 200-260 ºC, holding time of 0-40 minutes with the presence and absence of CH_3COOH as catalyst. The glucose content in liquid product was measured by HPLC. The solid fraction was analyzed for cellulose content by TAPPI method.

Effects of temperature, holding time and calcium carbonate content on glucose production were experimentally examined. The hydrolysis of cellulose is strongly dependent on the temperature. However, degradation of glucose could take place and be enhance by the increased temperature also. For effect of holding time, it was found that the longer holding time would result in the higher possibility of glucose decomposition. Thus cellulose should be treated with a short holding time. Calcium carbonate would behave as inhibitor, which retard hydrothermal reaction of cellulose, resulting in decrease in rate of hydrolysis. Therefore glucose yield was lower with the presence of calcium carbonate. It is suggested that calcium carbonate should be separated before hydrothermal treatment. The highest glucose yield of 0.68 % can be obtained from hydrothermal treatment of secondary pulp and paper sludge at temperature 220 ^{o}C and 20 minutes holding time. As a catalyst CH_3COOH could enhance hydrolysis rate of cellulose, resulting in gave higher percentage of cellulose conversion, glucose and 5-HMF yields.

Recommendation

The lignin and calcium carbonate of raw material on hydrothermal treatment are interested point from this works, therefore the method for removing calcium carbonate and lignin before hydrothermal treatment should be considered in future work. In addition, the method for increasing glucose yield should be considered also.

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APPENDICES

APPENDIX A

Calibration curve of glucose, 5-HMF and Ca^{2+}

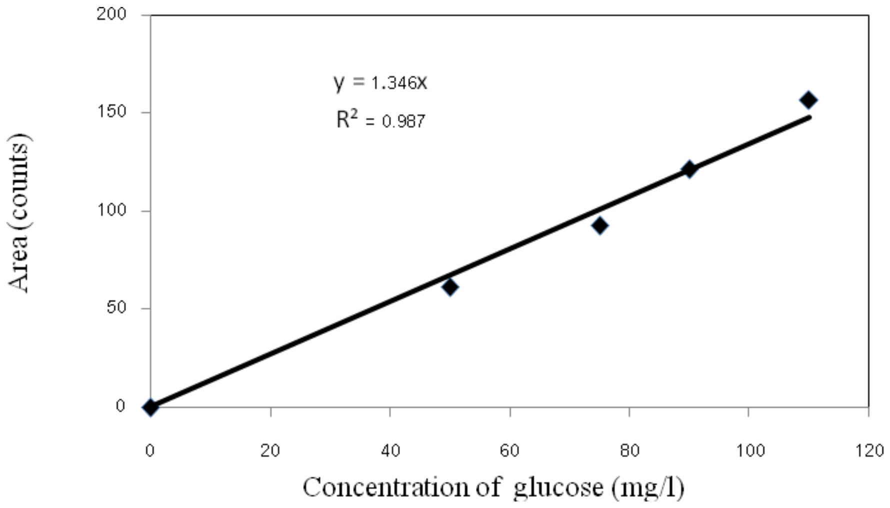

Figure A1 Calibration curve of glucose solution by HPLC

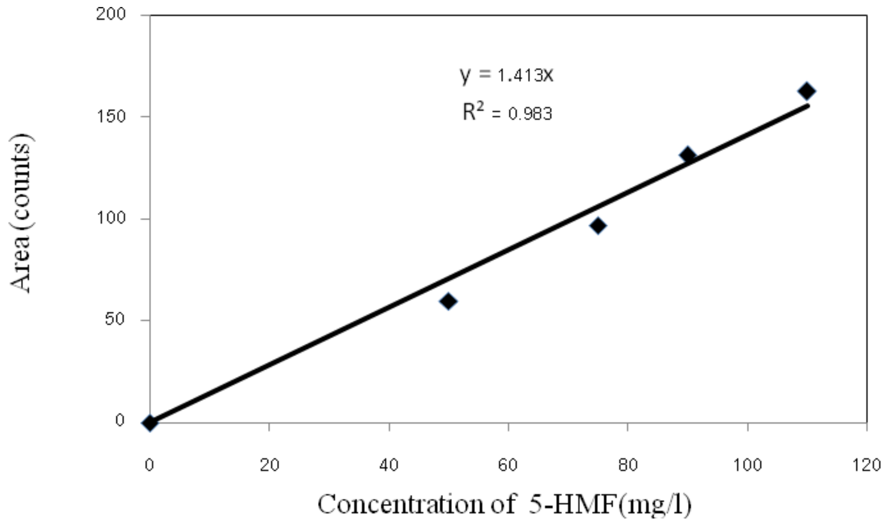

Figure A2 Calibration curve of 5-HMF solution by HPLC

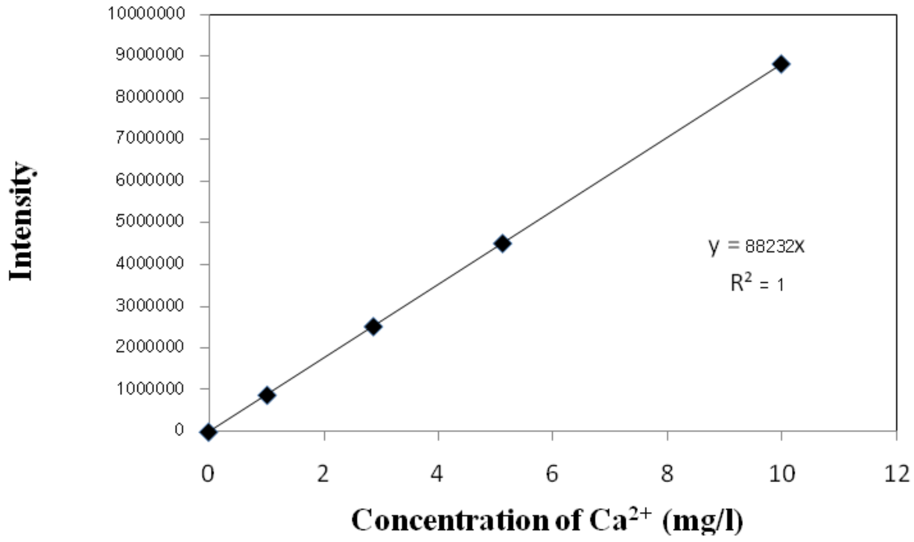

Figure A3 Calibration curve of Ca^{2+} solution by HPLC

APPENDIX B

TAPPI Method

1. Preparation of Holocellulose (Chlorite Holocellulose)

1.1 Scope

Holocellulose is defined as a water-insoluble carbohydrate fraction of plant materials. According to Browning (1967) there are three ways of preparing holocellulose and their modified methods: (1) Chlorination method (also ASTM Standard D1104); (2) Modified chlorination methods; and (3) Chlorine dioxide and chlorite methods. The standard purity of holocellulose is checked following lignin analysis.

1.2 Sample Preparation

Dry samples are oven dried for 24 hours (usually at 105°C) before milling. Wet samples can be milled while frozen in order to prevent oxidation or other undesirable chemical reactions. Samples are ground to pass 40 mesh (0.40 mm) using a Wiley Mill.

1.3 Reagents

- Acetic acid, reagent grade
- Sodium chlorite, $NaClO_2$, technical grade, 80%

1.4 Procedure

To 2.5 g of sample, add 80 ml of hot distilled water, 0.5 ml acetic acid, and 1 g of sodium chlorite in a 250 ml Erlenmeyer flask. An optional 25 ml Erlenmeyer flask is inverted in the neck of the reaction flask. The mixture is heated on a water bath at 70°C. After 60 min, 0.5 ml of acetic acid and 1 g of sodium chlorite are added. After each succeeding hour, fresh portions of 0.5 ml acetic acid and 1 g sodium chlorite are added with shaking. The delignification process degrades some of the polysaccharides, and the application of excess chloriting should be avoided. Continued reaction will remove more lignin but hemicellulose will also be lost. Addition of 0.5 ml acetic acid and 1 g of sodium chlorite is repeated until the fibers are completely separated from lignin. It usually requires 6 h of chloriting, and the sample can be left without further addition of acetic acid and sodim chlorite in the water bath overnight. At the end of 24 h of reaction, cool the sample and filter the holocellulose on filter paper using a Buchner funnel until the yellow color (the color of holocellulose is white) and the odor of chlorine dioxide are removed. If the weight of the holocellulose is desired, filter the holocellulose on a tarred fritted disc glass thimble, wash with acetone, vacuum-oven dry at 105°C for 24 h, place in a desiccator for an hour and weigh. The holocellulose should not contain any lignin and the lignin content of holocellulose should be determined and subtracted from the weight of the prepared holocellulose.

2. Preparation of α -Cellulose (Determination of Hemicellulose)

2.1 Scope

The terms; a -cellulose, b -cellulose, g -cellulose, cellulose, cellulose I, cellulose II, cellulose III, cellulose IV, cellulose V are defined in ASTM 1695-77. The term hemicellulose was introduced by Schulze method and defined as the cell-wall components that are readily hydrolyzed by hot dilute mineral acids, hot dilute alkaline or cold 5% sodium hydroxide.

2.2 Principle of Method

Extractive-free, lignin-free holocellulose is treated with sodium hydroxide and then with acetic acid, with the residue defined as a -cellulose. Thus the last fraction gives the hemicellulose content.

2.3 Reagents

- Sodium hydroxide solution, NaOH, 17.5%, and 8.3%
- Acetic acid, 10%, mix one part by weight of glacial acetic acid with nine parts of distilled water.

2.4 Procedure

- Weigh out about 2 g of vacuum-oven dried holocellulose and place into a 250-mLglass beaker provided with a glass cover. Measure 25 ml of 17.5% NaOH solution in a graduated cylinder. and maintain at 20°C.
- Add 10 ml of 17.5% NaOH solution to the holocellulose in the 250-mL beaker, cover with a watch glass, and maintain at 20°C in the water bath. Manipulate the holocellulose lightly with a glass rod with the flat end so that the specimen becomes soaked with the NaOH solution.
- After 2 min, manipulate the specimen with the glass rod by pressing and stirring until the particles are separated from one another. After the addition of the first portion of 17.5% NaOH solution to the specimen, at 5 min intervals, add 5 ml more of the NaOH solution and thoroughly stir the mixture with the glass rod, until the NaOH is gone.
- Allow the mixture to stand at 20°C for 30 min, making the total time for NaOH treatment 45 min.
- Add 33 ml of distilled water at 20°C to the mixture. Thoroughly mix the contents of the beaker and allow to stand at 20°C for 1 h before filtering.
- Falter the cellulose with the aid of suction into the tarred, alkali-resistant Alundum or fitted-glass crucible of medium porosity.
- Transfer the holocellulose residue to the crucible, and wash with 100 ml of 8.3% NaOH solution at 20 °C. After the NaOH wash solution has passed through the residue in the crucible, continue the washing at 20°C with distilled water, making certain that all particles have been transferred from the 250-mL beaker to the crucible. Washing the sample in the crucible is facilitated by releasing the suction, filling the crucible to within 6 mm of the top with water, carefully breaking up the cellulose mat with a glass rod to separate any lumps present and again applying suction. Repeat this step twice. The combined filtrate at this stage of the procedure may be set aside for the determination of b -cellulose.

- Pour 15 ml of 10% acetic acid (at room temperature) into the crucible, drawing the acid into the cellulose by suction but, while the cellulose is still covered with acid, release the suction. Subject the cellulose to the acid treatment for 3 min from the time the suction is released, then apply suction to draw off the acetic acid. Without releasing the suction, fill the crucible almost to the top with distilled water at 20°C and allow to drain completely. Repeat the washing until the cellulose residue is free of acid as indicated by litmus paper. Give the cellulose a final washing by drawing, by suction, an additional 250 ML of distilled water through the cellulose in the crucible. Dry the crucible on the bottom and sides with a cloth and then, together with the weighing bottle in which the sample was originally weighed, place it overnight in a vacuum oven to dry at 100-105°C. Cool the crucible and weighing bottle in a desiccator for 1 h before weighing.

2.5 Calculation and Report

Calculate the percentage of α-cellulose on the basis of the oven-dry holocellulose sample:

$$\propto cellulose\,(\%) = \frac{W1}{W2}x100$$

W1 = weight of the original oven-dry holocellulose sample.
W2 = weight of the oven-dry a -cellulose residue

3. Preparation of Klason Lignin

3.1 Scope

Klason lignin gives a quantitative measure of lignin and is not suitable for the study of lignin structures and some other lignin such as cellulolytic enzyme lignin, or Björkman (milled wood lignin) should be prepared for the study of lignin structure. About 10-15% of Klason lignin of non-wood sources could be protein, and the protein content should be subtracted from the Klason lignin value applying the Kjeldahl procedure. This procedure is a modified version of TAPPI T222 acid-insoluble lignin in wood and pulp (TAPPI, T-222, 1988). The lignin isolated using this procedure is also called sulfuric acid lignin.

3.2 *Reagents*

- Sulfuric acid, H2SO4, 72% and 4% by volume
- Fucose, 24.125% in 4% H2SO4 [w/w]

3.3 Procedure

Prepare samples and dry the sample at 45°C in a vacuum oven overnight. Accurately weigh out approximately 200 mg of ground vacuum dried sample into a 100 ml centrifuge tube. To the sample in a 100 ml centrifuge tube, add 1 ml of 72% (w/w) H_2SO_4 for each 100 mg of sample. Stir and disperse the mixture thoroughly with a glass rod twice, then incubate the tubes in a water bath at 30°C for 60 min. Add 56 ml of distilled water (use a 60-mL syringe). This results in a 4% solution for the secondary hydrolysis. Add 1 ml of fucose internal standard (this procedure is required only if five sugars are to be analyzed by HPLC as a part of the analysis). Autoclave at 121°C, 15 psi, for 60 min. Remove the samples from the autoclave and filter off the lignin, with glass fiber filters (filters were rinsed into crucibles, dried and tarred) in crucibles using suction, keeping the solution hot. Wash the residue thoroughly with hot water and dry at 105°C overnight. Move to a desiccator and let it sit 1 h and weigh to five places. Calculate Kason lignin content from weights.

APPENDIX C

Glucose Decomposition

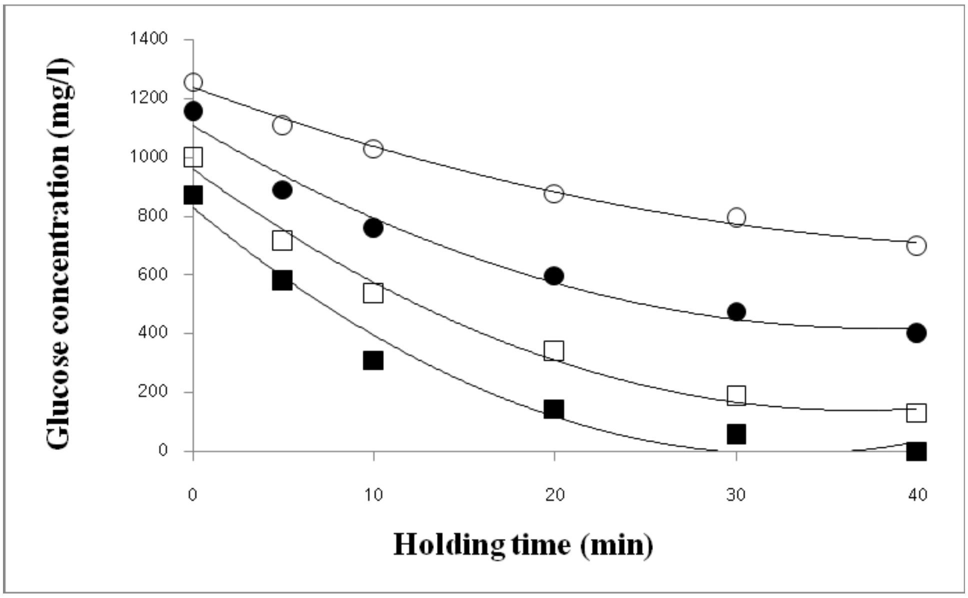

Figure C1 Decomposition of glucose: ○ 200 ºC, ● 220 ºC, □ 240 ºC, ■ 260 ºC

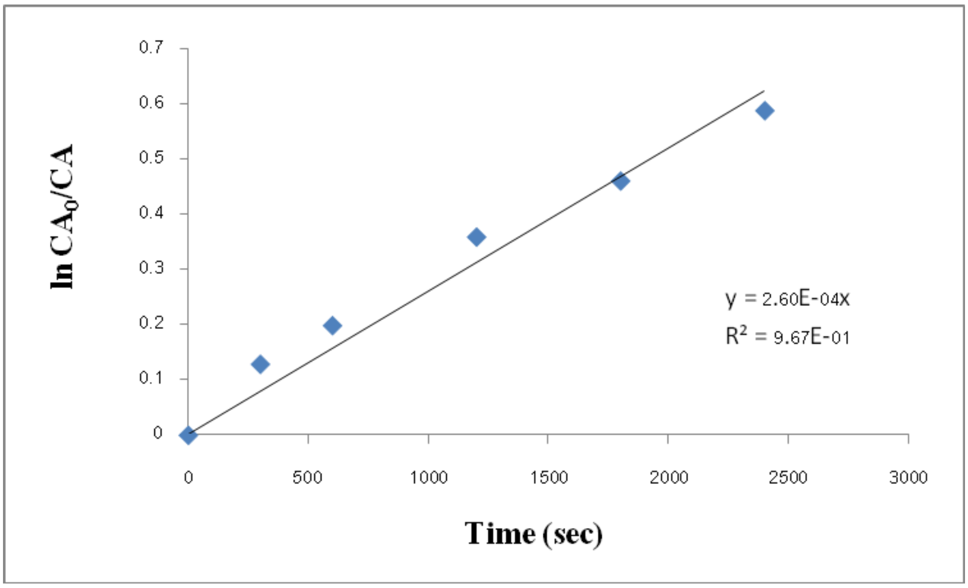

Figure C2 lnCA0/CA VS Residence time at 220 ºC for K value calculation

VITA

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List of publication

NawaponChariyaprasertsin, Yukihiko Matsumura, TawatchaiCharinpanitkul, "Conversion of Secondary pulp and paper sludge to Glucose by Hydrothermal Treatment", The journal of Metals, Materials and Minerals., Vol.23 NO.1, June, 2013.