AN ABSTRACT OF THE THESIS OF

JAMES ANDERSON PHILIPS for the degree of MASTER OF SCIENCE in CHEMICAL ENGINEERING presented on February 13, 1997. Title: Acid Catalyzed Conversion of Carbohydrates - The Preliminary Design of a Sustainable Technology: Strategy and Experiment

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The goal of this research was to make a contribution toward the development of sustainable technology for acid catalyzed conversion of waste carbohydrates into high carbon products. First, a set of rules for developing a sustainability technology are presented. These guidelines are based on the review of historic analysis of failures and successes of different technologies. New emerging ideas regarding sustainable development are also incorporated in this section.

Next, the experimental information is presented. Several waste materials are investigated as feed stock for the reaction: commercial paper products, corn cob, and sugar beets bagasses. Literature and experimental data suggest several reactions convert the carbohydrates. The reaction time depended on the water removal conditions, 1 to 40 minutes, which indicates this is the limiting step in the overall process. Data were taken under acid concentrations of 1 to 4 mole equivalent acid to 1 mole equivalent hexose sugar in the linked carbohydrate in the range of 100°C to 200°C. The analytical techniques used were: Differential Scanning Calorimeter(DSC), Infrared Spectroscopy (IR), Scanning Electron Microscopy (SEM). Elemental analysis show the final product composition is $C_6H_4O_2$. Initial testing suggest the product may have better adsorption capacity than activated carbon. Then, the information obtained in the experimental study is used to develop a new process for the acid catalyzed conversion of carbohydrates. The preliminary design of a pilot plant is presented.

Acid Catalyzed Conversion of Carbohydrates - The Preliminary Design of a Sustainable Technology: Strategy and Experiment

by

JAMES ANDERSON PHILIPS

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Chapter 1, Sustainable Technology

1.1 Introduction

The main goal of this thesis was to develop a sustainable technology for the acid catalytic conversion of carbohydrates into high carbon products. There were several objectives for this project . First, identify useful raw materials and their composition. Second, identify the reactions taking place. Third, investigate parameters that influence the conversion of carbohydrates. Forth, study the physical and chemical properties of the high carbon product. Finally, identify possible uses of the product and briefly investigate one.

In the development of these goals this thesis starts out with a review on technology as the first chapter. This is the ground work for development of sustainability in engineering. The second chapter is the background and experimental work done on the acid catalytic reaction of carbohydrates. The third chapter is the technology development. This section presents a preliminary technology to produce the reacted cellulose product and a quick evaluation of it.

1.2 Activity Toward Sustainability

Humans are living an unsustainable lifestyle. We are polluting, over populating, and using natural resources at an unacceptable rate. Efforts have recently focused on identifying and correcting some of the problems. The two main areas addressed here are minimization of pollution and natural resource utilization. The identified failures for these areas are design philosophies, technological failures, and human influences. Some of the main failures are reviewed and analyzed. The information is then used to develop a philosophy for the development of sustainable technology.

Conferences, Commissions and Movements

The world's communities has started paying attention to the sustainability of the world we live in. Conferences, Commissions, and Industry have developed ideas such as sustainability, technology transfer, appropriate technology, clean technology, and industrial ecology as a response to unsustainable practices. All of these ideas have sustainable technology elements. The main focus is longer term existence of people on earth. Some of the ideas are illustrated:

> The collective international trend started with a report by the World Commission on Environment and Development titled, "Our Common Future." The 1987 report was endorsed by 100 governments on the United Nations General Assembly. The report defined Sustainable Development (Beder S., 1994) as " development that meets the needs of the present without compromising the ability of the future generations to meet their own needs."
>
> The next global effort to address this was the 1992 United Nations Conference on Environmental and Development (UNCED), also known as the Earth Summit. The conference was represented by 178 governments (de Lemos H. M., 1992) and many nongovernment groups that addressed the topics of population, technology, and sustainability. It was said to be the largest conference ever. The nations were unable to agree on population or consumption levels, although several documents were made. Among those were the Rio Declaration on Environment and Development, Agenda 21, a statement on Forest Principles, and two conventions: one on Climate and another on Biodiversity. The Rio Declaration summarizes principles which the nations have agreed to base their practice in environmental and developmental issues. Agenda 21 is a guideline to sustainable development. From this preceding the US created the Presidents' Council on Sustainable Development.
>
> Another movement was begun by the "National Commission on the Environment" (Train R. E., 1993). One of their aims is removing regulatory obstacles to

environmental advantageous technologies. Some of their other aims include using tax incentives and direct federal funding to simulate technologies that will permit sustainability. The ideas for the future discussed by this commission are: a carbon tax, changing human ethics, and minimizing the stress on environment

This trend was followed by businesses looking into their future. One example was the 1993 Third Forum of the World Chemical Industries. The title (Popoff F., 1993) was " Major Challenges of the Next Century"- technologies and competitiveness, cooperation and competition in a global market , and relationships between the chemical industry and society. The main topics were sustainability development and technology cooperation between businesses. Another examples is a book written by the Business Counsel for Sustainable Development (BCSD). The book "Changing Course," focused on global business perspectives for sustainable development.

Next some of the ideas developed as a response toward sustainable development are presented. The topics cover are appropriate technology, clean technology, and industrial ecology. The ideas presented here appear under different titles throughout various disciplines.

Appropriate Technology

Many different philosophic ideas on what types of technologies are fitting have been documented: low-cost, intermediate, progressive, correct, and traditional. In the 1970's these evolved into the appropriate technology movement. Schumacher (1974) fathered the movement with his book " Small is Beautiful; A Study of Economics as if People Mattered." The movement focused on use of technology that was appropriate with considerations of; health, climate, biodiversity, ecology, social institutions, politics, culture, economics, ethics and the personal/spiritual needs of individuals (Beder S., 1994). The movement was said to have failed for several reasons: vested interests, and mainstream thinking and understanding of the classical process of technology definition and development.

Clean Technology

According to Clift R. (1995) "A clean technology is a means of providing a human benefit which, uses less resources and causes less environmental damage than alternative means which are economically competitive." The main elements in creating clean technology are: economic performance, resource lifecycle analysis, changing from a manufacturing to a service industry, and waste minimization.

Industrial Ecology

The concept of industrial ecology is one in which economic systems are viewed not in isolation from their surrounding systems, but in concert with them (Graedel T. E., 1993). As applied to industrial operations, this concept requires a system approach in which one seeks to optimize the total material cycle from virgin material, to finished material, to component, to product, to waste product, and to ultimate disposal. Factors to be optimized include natural resources, energy, and capital.

1.3 The System Failure

Macro Failure (The system philosophy failure)

Environmental problems have become apparent to everyone in the last several decades, but they originated on the large scale with the beginning of the industrial age. The pollution caused by industrialization was not a failure of the designer or the system, it was the failure of the system philosophy. Manufacturing plants were designed to make products, not to be environmentally benign.

Micro Failure (The technology failure)

Environmental problems can also be contributed to technology failure. Technology failure can be divided into two main categories: system design failure and implementation failure. System design failures are related to inadequate or wrong design of technology. System design failures are typically easier to identify and correct (through implementation of technology design principles\rules) than implementation failures. Factors leading to implementation failure are outside the technology, and are more numerous, diverse and dynamic than the factors of system design failure. Implementation failures are technology failures caused by; policies, politics, culture, economics, human factors, and coupled effects. Other design technology topics that need to be considered because of their potential for failure include closed loop technology, lifecycles, and technology transfer. These factors are briefly identified and discussed.

Policies and Politics

Policies and politics can both cause similar technology failures. For instance, many countries or businesses do not always support clean technologies by politics or policies. End of pipe pollution control treatment is a prime example. Pollution problems that cause fines and legal problems are quick fixed by end of pipe treatment. This treatment is often a wasteful use of resources because it is technology designed to fix technology. The Organization for Economic Co-operation and Development (OECD), a multinational organization, found 80% of pollution control investments were for end of pipe treatment (Beder S., 1994). Cleaner technologies are not always available, but when they are, they are not chosen for several reasons, among which are: government regulations, political influences, company policy, and cost.

Culture

Culture barriers can cause technology to fall short of potential operation. An example is clean drinking water. Third world countries in Africa and Latin America are deficient of clean drinking water. The American solution would be to build water treatment plants. The system would filter, flocculate, sanitize, adjust mineral content and pH levels. This type of system works appropriately in America, but it would fail in most third world tribal communities.

There are several reasons why this type of technology would fail in most tribal communities. First, these societies do not have the necessary infrastructure. Second, they may not want it for cultural reasons. Next, there are human resource problems like; hiring qualified technicians to run and repair the system, gaining acceptance from the community, and cost. Other problems encountered may involve a belief or a religious Sabbath.

One example of applied technology with cultural considerations outlined here are some of the wells used by third world countries. The special wells are designed by highly industrialized nations with the outlined problems in mind. In this case, a typical water system (Valenti M., 1991) consists of a capped well with a hand pump that is occasionally disinfected with chlorine. This design is not as safe or efficient at delivering water, but it fits in better with the culture as compared to standard American water technology.

Economics

Economics elements are one of the more obvious reasons for technology failure, although other factors complication the failures. Advancement in technology, supply, demand, and politics are only a few of the causes that influence economic failures of technology. Technology advancements can have impacts such as rendering a production infrastructure useless. This can waste resources and hurt businesses especially if there was a large capital investment. Changes in supply or demand are problems that can devastate any technology's economics. A shortage in resources are of the most concern here. Politics are another cause of the economic failure of technology. For instance, much technology is developed under government grants or incentives. If a political influence changes the funding, the technology can deteriorate or never reach its potential. Solar energy incentives cut by the Reagan administration is one example of this unfortunate development.

Human Factors

Human factors are one of technology's worst enemies because they can cause technology to fail due to bias. Some of the identified factors include; technology trajectory, appeal, and personal perception of power. Technology trajectory defined by Beder S. (1994) is technology that is developed to fit a paradigm. If the technology does not fit the paradigm, then it is ignored by most of the mainstream professionals. This impedes creative thinking and ingenuity. Human appeal and personal perception of power are factors that cause people to act on desires instead of practical reasoning.

An example that illustrates these factors is the automotive industry in the US. Oil companies want people to buy oil, gasoline and other petroleum products. Car companies want people to buy cars. They design cars to fit people's lifestyle and desires. They advertise the cars to have appeal and freedom. People see autos as symbols of freedom and personal power. The cost and resources used for transportation are compared to transportation and satisfaction gained by driving. Often, mass transit is a cheaper method of transportation that is discarded because people want to drive themselves. For example, in 1990, the US public transit was used by 5.3% of the population for transportation to work. This industry also illustrates technology trajectory. Different modes of transportation like electric cars were mainly ignored until resent laws called for alternatives energy for transportation. Each one of these factors can cause applied technology to fail because of bias or desires of individuals.

Coupled Effects

Technology application failure is seldom caused by one factor. The different factors coupled with other elements like infrastructure and technology advancement often cause failure. For instance, a past American idea was the "bigger is better" principal. People, businesses and governments followed this until about 10 years ago, at the fall of the main frame computers to personal computers. This point in history is also marked by VCR's competing with movie theaters, and photocopy machines displacing conventional printing.

Traditional wisdom suggested it was more economically advantageous to use one large system than several small ones for the same results - a "natural monopoly" for large systems (Alamaro M., 1994). This idea is often true, but it fails. A good example is the computer industry in business. Main frame computers are the cheapest computing tools if there is a large demand, although personal computers are dominating businesses with large demands.

Alamaro M. (1994) suggested one reason for the change from large systems to small ones is the technology evolves into common information. Some of his other reasons are; small capital investment, convenience of mass production of small systems versus customization of large systems, reduced infrastructure, and just in time operation. Some of the advantages of small systems are; personal perception of power, convenience, increased technology, accelerated technology, innovation, incremental output capacity, and time saved.

Other Ideas That Deserve Attention

Closed Loop Technology (Cogeneration/Waste Minimization)

Resource utilization can influence the failure or success of a technology when one of the goals is sustainability. Resources that can be commonly saved or better utilized are heat and materials. The common terminology for these are cogeneration and waste minimization. Cogeneration is the recovery of energy from process heat sources. Waste minimization is reduction of waste materials. Both of these can contribute to pollution, either thermal or physical. Often the decision to proceed with cogeneration or waste minimization is based on financial gain and the type of problems anticipated. This type of decision is often misleading and can cause technology to fail, especially if the technology was designed with a long term goal of sustainability. Closer partnerships with businesses can lead to better resource usage.

One example that illustrates a partnership (figure 1.3.1) is the Danish Kalundborg's "Industrial Symbiosis" (Knight, 1993). The collaboration is between; a coal fired power plant, a fish farm, a pharmaceutical plant, a refinery, a plaster board plant, and public housing. The coal fired plant supplies warm water, hot water or steam to all the partners of the collaboration except the plaster board plant. The coal plant also produces fly ash and gaseous sulfur. The fly ash is collected and sold to cement makers as a filler. The sulfur is scrubbed and reacted to gypsum which is sold to the plaster board plant. The refinery supplies surplus gas, cooling water and gaseous sulfur removal to the coal fired plant. Further use of resources is seen by the pharmaceutical plant which makes fertilizer supplement from their sludge, and the refinery which supplies sulfur for sulfuric acid production. Typically, coal fired power plants convert about 40% of the energy in coal to electricity. Collaboration like this is said to increases the coal energy efficiency usage be around 90%.

Technology Transfer

Availability of information is important for technological success. The trade of technology is beneficial to everybody for several reasons. First, the most efficient use of resources can be achieved by increasing the resource life, shortening development time which cuts cost. Second, common needs can be shared like accessible infrastructure and specialization expertise. Third, technical advancement by combined efforts is greater than advancement by individual efforts.

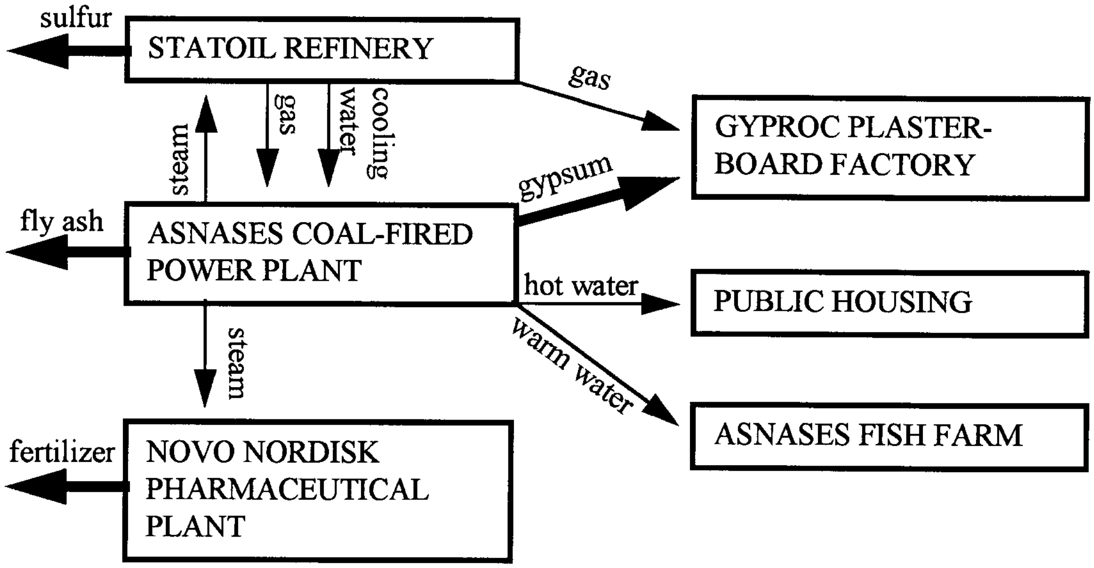


Figure 1.3.1, Kalundbourg's Industrial Symbiosis

Lifecycles

The lifecycle design of products is another potential downfall of technology. Businesses typically design products with a useful life. After the life, the products are often scrapped or recycled. Some businesses design their products with maximum profit as their only agenda. The short lived product may have produced a high profit, but resources are wasted. Even if the product is recycled, the energy to recycle it is lost. A great idea that came out of this is product stewardship. This is currently practiced in Germany with product packaging. The distributors, manufacturers and retailers who handle a product are responsible to collect and recycle the packaging. If businesses shift from a manufacturing to a services industry, the objective of long product life will benefit and be developed by the businesses.

1.4 Sustainable Technology Philosophy and Objectives

Reflecting on the information presented, I have coordinated a system design philosophy for sustainable technology. The system consists of goals, objectives, and evaluation tools.

Goals

The purpose of presenting and analyzing this information is to identify the success and failures of technology. The technology we design must work in a sustainable harmony with the world in which we live. People have been trying to achieve sustainability, but they have often failed for a variety of reasons. The general goal for sustainable technology is:

Technology that fits with society, the earth's ecosystems, with minimal use of resources, minimal impact on the environment and maximum yield of used resources.

Objectives

In the development of sustainable technology there are several groups of objectives.

Social objectives:

- Government regulations and policies aimed at helping sustainable technology
- Regulated political influences
- Control of technology trajectory and vested interests
- Proactive education of the people
- Change in human ethics, appeals, and attitudes

Business objectives:

- Dynamic evaluation of the business system elements
- Shifting from a manufacturing to a service industry

Technology objectives:

- Economic performance
- Meshing with business practices
- Decentralization of investment
- Minimum infrastructure demand
- Size of operation
- Clean technology instead of end of pipe treatments
- Closed loop technology (waste minimization/cogeneration)

This list of objectives are a present day overview of anticipated problems. As the problem complexity changes with time so will the objectives, indicating the list will need to be dynamically updated. If these objectives are not evaluated and updated, the potential for some type of failure increases. Despite the fact that objectives are quantified, different design approaches will yield independent solutions. Therefore, when technology designs are compared an assessment tool is needed.

Assessment Tool

Above are the elements of our technology development. When technologies are compared, one useful tool is the lifecycle assessment (Clift R., 1995). The life cycle assessment typically involves four steps: goal definition, inventory, impact assessment, and improvement assessment. The steps define a system and methodology to evaluate the best technology. Goal definition starts with defining a system boundary on a per unit basis for comparison. For example, if glue were being compared the comparison would be on surface area glued and not the mass of glue. The system boundary is defined as all the material and energy used or created by the product from the raw or recycled material stage to the disposal or recycle stage. Inventory means quantifying the systems boundary flows. The impact assessment analysis estimates the resource depletion and environmental impact caused by the system. Improvement assessments are comparisons of technology.

1.5 Summary

The most important objectives for sustainability are: attitude adjustments, and education of the people. In my opinion, cutting back on resource usage is the most difficult component to control. If people are made aware of what is happening to the resources of the world, then they may change their habits. An example of this is illustrated in fusion technology. The argument is that if fusion is developed, then we will have a large supply of clean cheap power. This also will save natural resources like oil and coal. Global warming will decrease due to less combustion of carbon based fuels. This is all true and most people would like this. What people don't understand is how fusion can contribute to thermal pollution. This brings us back to global warming, will it be worse than now? The solution is to slow down!

Some other ideas which deserve further consideration and development for sustainable technology implementation are; technology transfer/cooperation, product stewardship, carbon taxes, resource taxes, and changes in laws and ethics. The driving forces for these ideas will need to be developed , but ideas like these will help in attaining the goal of sustainability. Implementation of sustainability will be a long term process. Goals like this are often most successful under a total quality management system like the Deming system.

Chapter 2, Experimental and Theoretical Work

2.1 Conversion of Cellulose

Cellulose is the most abundant source of carbon on the earth. In the US, the potential energy in the annual biomass is equal to the annual energy consumption (Antel M. R., 1983). Finding an efficient method of converting cellulose into a useful storable energy source like a liquid fuel or a useful chemical is under investigation. Several different methods to recover the energy in cellulose are outlined in table 2.1: combustion, hydrolysis, fermentation, and pyrolysis. The conversion efficiency of biomass to chemicals or a liquid fuel is below 45%. This indicates that further research is needed in this area.

Process	Product	Approximate Overall Efficiency *
Direct combustion [1]	Steam	65%
Direct combustion [1]	Electricity	25%
Gasification, with oxygen [1]	Medium Btu gas	60%
Gasification, with air [1]	Low Btu gas	50%
Gasification [1]	Steam	65%
Pyrolysis [1]	Pyrolytic oil, char and low Btu gas	45%
Anaerobic digestion [2]	Medium Btu gas	50%
Ethanol fermentation [3]	Ethanol	30%

Table 2.1.1, Biomass Conversion Processes (Robinson J. S., 1980)

* Based on the biomass input (higher heating value) converted to fuel, less the required fuel needs of the conversion process.

[1] Up to 50% maximum moisture without drying(e.g. wood chips, field dried agriculture residue).

[2] High moisture (sewage sludge, aquatic biomass, etc.)

[3] Sugars(sugar cane juice, molasses, hydrolyzed cellulose, etc.)

This thesis investigates the acid catalyzed reactions of carbohydrates like paper products, sugar beet pulp, and corn cob. Possible products from this material are liquid fuels, gaseous fuels, chemicals, adsorbent materials and fertilizers. Further processing of the reacted cellulose is believed to result in products similar to coal processing. Liquefaction is one method that may have promise for this material. The liquid products may be useful as chemicals or fuel. Gasification is another possibility for this material. This material is believed to have less functional groups than coal. This indicates a smaller array of compounds would be produced from further processing of this material compared to coal.

Introduction to Acid Catalyzed Conversion of Carbohydrates

Acid catalyzed dehydration is a process that has potential application in the conversion of waste carbohydrates into useful products. All carbohydrates are believed to react similarly in this process. The products have characteristics similar to materials like young coal, activated carbon, and humus. The goals of this thesis are to develop a technology to produce this product and find uses for it. The objective in this research is to develop sustainable technology that can convert waste cellulose into the product, and investigate potential applications of it.

The main conversion mechanism of this process consists of acid catalyzed dehydration reactions and water removal from the system. Other operations in this process are steps that support the main reaction. This section studies these steps: materials, preparation, unit operation, and product characteristics. The choice of unit operations corresponding to these process steps are given in chapter 3.

The reaction starts out by saturating the carbohydrate material with aqueous acid. After the acid has penetrated the material, it is exposed to heat which evaporates the water. The reaction proceeds as water is eliminated from the system, and takes approximately the same time as drying the material. Experimentally it was noted that when water is not eliminated from the system, the reaction is slowed or stopped. The overall reaction scheme is illustrated in figure 2.1.1. This scheme comes from elemental analysis of the several different initial and final materials. This process consists of heat transfer, mass transfer, and reactions. The heat and mass transfer are complicated by geometry and changing macrostructure (as seen in the ESM studies). The acid catalyzed dehydration reactions are probably reversible reaction as shown in figure 2.1.1. This indicates that the rate of water removal could control the mechanism in this reaction, although the heat transfer mode most likely plays a role. Another example of a controlling mechanism would be formation of hydrolysis products if little or no water was removed, although this was avoided. Other possible reaction mechanism, covered in section 2.2, are: pyrolysis, polymerization, or crosslinking.

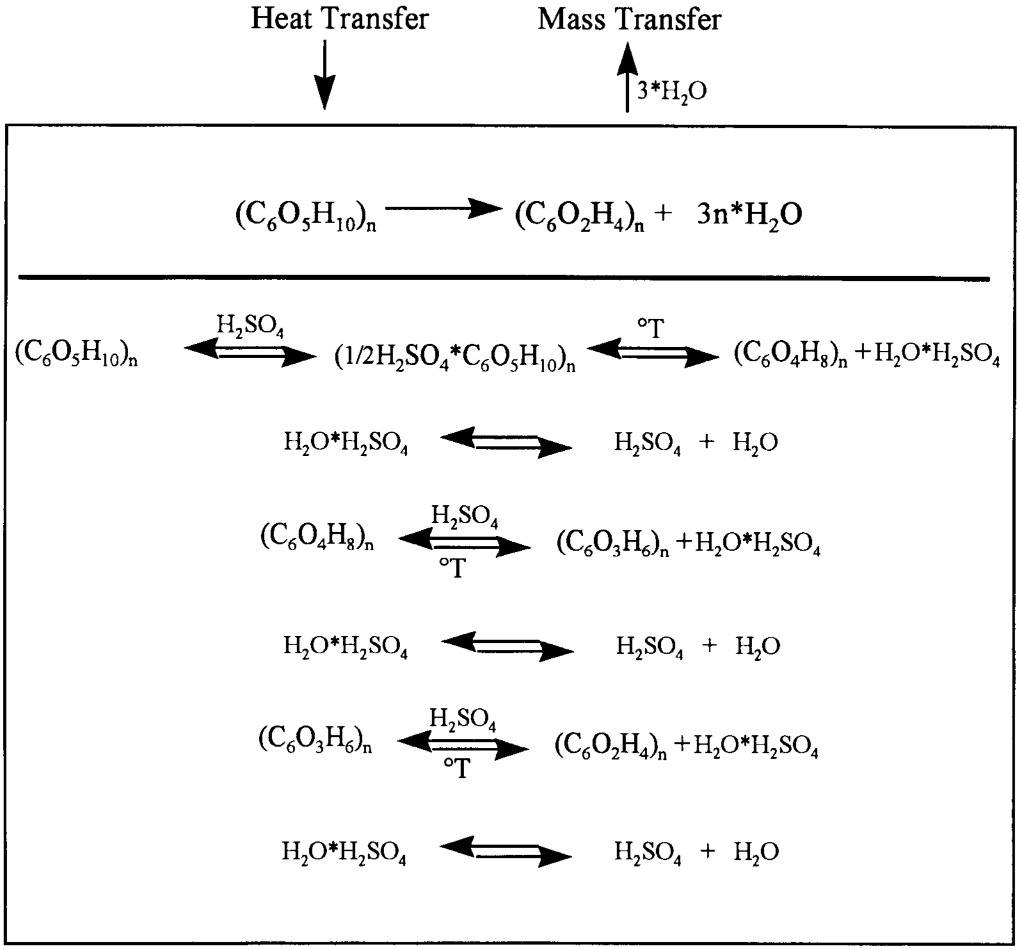


Figure 2.1.1, Conversion Process

2.2 A Review of Mechanisms for Conversion of Cellulose

Many studies have focused on reactions of cellulose and hemicellulose for production of chemicals such as; furfural, acetone, levoglucosan, glycolaldehyde, levulinis acid, formic acid, butanol, ethanol, methane, and hydrogen. Studies have concentrated on hydrolysis, fermentation and pyrolysis of cellulose, hemicellulose, wood, and many types of agricultural waste. There have been other studies of polymerization of sugars and starches. A crosslinking reaction mechanism has been indicated in some cases. A hypothesis is presented for the acid catalyzed reaction studied here. The common link between these areas of research is the investigation of catalysts to enhance the reactions and the crosslinking or polymerization.

Hydrolysis

One main area of research has been acid catalyzed hydrolysis of cellulose to sugars. Many researchers have focused primarily on the production of ethanol from the glucose. There have been studies of glucose conversion (figure 2.2.1) to levulinic acid, hydroxyl methyl furfural (HMF), acetone, butanol, and other various acids.

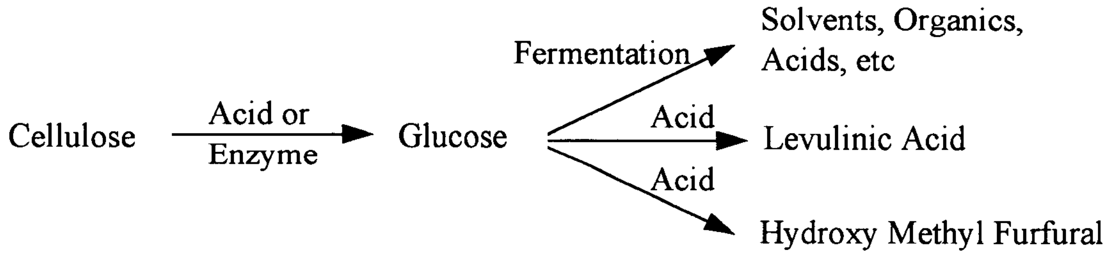


Figure 2.2.1, Cellulose Processing Path

Other studies have explored conversion (figure 2.2.2) of hemicellulose to furfural and other products

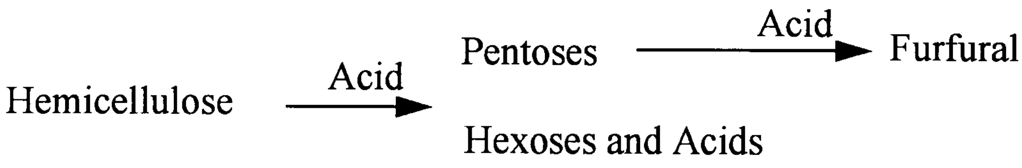


Figure 2.2.2, Hemicellulose Processing Path

Hydrolysis is frequently associated with a solid residual, often termed humic substances. The solid product is melanoid (black pigment substance) and mostly insoluble in acid or base. Hydrolysis research that yield humic substances (Riera F. A. et al., 1991) are made with catalysts such as salts (aluminum sulfate, calcium chloride and zinc chloride) and acids (sulfuric, hydrochloric and phosphoric). Some examples of humic substances made during hydrolysis are sighted. Nelson M. L., Conrad C. M. (1948) reported insoluble residuals in acid hydrolysis of cellulose. Philipp B. (1947) presented a method to remove the humic substances from acid treated cotton. Garves K. (1981) reported the products of mainly HMF, levulinic acid, formic acid and humic substances from hot sulfuric acid treatment of glucose. Riera F. A. et al. (1991) found furfural and humic substances as products from hot pressurized hydrolysis of corn cob.

Pyrolysis

Another branch of researchers have focused on thermal decomposition of cellulose. Pyrolysis of cellulose (Antal M. J,, 1995) forms many organic species and a complex char. Some of the products found are; levoglucosan, glycolaldehyde, water, carbon monoxide, carbon dioxide, butanol, ethanol, methane, hydrogen, furans, low molecular weight carbonyl compounds, and complex polymers. Catalysts are used for selectivity of the products. Currently, a reaction pathway model for cellulose pyrolysis has been proposed as shown in figure 2.2.3:

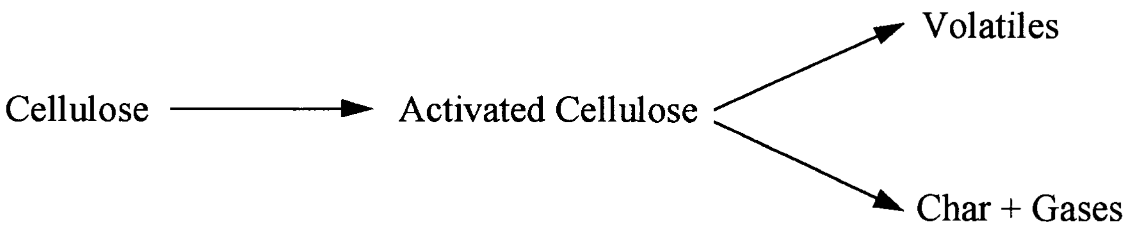


Figure 2.2.3, Pyrolysis Pathway (Bradbury A. G. W., et al., 1979)

Some of the catalysts that play a role in pyrolysis are; salts, metals, H^+ and moisture. Salts and metals (Richards G. N., 1991) have a large effect on selectivity of products. The salts and metals selectivity mechanism is unknown. Temperature weakly influences the selectivity in the presents of metals and salts. Pretreatment with sulfuric acid (Piskorz J., et al., 1989) has shown increased selectivity. This acid pretreatment typically reduces salts and metals as shown by a reduction in the ash content of the starting material by 90%. The hydroian ion (H^+) is believed (Antal M. J., 1995) to affect dehydration of cellulose. Moisture was found to catalyze hydrolysis (Mok W. S. L., et al., 1992) of unreacted cellulose under pyrolysis conditions.

There are two main mechanism theories for pyrolysis of cellulose: intermolecular dehydration (cross linking), and char free depolymerzation (volatilization). Pyrolysis reactions were shown (Broido A., Nelson M. A., 1975) to be a combination of the two. In this study the depolymerzation reaction formed no residue, where as the dehydration reaction formed 36% char. The dehydration reaction (Antal M. J., 1983) dominates at lower temperatures and produces mainly: CO, CO_2, H_2O, and char. The residual, known as char, elemental analysis (Broido A., Nelson M. A., 1975) revealed: 86% C, 2.4% H and 1.6% O.

Pyrolysis of mono and oligosacchrides is known to produce over a hundred compounds. The principal reactions are dehydration's evolving water. One example (Brinkly R. W.,

1988) is pyrolysis of D-glucose (figure 2.2.4) which produces HMF and 1,6-anhydro-β-D-glucopyranose commonly known as Levoglucosan - an exopoxide.

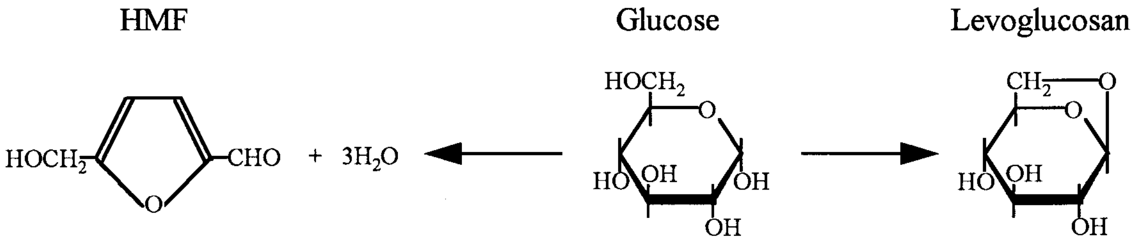


Figure 2.2.4, Glucose Conversion Pathway (Brinkly R. W., 1988)

Polymerization

Polymerization's of sacchrides are known to proceed between several functional groups. The main polymerization of sacchrides in an acid environment is between hydroxyl groups reacting with functional groups such as: aldehydes, expoxides, and carboxylic groups.

Sugars in a strong acid medium are known to degrade to solid melanoids. Hexose sugars react in high acid concentration (figure 2.2.5) to a dehydration products like of HMF and 3 water molecules (Brinkly R. W., 1988). Pentose sugars under the same conditions are converted to furfural and water (McMurry J., 1988). Cellulose is also known to react and produce HMF (Biermann C, 1993) and water in a 25% sulfuric acid solution. These products are known to polymerize in an acid medium (Parsons J. W., 1989).

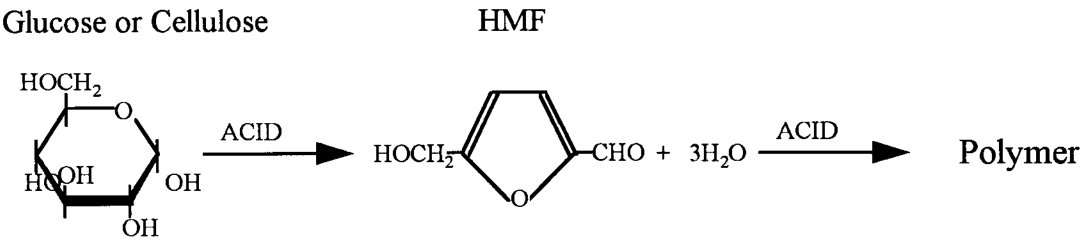


Figure 2.2.5, Dehydration Pathway

Mora P. T., et al. (1958) studied acid catalyzed polymerization of glucose at 140 to 170°C in a vacuum. The vacuum was necessary to remove water so the reaction would proceed. The polymerization took place between a glycoside hydroxyl group and a aldehyde (figure 2.3.6) from mutarotation, which means the polymerization is not limited to glucose. An interesting note in further research (Mora P. T., et al., 1958) suggested a high degree of polymerization of glucose was favored by: acid catalysis at a concentration that does not cause side reactions, high temperature, effective elimination of the water produced during the reaction, high concentration of sucrose, sufficient mobility of the monomer and polymer, absents of oxygen and other conditions that may caused degradation, and uniform reaction conditions.

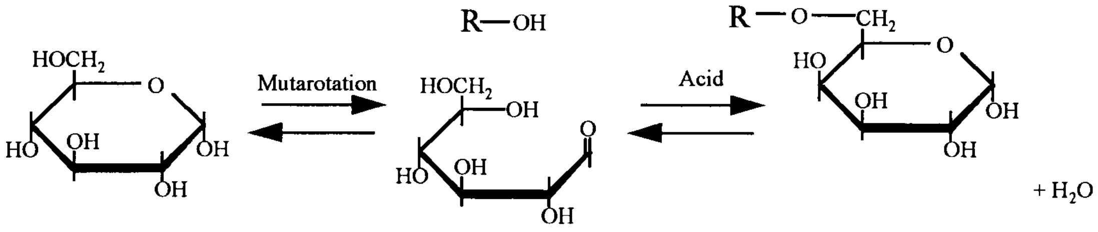


Figure 2.2.6, Murarotation Polymerization (adapted from Mora P. T., et al., 1958)

Another known ether linkage polymerization (Greenwood C. T., 1967) is formed from exopoxides and hydroxyl groups (figure 2.2.7)

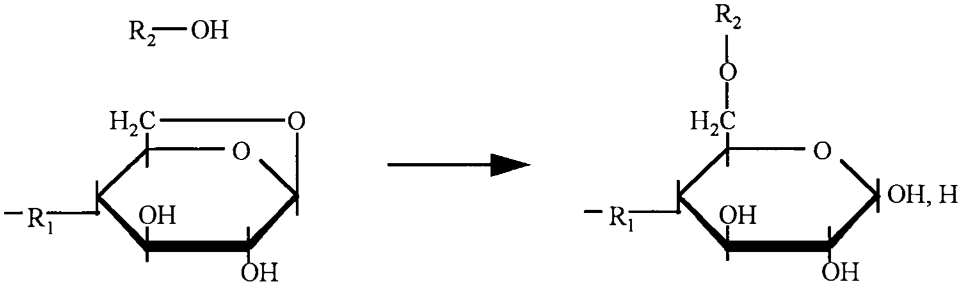


Figure 2.2.7, Expoxide Polymerization (adapted from Greenwood C. T., 1967)

Jayme G., Lang F. (1963) found esterfication (figure 2.2.8) always occurs to some extent for cellulose in sulfuric acid. Esters can form or hydrolyze as a function of pH as do lactols (Bloom P. R. Leenheer A., 1989). Ester linkage will also hydrolyses (Pigman W. W., 1948) in the presents of sulfuric acid, degrading the linkage.

$$R_1-\overset{\overset{\displaystyle O}{\|}}{C}-OH + HO-R_2 \longrightarrow R_1-\overset{\overset{\displaystyle O}{\|}}{C}-O-R_2 + H_2O$$

Figure 2.2.8, Ester Linkage (adapted from Jayme G., Lang F., 1963)

Other researchers have focused on different aspects of pyrolysis polymerization. Durand H. W., et al. (1958) polymerized glucose in the solid state with a dry acid catalysts. Hounimer Y., Patai S. (1969) found 18 % of the collected water in a dehydration reactions for pyrolysis of glucose resulted in carbon double bond formation. The same acid catalysis crosslinking reactions have been extended to starches (Greenwood C. T., 1967).

Research of noncellulose carbohydrate have focused on polymerization reactions at temperatures less than 200°C. Levoglucosan (Carvalho J. D. S, et al., 1969) and other pyrolysis products (Antal M. J., 1983) readily undergoes polymerization in the presents of catalysis. The products formed are complex polymers, H_2O, CO_2, CO, furans, and low molecular weight carbonyl compounds. Catalysts used in this work were zinc chloride and platinum black. The main difference between this reaction and acid catalyzed polymerization reactions of glucose is the necessity to removal of water for the glucose to polymerization.

Thermal Crosslinking Reactions

Thermal crosslinking reactions studies of cellulose showed results similar to pyrolysis. Philipp B. (1981) showed thermal hydrolytic degradation is clearly increased by the presents of an acid. Philipp B. also found that extend exposure of cellulose to high temperatures inhibits determination of the degree of polymerization because the formation of insoluble crosslinked products. A crosslinking of intermolecular glycoside bonds was suggested (figure 2.2.9) which agrees with the work of Back E. L. (1967) and Mora P. T., et al. (1958). Back E. L. (1967) also found that cleavage and crosslinkage occur simultaneously on heat treatment of cellulose and hemicellulose, and that crosslinking reactions are catalyzed at a low pH.

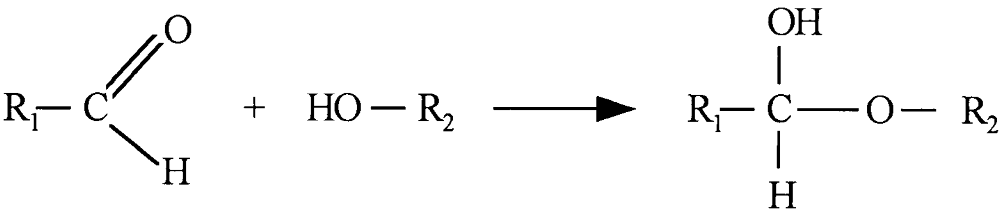


Figure 2.2.9, Thermal Ether Linkage

Other Reactions

Several nonconventional reactions have been suggested for acid catalyzed reactions of cellulostics. Cellulostic materials (Nevell P. T., 1963) react to furfural and carbon dioxide in an acid medium. The furfural undergoes further reactions. Garves K. (1981) further indicated the loss of one CO_2 molecule per anhydroglucose unit is conceivable, or the oxidation-decarboxylation-hydrolysis of cellulose could lead to furfural. They concluded that continuing reactions between dissolved carbohydrates and aqueous acid leads to products of dehydration. Their work showed that higher reaction time and higher temperature increased the formation of insoluble residuals.

The Sperry Hypothesis

Carbohydrate converted to high molecular weight polycarboxyl acids has been shown (Patents: 2881211, 2894940, 2956948, 2976235) to proceed by an acid catalyzed reaction. Initial work by Sperry R. L. (1996) showed conversion of cellulose to solid char resins proceeded in a high acid concentration. Sulfuric and Hydrochloric acids were shown as good catalysts in the reaction , although other acids were believed to work. Further work by Sperry R. L. (1996) showed that acidic salts (patent 3932166) catalyze the reaction also. Additional reaction of the char in a NaOH environment at elevated temperatures yielded high molecular weight polycarboxyl acids.

The acid catalyzed reaction is hypothesized to be a crosslinking mechanism that eliminates water. The theoretical pathway suggested by Sperry R. L. (1996) shows carbohydrate conversion as figure 2.2.10.

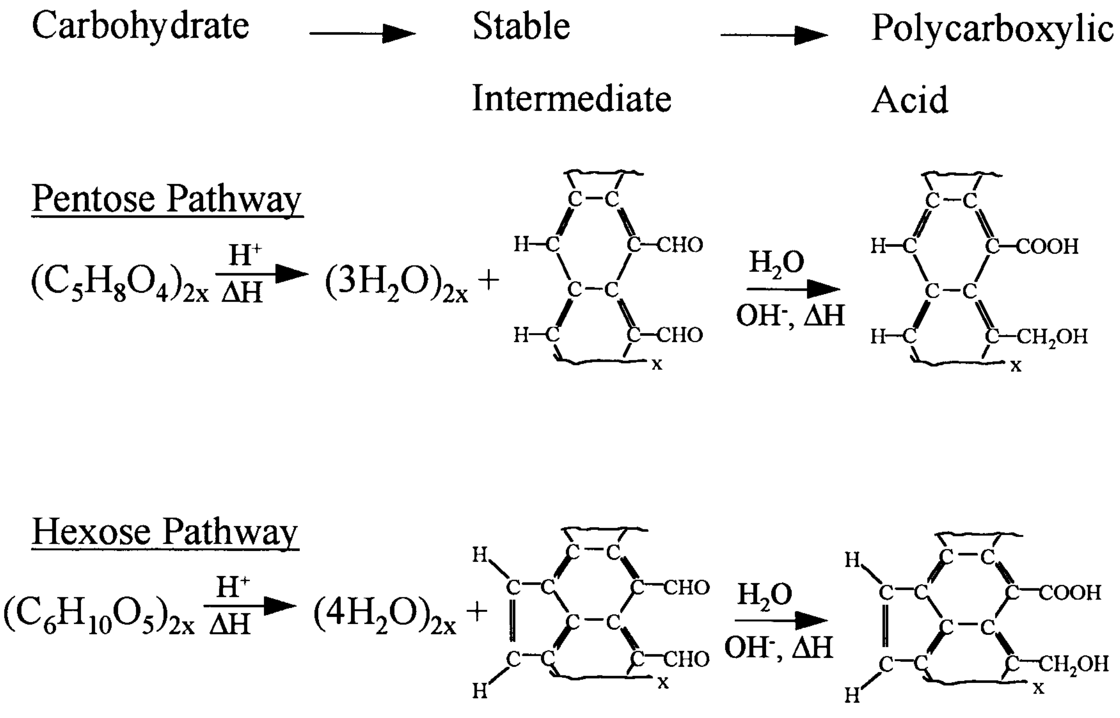


Figure 2.2.10, Carbohydrate Product Path (Sperry R. L., 1996)

The intermediate product is black and mostly insoluble in all solvents tested (organics, and boiling caustic); shows no signs of a melting point and appears inert. Elemental analysis of the intermediate done by Rayonier, Inc. in the 1960's gave; 78 to 80% C, 18 to 20% O, and 2 to 3% H. Rayonier also inferred, from infrared analysis that oxygen is present only as a carbonyl group such as carboxylic acid and alcohol groups in the polycarboxylic acids (Sperry R. L., 1996).

Reaction of the intermediate in caustic is believed to convert the aldehyde groups to alcohol's and acids on the polymer by the Cannizzaro reaction. The reactant is mixed with aquaous NaOH in a sealed bomb and reacted at temperatures around 500°F. The products are soluble in a basic solution and precipitate in an neutral to acid solution. Further reaction under the same conditions are believed (Sperry R. L., 1996) to decarboxylate the polymer as shown in figure 2.2.11. Acid numbers in the range of 205 to 210 indicate linear polymers with one carboxylic acid for every 12 carbons (Sperry R. L., 1996). This reaction should work on many carbohydrates; Cellulose, Hemicellulose, Starches, and Sugars.

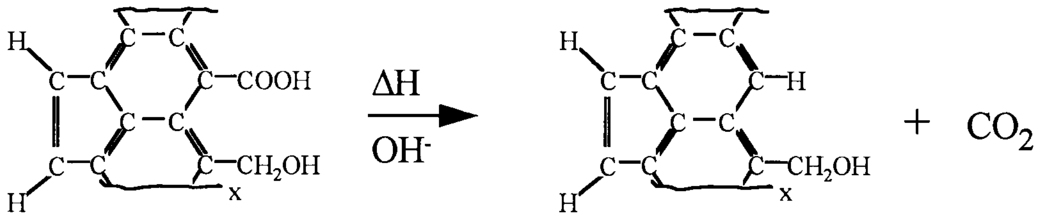


Figure 2.2.11, Char Solublization Reaction (Sperry R. L., 1995)

2.3 Raw Material Study

This research is based on dehydration and polymerization of hexose and pentose polymers like cellulose and hemicellulose. With this and economic considerations we have decided to investigate the materials that are naturally abundant in our economy. This section describes the raw material, preparation and handling.

The main criteria for selecting the material was the quantity of linked sugars such as in cellulose. Some other criteria for selection are: cost, renewable sources, waste materials, low contaminates, low ash, and low water. There are many sources that meet this criteria: paper products, rice hulls, melon shells, straws, corn stalks, corn cobs, grasses, woods, and bagasses (sugar beets, and sugar cane).

This study has focused on the use of paper products, corn cob, and sugar beets. The reason for using these products are only for preliminary testing and the convenience of known composition of cellulose and hemicellulose. Paper towels were chosen to represent waste paper products without the contaminates. The corn cobs and beets were chosen to demonstrate the use of waste agriculture products.

Paper Towels.

The main reactants used in this study were paper towels. Paper towels have cellulose/hemicellulose composition in the range of Kraft pulp. Table 2.3.1 outlines the average composition range of 10 types of pulp from two pulping processes

Source	Material as reported	Wt % cellulose	Wt % hemicelulose
Reeve F. A., et al., 1989	Sulfide pulp	85 to 91	9 to 15
	Kraft pulp	72 to 82	18 to 28

Table 2.3.1, Pulp Composition

The material was never washed. It was believed to have a small amount of whiteners and other fillers. This can be seen by putting some phenolphthalein in 500 ml of distilled water, stirring in two paper towels, and allowing them to set. After several minutes at

15°C the water shows a small change in color, indicating a basic solution. The measured pH is 8. The buffer capacity is small and was ignored. When wet the paper towels were 150 to 300 wt % water. The carbon analysis revealed the paper towel to have about 43 % carbon, the same range as alpha cellulose.

Pulp

Three main types of pulps were used from Pope & Talbot: bleached, brown wash pulp, and the short reject fibers. The bleached pulp contains about 4 wt % water and consisted of two types: sawdust and a blend (50% sawdust 50% hardwood). The short fibers were rejects that were pumped out of the plant through the sewage system. The short fibers and brown wash pulp were dried at 60°C. Higher temperatures caused a reaction in the brown pulp making it smell strongly of black liquor. The pulp was stored in polyethylene bags. The carbon analysis of the bleached pulp showed 43.8% carbon.

Analytical grade α Cellulose

Alpha cellulose was obtained from SIGMA chemical company (No. C-8002 lot 35F-0803). The alpha cellulose material was approximately 99.5% alpha cellulose. The material was stored in the original package to prevent contamination. When wet the material was 150 % to 350% water. Carbon analysis showed 43.3 % carbon compared to the 44% theoretically.

Cotton Fiber Paper

Cotton paper was obtained in the form of resume paper from Southworth. The paper was 100% cotton fiber paper, and contained approximately 90% cellulose (table 2.3.2). The hemicellulose content is unknown.

Source	Material as reported	Wt % cellulose
Cowling E. B., Kirk T. K., 1975	Cotton Fiber	90

Table 2.3.2, Cotton Fiber Composition

Corn Cob

Dried corn cob from a feed store, sold as pet bedding, was one material tested. The dried material was in the form of semi-square pellets about 0.4 cm in diameter. Several composition are reported in table 2.3.3. When wet, the material is 200 to 300 wt % water and rigid in shape. The carbon analysis showed this material to have 47.6% carbon.

Source	Material as reported	Wt % cellulose	Wt % hemicellulose
Okeke B. C., Obi S. K. C., 1994	TZSR-W (Cob)	34.8	38.1
	Amiacha (Cob)	39	41.7
Foley K. M., et al., 1981	Whole Cob	41.2	36
Ladish M. R., et al., 1983	Corn Cob	36.5	28

Table 2.3.3, Corn Cob Composition

Fresh corn cob from the local market was used in several experiments. The corn was cooked whole in boiling water for 10 minutes. The kernels were removed and the cob

was refrigerated in a plastic bag. The wet material contained 150% to 300 % water. The carbon analysis showed the washed and dried cob to be 48.1 to 48.6 % carbon.
In preparation of the fresh cob, the kernels were removed. While wet, the cob was ground in a meat grinder. Next, the ground cob was rinsed twice to remove the remaining skins in a 4 to 1 DI water/wet cob volume. In the same volume the cob was boiled in DI water for 10 minutes. In each case the top half of the water was decanted off with the remaining skins. The remaining cob was separated from the water and rinsed with a volume equivalent of DI water. This was executed in a step wise fashion and termed 1X for one boiling cycle.

Washing of the material was studied in an effort to eliminate acid reacting with contaminant in the cob. The washing study consisted of measuring the buffering capacity of washed cob. The corn cob was dried to get the weight, then rehydrated for 2 or more hours. The sample for each titration was 14 grams of dry corn cob in 500 ml of DI water. The titration was measured with a pH meter (described in Appendix A). Incrementally 0.1 ml to 0.5 ml of 0.34 N NaOH were added in a stirred beaker and allowed to equilibrate with the cob for 10 to 15 minutes. The results are shown in figure 2.3.1.

Sugar Beets

Sugar beets bagasses were obtained from Amalgamated Sugar Company in Nampa, Idaho. This material is sold primarily for animal feed. At the plant, the beets were process to remove the sugar and coated with a process sugar waste. The dry beets were delivered as dry fibers 0.5 to 3 mm thick and 1 to 3 cm long. When wet they swell to 200 to 300 wt % water and have many pores. The cellulose composition are 20 to 24 wt %, and hemicellulose are around 25 wt % (table 2.3.4). The carbon analysis for unwashed beets was 43.8% and for washed beets (2 cycles of washing) was 44.6 %. The 1.8 wt % nitrogen was high relative to the other materials tested.

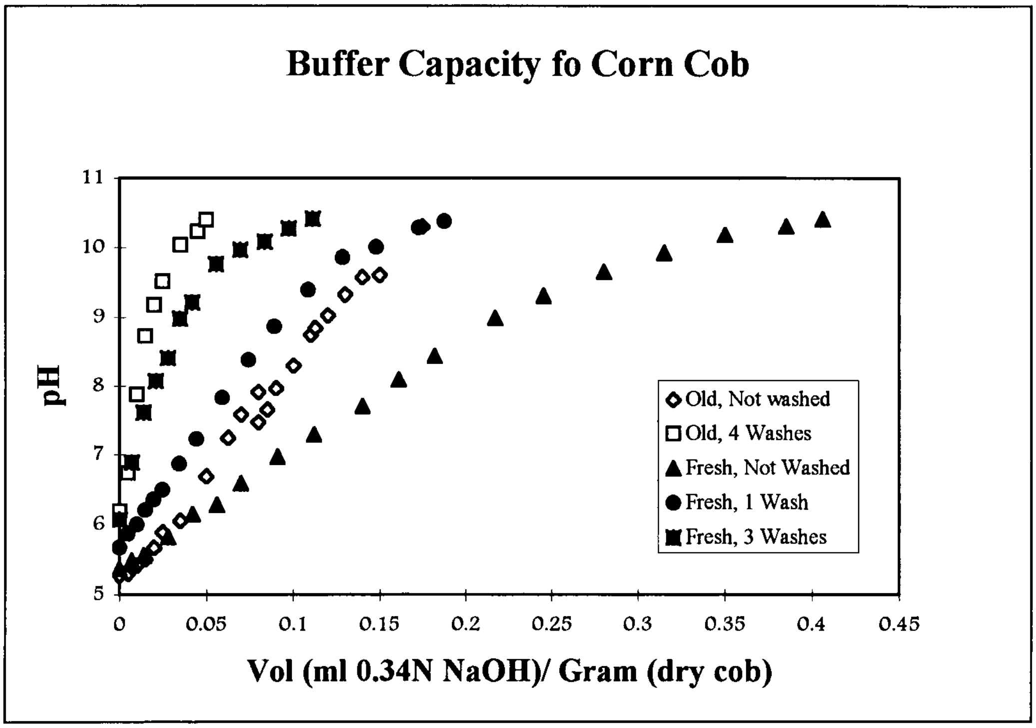


Figure 2.3.1, Buffer Capacity of Corn Cob

Source	Material as reported	Wt % cellulose	Wt % hemicellulose
Bertin C., et al,, 1988	Sugar Beet	20	25
Wen L. F., et al., 1988	Sugar Beet Pulp	24	25.6

Table 2.3.4, Sugar Beet Composition

The sugar beets washing cycles was studied similar to the corn cob. The beets were allowed to saturate with water for 6 hours. They where then rinsed and boiled in a 4/1 DI water/wet beets volume ratio for 10 to 15 minutes. The first washing removed most of the residual sugar on the beets. The second washing did not show much sign of contaminant removal in water color or buffering capacity. The washing for the beets was not pursued because there was an insignificant change after the second washing. This was probably due to the leaching process that removed the sugar. The beets have more buffer capacity than the cob as can be seen from figure 2.3.2. The higher buffer capacity of the beets may be explained by a higher residual fertilizer since the nitrogen content for the beets was higher than the cob.

Other Possible Materials

Several other reported composition in agriculture waste are listed in table 2.3.5. None of this material was used, but all of it seems candidate and worthy of mention. More detailed information is given in the referenced papers.

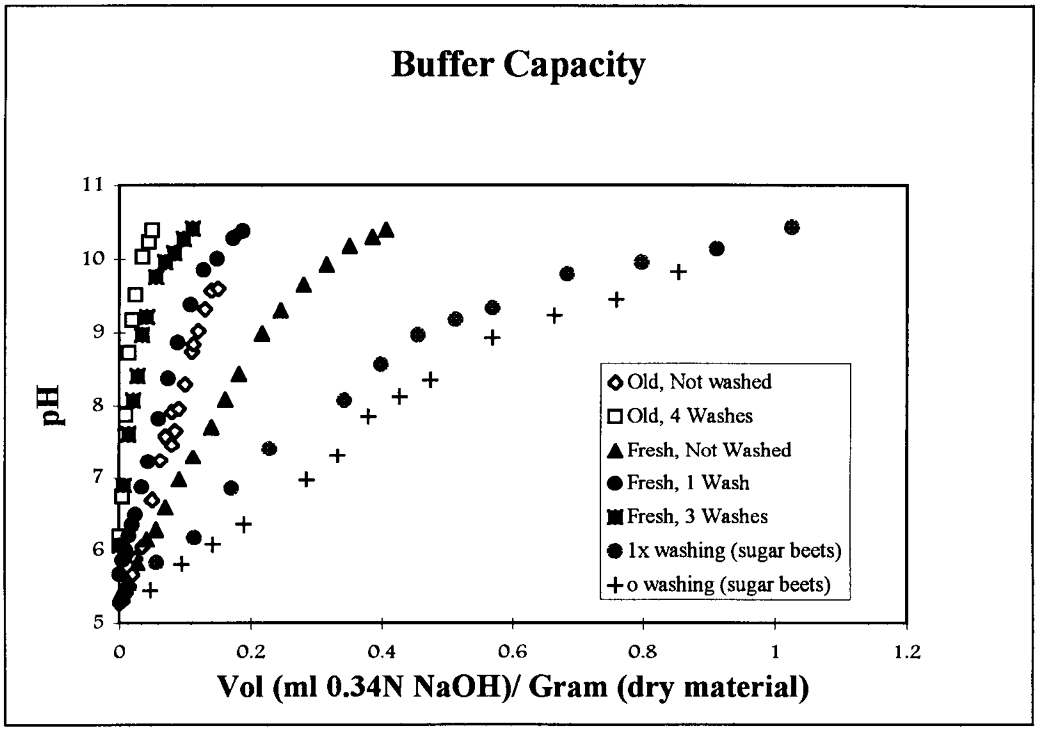


Figure 2.3.2, Compared Buffer Capacity

Source	Material as reported	Wt % cellulose	Wt % hemicelulose
Okeke B. C., Obi S. K. C., 1994	Rice Hulls	24.0 to 29.8	12 to 14.4
	Melon Shells	34.5	18.6
Ladish M. R., et al., 1983	Straw	34 to 42	12 to 31
	Corn Stalk	33.5 to 38	26 to 32.6
	grasses	14.4 to 24.5	27 to 30
	Woods	23.5 to 37.3	38 to 50.8
	Bagasses*	38	34
Singh A. et al., 1984	Bagasses*	42	28

Table 2.3.5, Miscellaneous Material Composition (* Bagasses could be sugar cane or sugar beet)

2.4 Material Preparation

There were several considerations for material preparation. The material was subject to acid addition, prereaction acid consumption, soaking, and drying. The methodology is covered in this section.

Material Drying

The initial reactants often contained residual water. In most cases a test portion of the material was dried in an oven to determine the moisture. This was done because the structure and reactivity of the cellulose is known to change if it is completely dried (Green, 1963). Prior to use, the filter paper was dried in a 110°C forced convection oven for 1 hour. After washing the reacted material and filter paper, they were dried in a forced convection oven for 2 to 12 hours. Next, the samples were placed in a desiccator to cool and be weighed.

Acid Addition

The acid addition percent was chosen based on the acid equivalent per sugar group, and the fluid capacity of the material. The fluid capacity was checked with water. The acid concentration is then calculated from the fluid capacity and the minimum amount of cellulose and hemicellulose from literature (assuming a pentose molecular weight of 140 per hemicellulose sugar). The acid addition changed depended on the experiment.

Usually the acid solution was added to the material and worked in by hand, or with a spatula.. In initial experiments the acid solution was applied in excess. The excess was removed mechanically by a set of rollers. This was dropped due to the belief of adsorption of the acid.

Soaking

The concern of molecular diffusion of the H_2SO_4 into the cellulose was addressed by soaking the material in the acid solution. The material was covered and soaked at 10°C. Soaking times varied from 5 minutes to several days. The effects of soaking on weight loss or acid loss were not detected as long as the material was completely wetted.

Water Removal

It was suggested that evaporating the water from the material helped the reaction proceed faster. There were two methods used to achieve this. The first approach was to allow the acid wetted material to sit in the ambient (10 to 30°C). The samples were placed out of direct sun above the vent hood in Gleeson 310. The second method used a vacuum to quickly remove the water. A titration on a vacuum dried sample showed no acid loss on a

90% water removal process. The drying changed the cellulose to a easily powered material known as hydrocellulose. The dried material reacted faster than undried material and yielded equivalent products.

Acid Consumption

Acid consumption was measured in two ways. The most common was titration of the solid in a mixing beaker of DI water. The titration was done with NaOH over a period of several hours to several days. A pH meter was used to determine the end point (pH=7). After completion of the titration, the solid was separated from the liquid in a Buchner funnel and washed. The washing proceeded in 1 or more cycles of: 500 ml boiling DI water pored through the filter, and a rinse of DI water. The Second method involved sequential washing of the solid with boiling DI water. The washings were carried out until a neural leachate was yielded.

2.5 Experimental Apparatus

Five different experimental apparatus and methods are described.

Forced Convection Reactor

A reactor (figure 2.5.1) was constructed from Pyrex glass. The reactor was designed so the top and bottom are sealed together with a Teflon gasket. The bottom section was loaded with 1 cm layer of reactant. The top section had an opening so a 1 inch OD glass adapter could be inserted. The joint was sealed with a Teflon gasket. The top adapter had an opening for air. The flow of air through the reactor was controlled by a glass distributor in the shape of a funnel. The second opening in the adapter was connected to a glass condenser which delivered the condensate to a vessel. The condenser was cooled with tap water at 10°C.

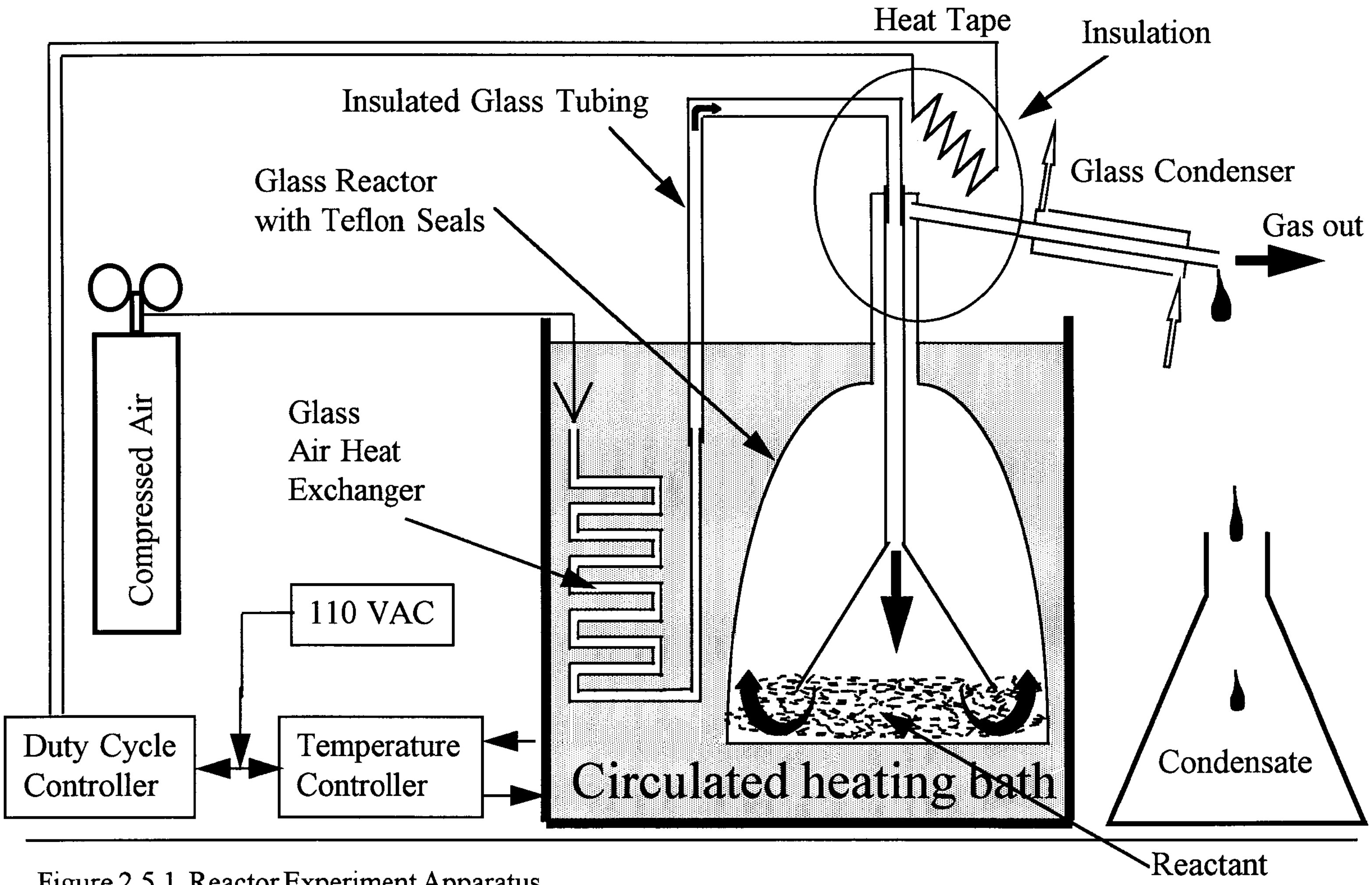


Figure 2.5.1, Reactor Experiment Apparatus

The reactor was placed in a temperature controlled forced convection heating bath. The heating bath was filled with 50% anti freeze and 50% water, and covered. Compressed air was fed through 5 ft of glass tubing (formed in circular shape to fit the bath) as a heat exchanger. The heat exchanger was connected to the gas inlet of the reactor by a Teflon coupling. The exposed glass tubing leaving the heating bath was insulated. The exposed reactor top and the glass adapter were covered with heating tape and insulated. The heating tape was connected to a 110 Volt duty cycle controller.

During operation, the duty cycle for the heating tape was adjusted so there was no refluxing on the glass. The circulated bath temperature was set at 102°C. The air leaving the glass heat exchanger was at 100°C. The regulated air pressure was set so 10 ml/s of air were collected in a graduated cylinder. The reactor temperature was measured at the surface of the glass with a bulb thermometer. The experiments ran 2 to 3 hours in a vented hood.

Packed Bed

A 24 inch tall, 3 inch ID Pyrex bed (figure 2.5.2) was constructed. The heating apparatus was placed in the bottom 12 inch Pyrex container. The 12 inch reaction section of the bed was coupled to the heating section with two Teflon seals.

The heating section consisted of several components. A 1000 watt heating element heated the incoming air. The heating element was placed in a 5 inch section of 1.5 inch ID cast pipe. Compressed air passes over the nichrome heating coil to a course screen. The screen supported a 7 inch section of 1/2 inch ceramic intalox saddles. A stainless steel wire mesh separated the heating from the reactant section.

Thermocouples were placed at the exit of the heating pipe and on top of the packing. The heating element power was controlled by a Rheostat. The compressed air was regulated,

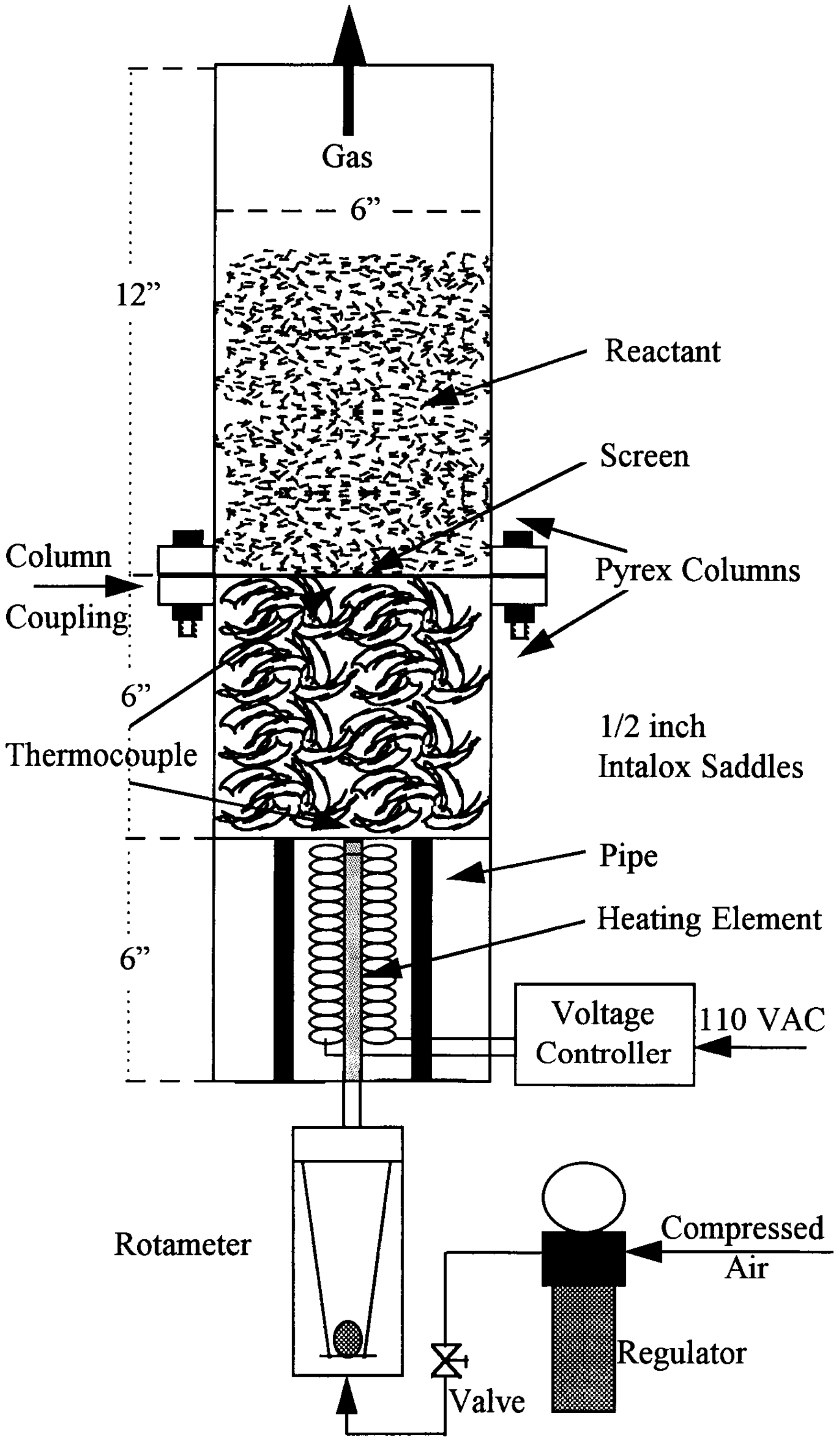


Figure 2.5.2, Packed Bed Experiment Apparatus

controlled with a needle valve and measured with a rotameter. The bed was insulated with fiberglass insulation.

The air flow was set at 1000 mL/min. The bed was preheated to operation temperature and run in a vent hood. While the system was operating the reactant was dumped in through a large funnel. The entering gas temperature was monitored underneath the distributor by the thermocouple. The bed temperature was monitored with a mercury bulb thermometer momentarily placed in the area of interest.

Microwave

Samples were placed in a Pyrex petri dish (figure 2.5.3) and covered with a Pyrex container. The container and the petri dish were placed so air could enter or escape. The top of the container had an opening to attach a glass tube. A glass tube connected the container to the cold finger condenser outside the microwave. The cold finger condenser was covered with dry ice and attached to a scrubbing system. A vacuum source was connected to contact the off gases from the reaction with the scrubbing system. Vacuum measurements for the operating conditions are labeled on figure 2.5.3. Sodium hydroxide was used in the scrubber to recover carbon dioxide.

The reactant was placed in the petri dish and covered with the container. The vacuum was turned on at the same time as the microwave. The scrubbing system was a 500 ml flask that contained 4 inch of 8 mm glass balls and 1 M NaOH. The gas was channeled through the packing in the scrubbing system. The system was operated 3 feet away from a vent hood with the dry ice 1 foot closer to the hood than the system air intake. In order to get a background level of CO_2, the same setup was run with new NaOH solution with no reaction for a corresponding time. The reaction varied from 1 to 6 minutes per experiment.

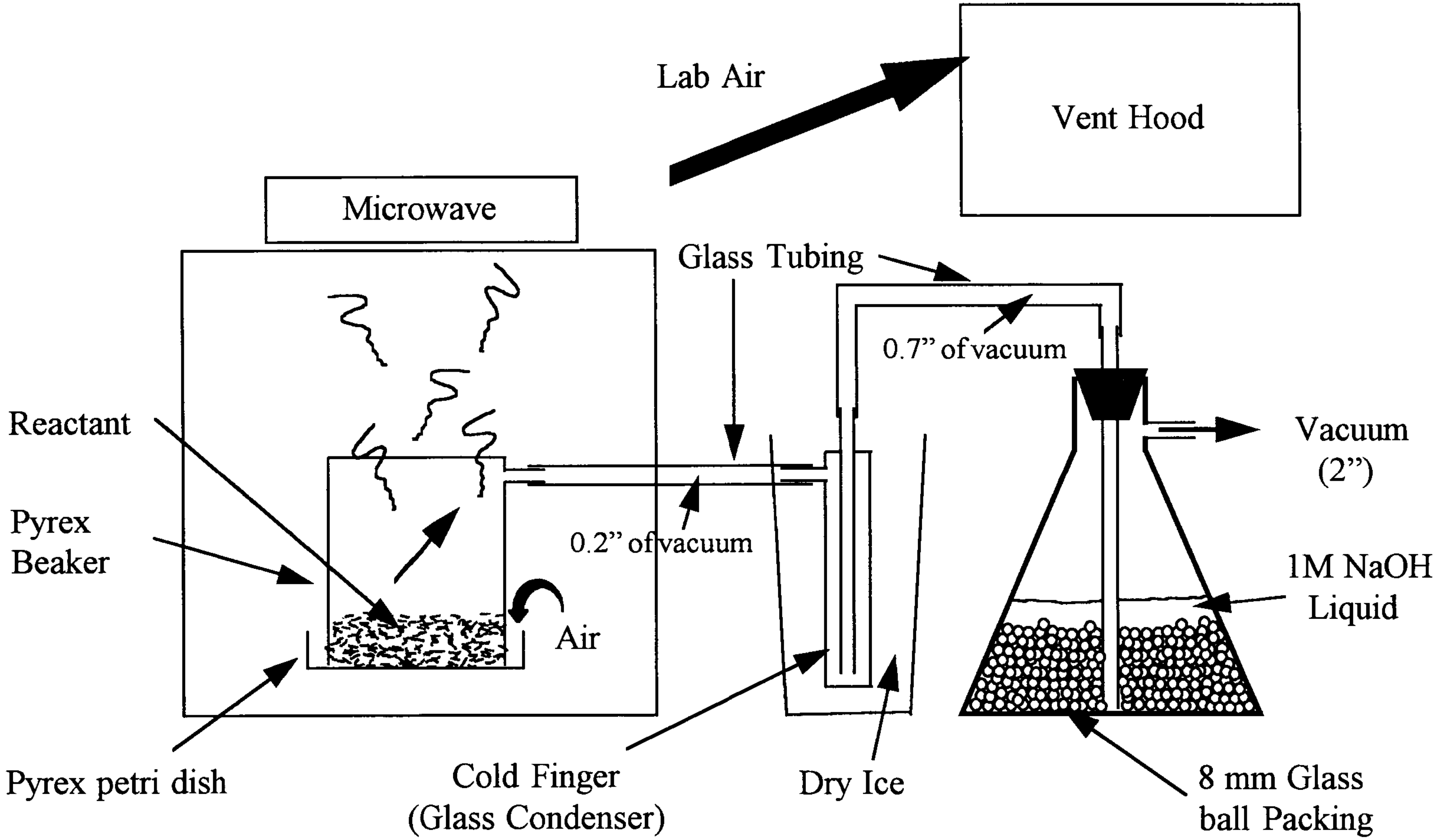


Figure 2.5.3, Microwave Experiment Apparatus

Vacuum Oven

The vacuum oven used was manufactured by the National Appliance Company. The chamber was 8 inch by 8 inch by 12 inch. The oven was preheated. The reactant was put in a petri dish and placed in the oven. The vacuum reached 29 inches Hg at 1 minute after starting the experiment. The temperature was monitored by an internal thermometer seen through the glass door. The reaction was run for 30 minutes.

Forced Convection Oven

The oven used was a Thelco 160DM microprocessor controlled forced convection oven. The chamber dimensions were 39 cm x 47 cm x 84 cm. One shelf was placed at 11.5 inches and another was placed at 21 inches below the inside top of the oven. A forced convection hood was placed over the oven to remove gases.

The convection pattern for the oven was studied by drying three samples evenly placed on the two shelves. Initially the temperatures measured at 102°C in all four corners on each shelf when the oven was set at 100°C. The temperatures were measured by a thermocouple and two different mercury bulb thermometers. Position 1 corresponds to the right hand side and position 2 to the middle. The results (figure 3.5.4) show the top shelf to be slightly faster at drying than the bottom shelf. The paper towels were crinkled up to fit into 4 inch diameter by 0.5 inch deep Pyrex petri dishes.

The experiments were executed in several different ways. In some cases the material was laid out on a 8 inch x 12 inch preheated Pyrex dish and placed in the oven. In other cases, the material was placed in Pyrex petri dishes and put in the oven. When simultaneous experiments were conducted the spacing between dishes was equivalent to the dish size. The oven was vented out the top by an adjustable vent. The vent was always wide open except at temperatures greater than 190°C.

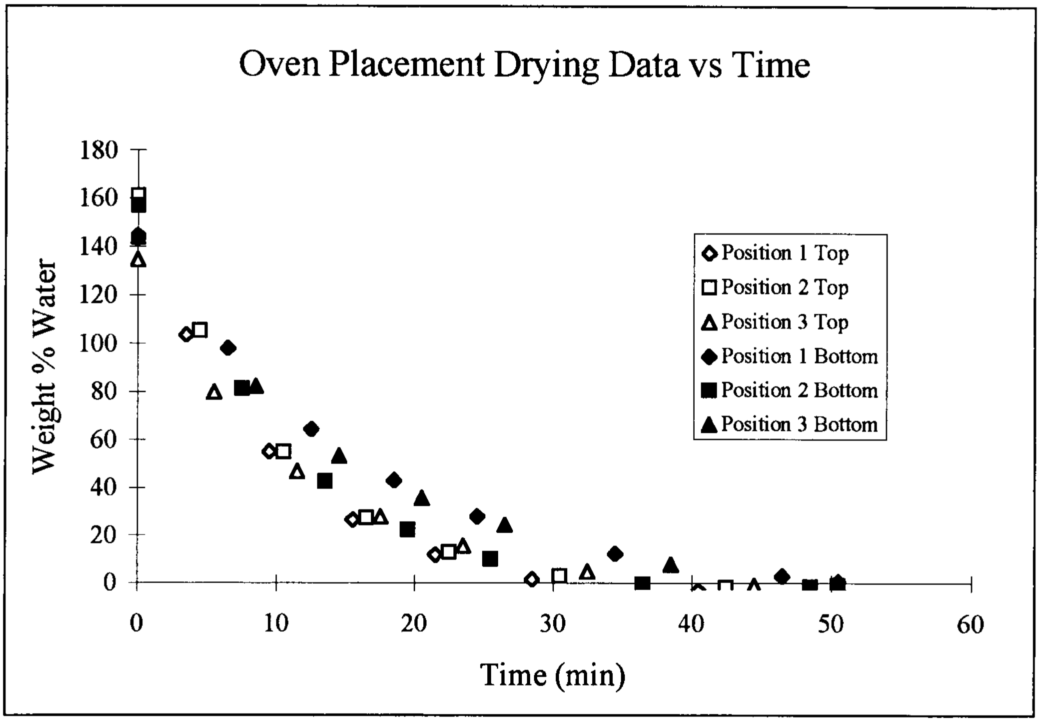


Figure 2.5.4, Drying curve for the Forced Convection Oven at 100°C

2.6 Parameter Studies

The study of process variables was done to understand controlling factors. The variables studied were; reaction temperature, reaction time, acid concentration, and pretreatments. The criteria for evaluation of variables was; acid loss, weight loss, carbon loss and carbon concentration.

The symbolism used in this section is consistent throughout the figures. Each point on the figures represents a single experiment. A line connecting the series markers indicates everything remained constant within the series, except reaction time. Aging time is denoted as "hrs aging." The reaction temperature is listed in the legend as a Celsius temperature. Acid concentration applied to the raw material is denoted as "acid equivalent/hexose" and "eq/hex."

Acid Loss

An acid loss study was done simultaneously with various aged papertowels. Figure 2.6.1 represents these experiments in the forced convection oven. Three experimental series were run at 110°C and aged at: 0, 66, and 135 hours. These experimental sets are close in acid loss with the nonaged material showing the most acid loss. This maybe due to experiential error. If aging significantly affected the acid loss then the longer aged material would be expected to have more acid losses. The main conclusion is aging does not affect acid loss.

Two other factors that affect the acid loss are temperature and reaction time. The reaction time effects are illustrated by following any isothermal reaction experiment in figure 2.6.1. For example, the 160°C, 68 hrs aging experiments shows 30% acid loss at 20 minutes which increases to 65% acid loss at 30 minutes. The temperature change effects are illustrated by the higher acid loss for higher temperatures bases on the same reaction time. For instance, at 20 min. the acid losses are; 0% at 110C, 30% at 160C, and 75% at 200C.

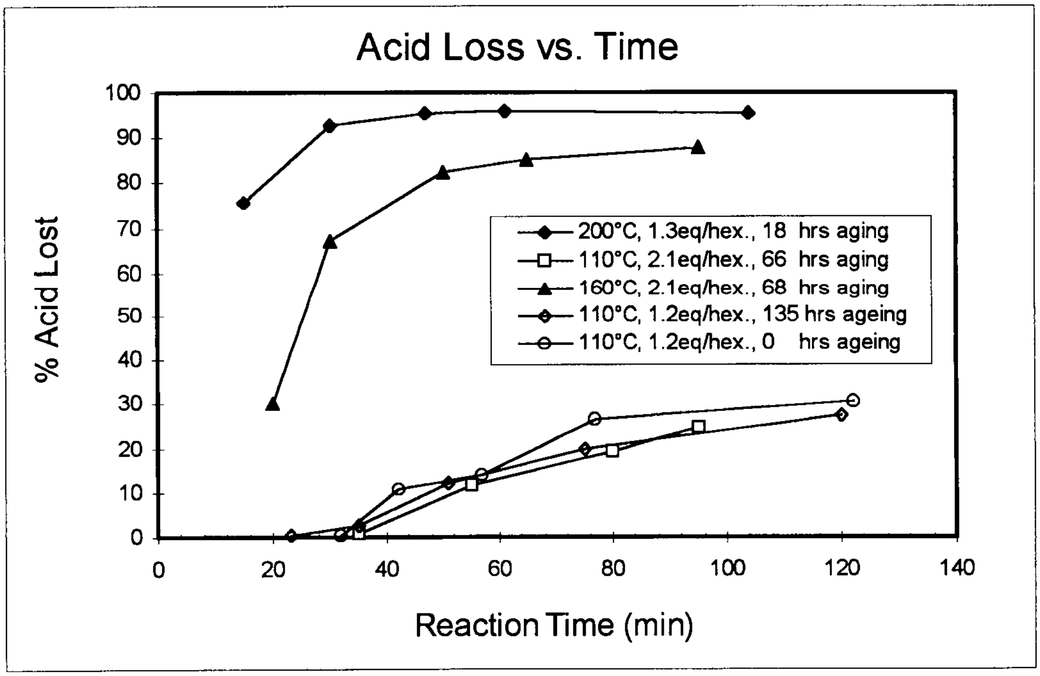


Figure 2.6.1, Acid Loss for Papertowels

Acid Concentration

The acid concentration played a significant role in the conversion of cellulostics materials to high carbon products. Figure 2.6.2 summarizes the weight reduction as a function of acid equivalents per hexose for many different reactions. The Acid equivalent per hexose was calculated from the moles of acid and the weight of the material. The material was treated as if it were molecules of hexose in a cellulose structure $C_6O_5H_{10}$ (mw162). The series represents the different reaction methods: microwave, forced convection oven, packed bed, reactor, vacuum oven, and vacuum drying followed by convection oven.

The scatter from figure 2.6.2 was caused from several things. First, this graph is a summary of many experiments. The starting materials are from cellulose sources like; sugar beet, corn cob, and paper products. Second, often in a series of experiments one or two experiment was stopped before complete reaction in order to follow the conversion curve.

The microwave method showed the highest most consistent method of conversion for several reasons. First, the microwave experiments were done with the maximum conversion as a goal. Second, the microwave experiments were all paper products. Third, rapid heating may have played a role.

The dependence of acid equivalents on weight loss is further illustrated from figure 2.6.3. The lines through the series were left out for clarity of the graph. This figure shows the weight loss of paper towels as a function of acid concentration for the forced convection oven. At 1.3 acid equivalents, higher temperatures were the only variable that increased the weight loss between different experimental series. This can be seen by comparing the

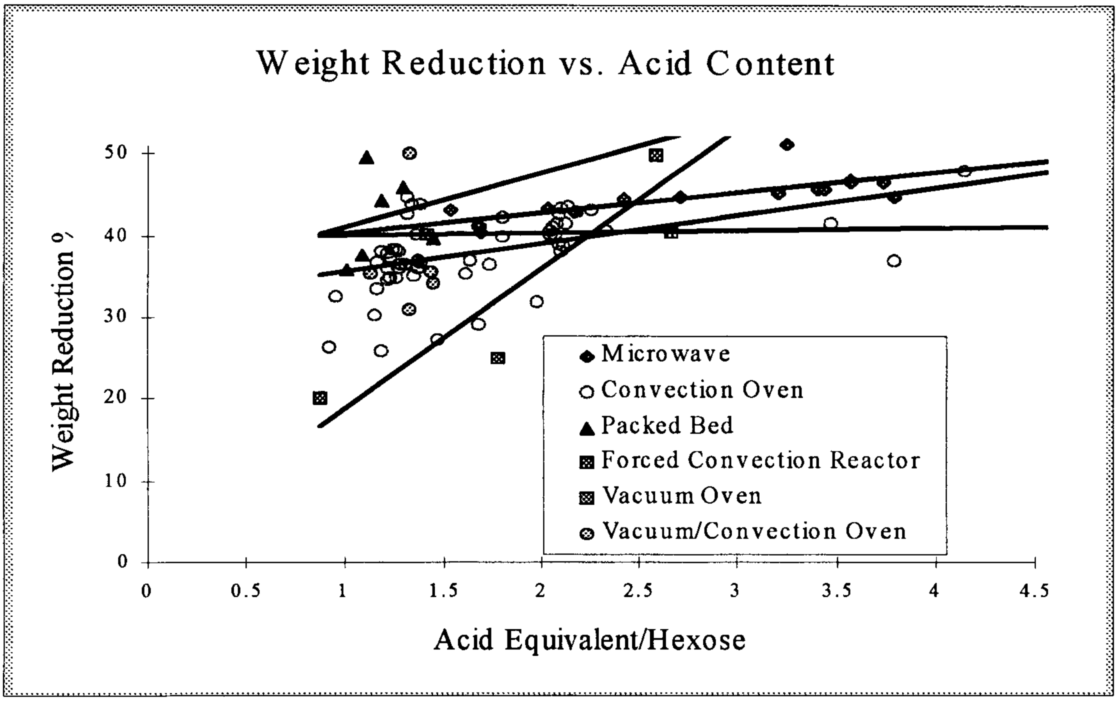


Figure 2.6.2, Weight Reduction for Different Materials

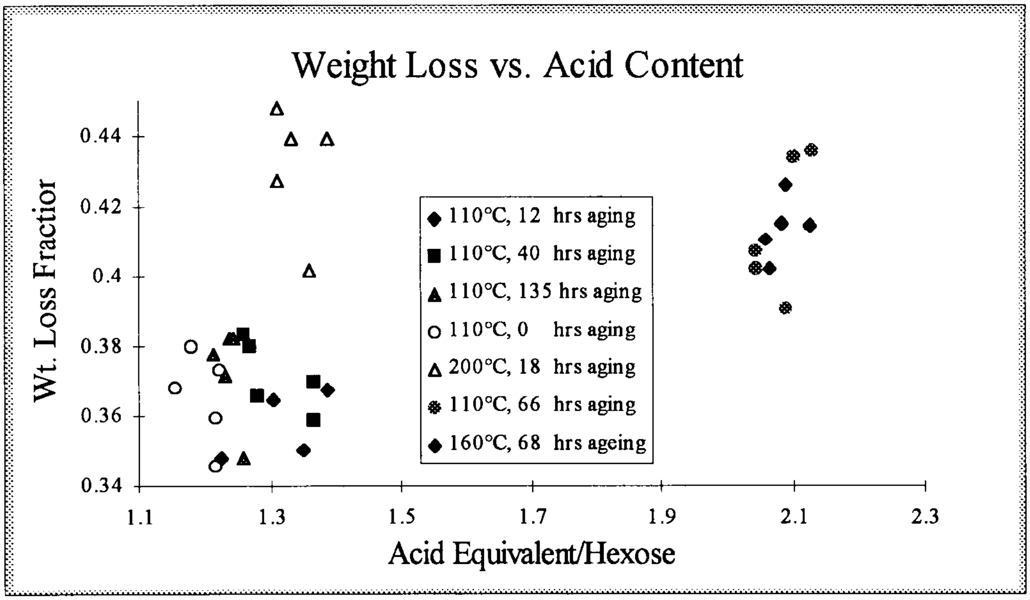


Figure 2.6.3, Effects of Acid Concentration in a Forced Convection Oven

200° C experiments to the 110° C experiments. The spread within the series can be correlated to reaction time. When the acid equivalents are increased to 2.1 the average conversion increased 5 percent, and the temperature has less effect.

Reaction Time

The reaction time was studied in the forced convection oven. Figure 2.6.4 summarizes the results of paper towels in petri dishes for various conditions. The first experiment in most series was removed before the material was completely reacted, as could be seen by a white color in the reacted material. This figure shows how the effects of aging change the reaction time. The figure also shows the higher weight loss at higher temperatures and higher acid concentrations.

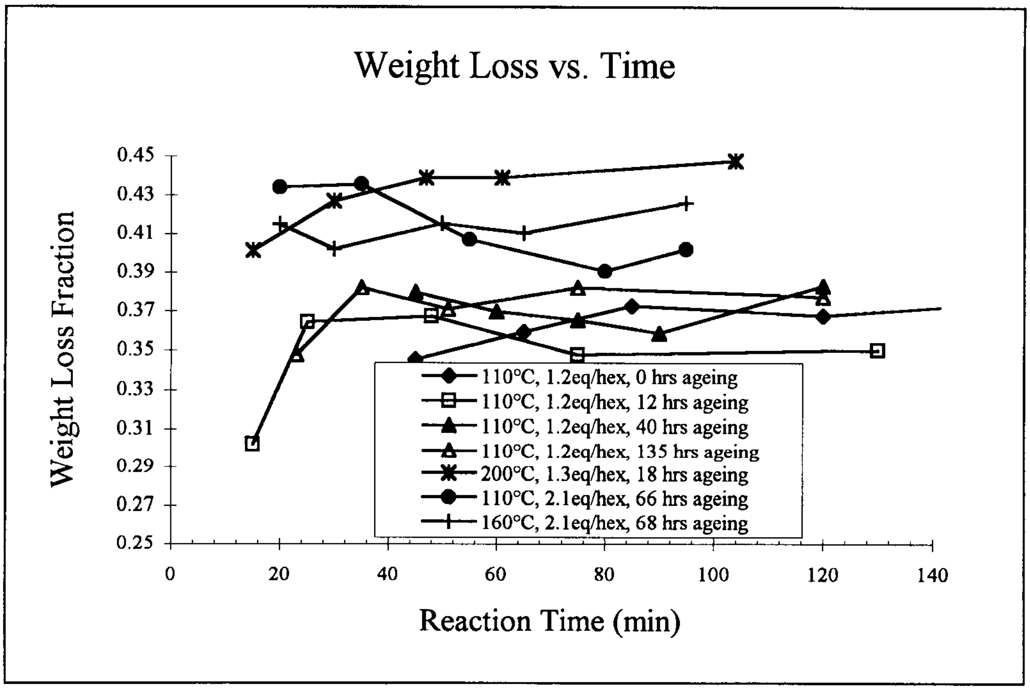


Figure 2.6.4, Convection Oven Conversion (110°C)

Aging was studied to determine effects on reaction time in the forced convection oven. Figure 2.6.4 shows that the unaged material at 110°C is approaching 35% weight loss after 45 minutes and the 12 hour aged material is approaching 35% weight loss after 25 minutes. This is due to the evaporation of water from the acid solution on the solid. The water loss in aging ranged from 35% to 91% of initial water. The water loss also depended upon the acid concentration, aging time, and humidity. For instance, after 12 hours of aging, 37% of the initial water is present, and after 135 hours aging 35% of the initial water is present. The main effect of aging is the decreased time of reaction.

An interesting feature is the maximum in the series data sets. This maximum has emerged several times. One explanation can be experimental error. Another explanation could be maximum hydrolysis yield before another reaction dominates.

A comparison of drying and conversion for the forced convection oven is shown in figure 2.6.5. The data series that has Position X, Top/Bottom is referring to the position in the convection oven. The first position refers to the right hand side and the third position refers to the left side. Top is referring to the upper oven rack and bottom is referring to the lower oven rack This data shows the reaction takes place as the drying is near complete. The average conversion time per paper towel in the forced convection oven is about 40 minutes compared to 3.5 minutes in the microwave with forces convection.

Carbon Loss

Solid phase carbon loss (figure 2.6.6) was analyzed for several different samples. The carbon loss was calculated from the carbon analysis and weight of the initial and final product. There was a small solid loss in the washing process that was unmeasured. The comparison of carbon loss and acid concentration shows an increase in carbon loss as the acid content of the material is increased. This indicated there is some optimum acid concentration to be used on the material to reduce product loss.

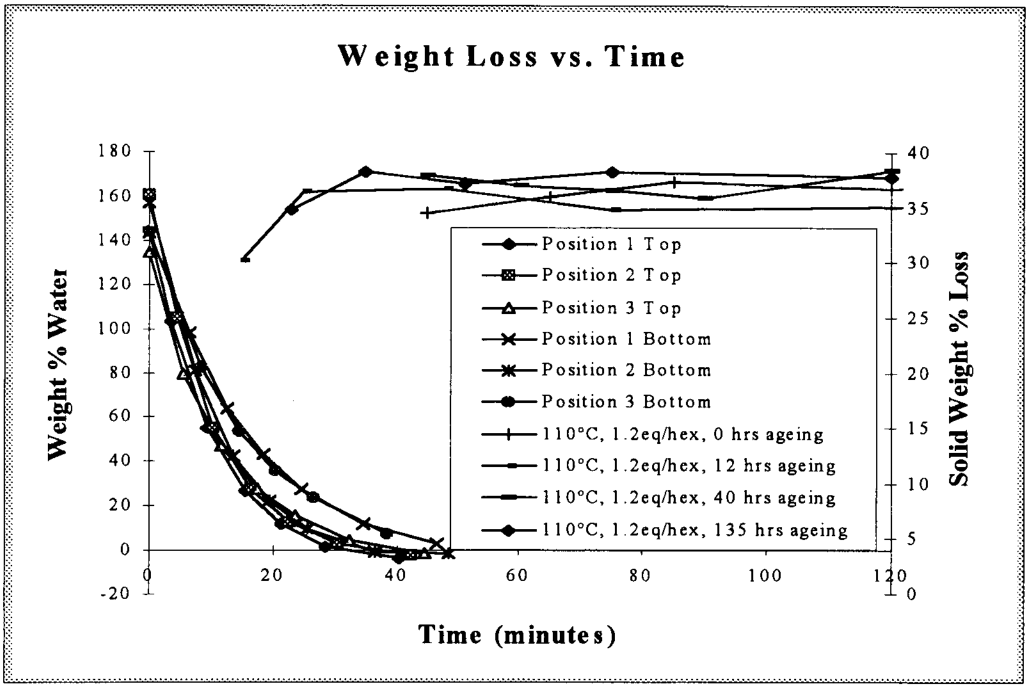


Figure 2.6.5, Compared Conversion Time and Drying Time.

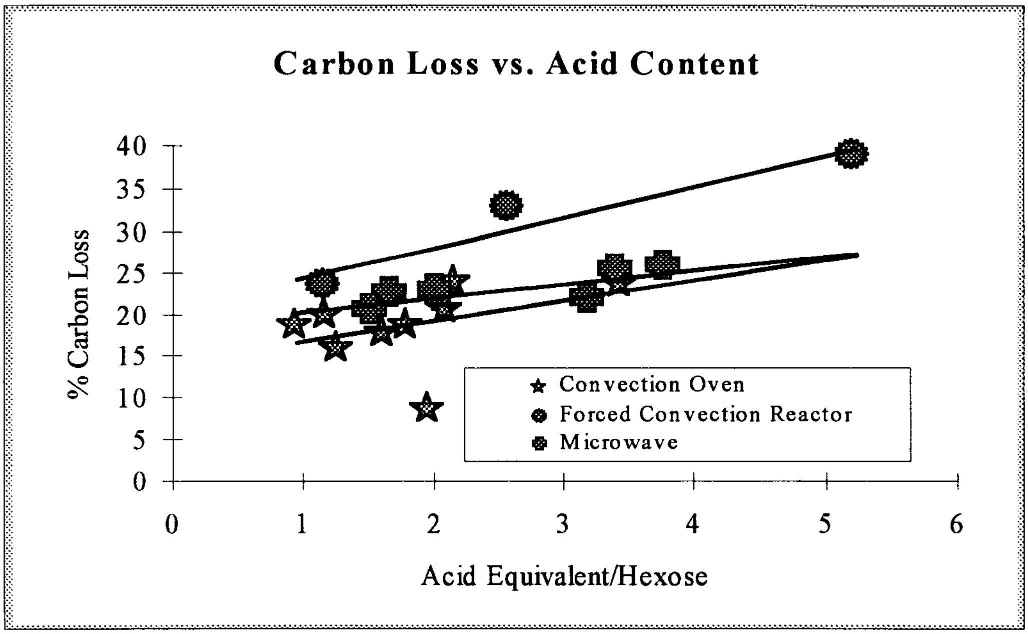


Figure 2.6.6, Carbon Loss for Different Materials

The forced convection reactor shows a much higher carbon loss trend than the other methods. One major difference between forced convection reactor and the other methods is the starting material. The forced convection reactor data is from corn cob and the other data is from paper towels. One of the main differences not shown in this figure is the reaction time. The average time was: 3.5 minutes for the microwave, 40 minutes for the natural convection oven, and 2 hours for the forced convection oven.

2.7 Structural Studies

Differential Scanning Calorimeter (DSC)

One of the analysis that reveals some structural information was the Differential Scanning Calorimeter (DSC). Instrumentation for DSC equipment records the difference in energy required to raise a sample temperature at the same rate as a standard. The information acquired can then be calibrated to a direct measurement of the heat of reaction or transition.

Figure 2.7.1 is a DSC of α-cellulose after preparation as described in Appendix A. Figure 2.7.2 is a plot of experiment 150 which was reacted from the α-cellulose in the reactor. The results from the analysis are typical of the general dehydration experiments. Figure 2.7.3 is another DSC of experiment 150.

The important observation about these analysis is the endothermic peak around 200°C. The significance of this is illustrated in other work with cellulose. Kilzer (1964) showed that at 100°C a change resulted from residual water evaporating. Following at 200°C to 280 °C, cellulose has a slight endotherm (although the range of 230°C to 320°C has been adopted by others (Antal M. J., 1983)). The endotherm results from a dehydration reaction that produces water and a double bond or an ether crosslinking (Philipp B.,

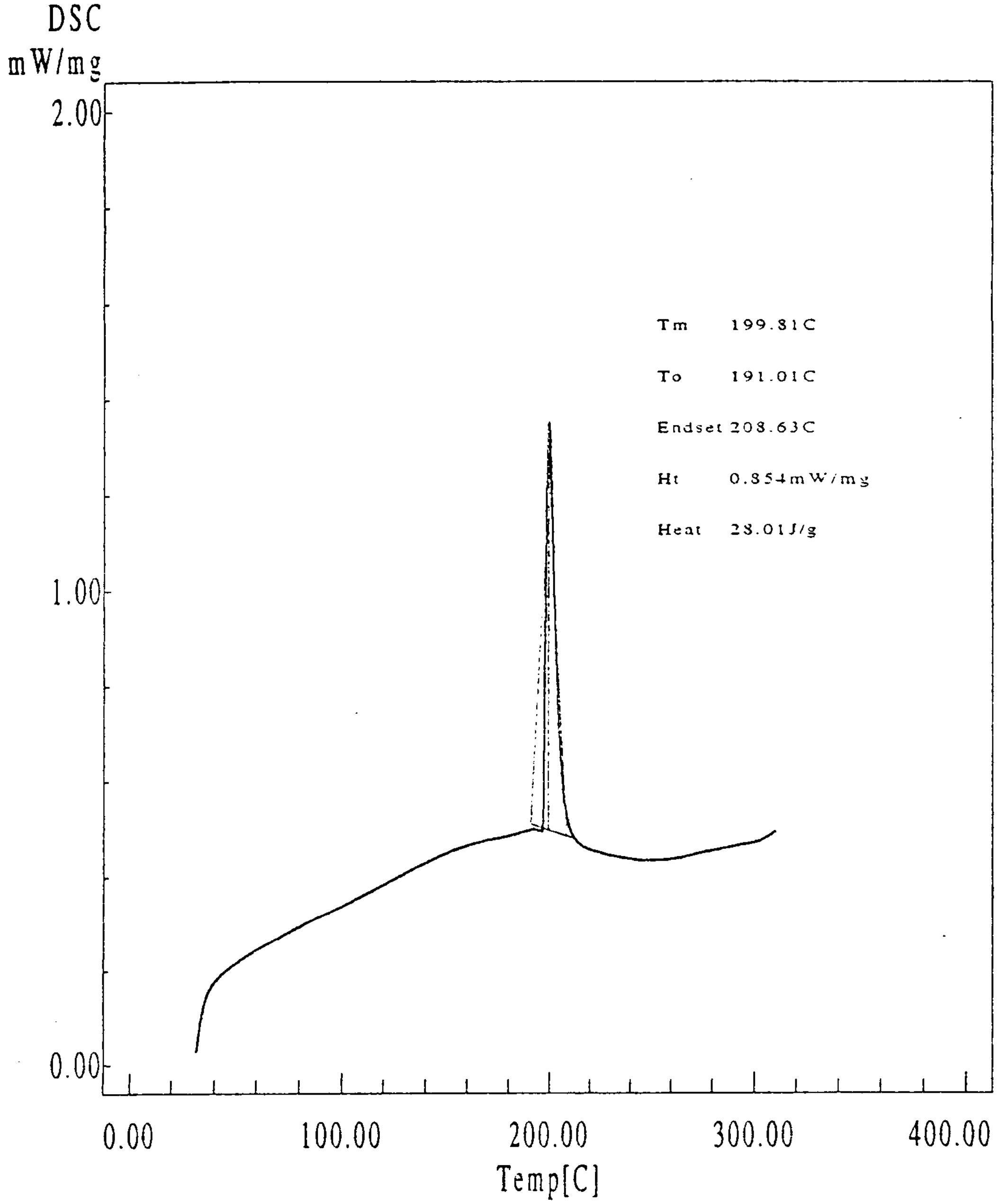


Figure 2.7.1 DSC of α Cellulose

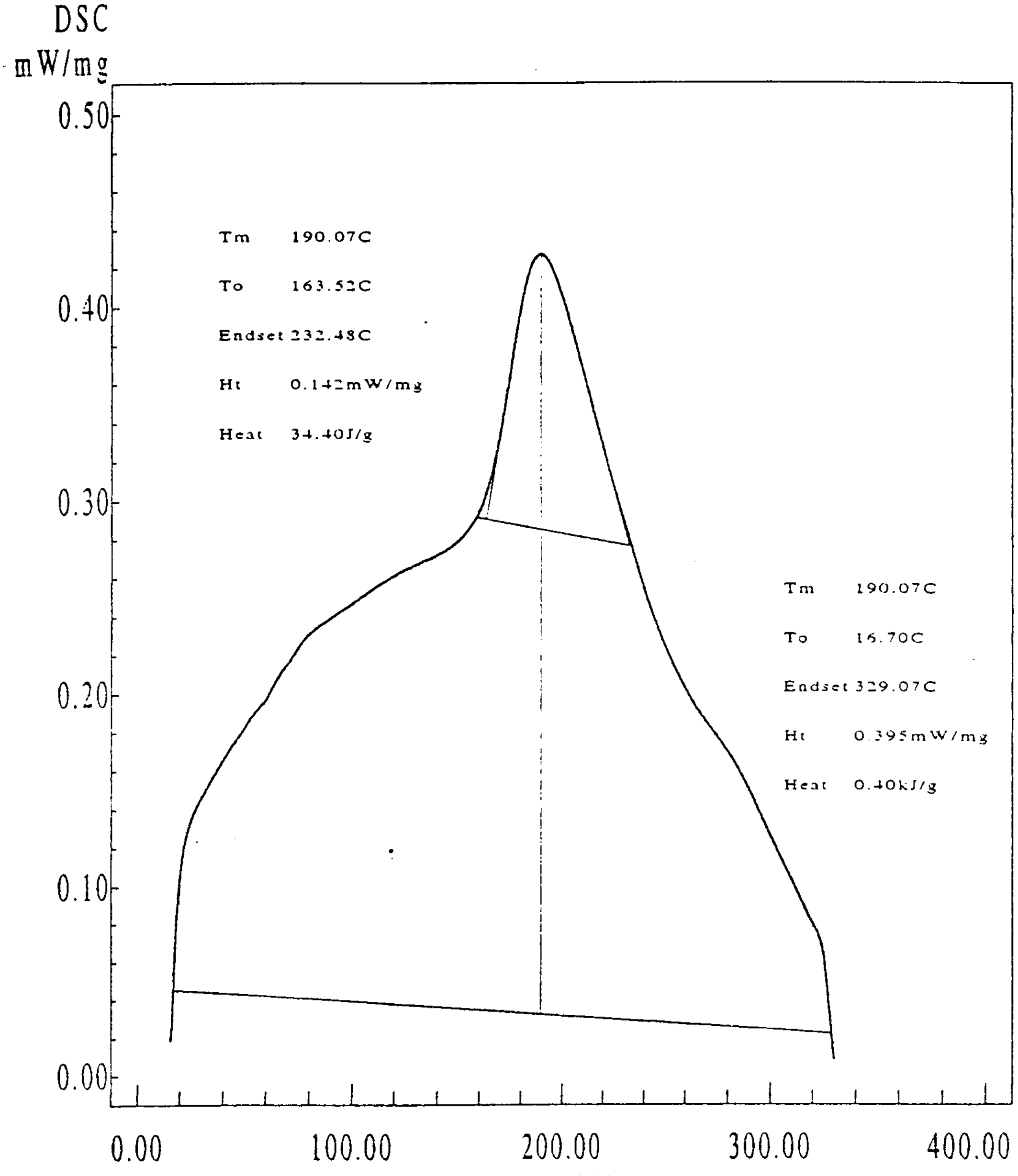


Figure 2.7.2 DSC of reacted α Cellulose

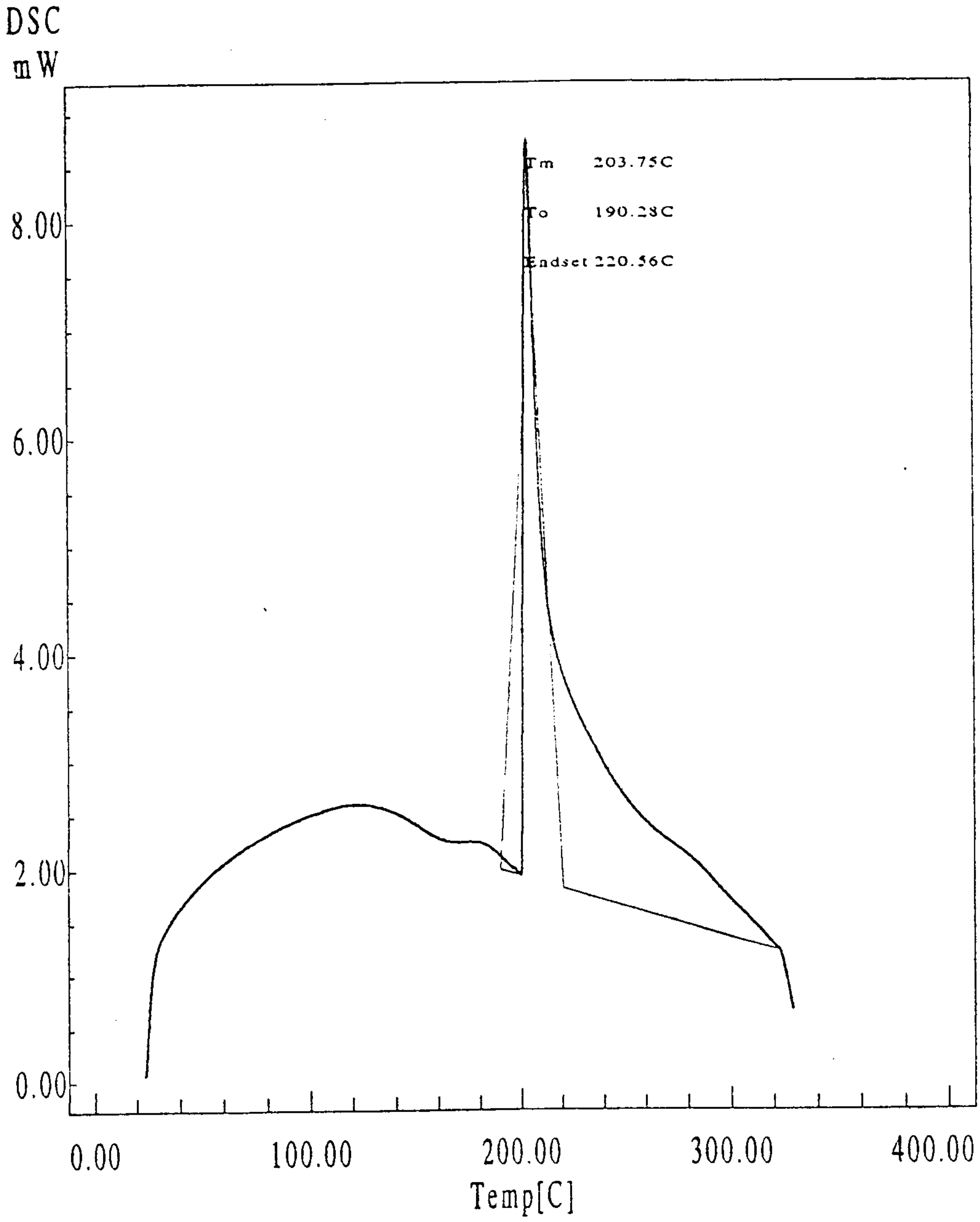


Figure 2.7.3 DSC of reacted α Cellulose

1981). This is shown in section 2.2. The large endotherm range is caused by contaminants like salts, metals, or H+ that catalyze the reaction.

Figure 2.7.1 and 2.7.2 maximum peaks fell within 10°C of each other, with quite a bit of spread at the base of the reacted material. The heat of reaction for the a cellulose and the a cellulose product are within 20%. Figure 2.7.1 and 2.7.3 maximum peaks fell within 5°C of each other, with very little spread. The weight of Figure 2.7.3 was lost but was the same order of magnitude as 2.7.2. Therefore, the heats of reaction are expected to be close. The approximate peak locations and corresponding heat of reaction suggest a like functional group arrangement and crosslinking in the reacted and unreacted material.

Scanning Electron Microscopy (SEM)

SEM is a method to get detailed surface information on the submicrometer size. The typical analysis involves sweeping a surface with a finely focused beam of electrons. The beam is scanned in a pattern like a cathode ray tube. The signal given off from the surface can then be processed in a stepwise method. SEM was used to illustrate the change in material from the reaction. Studies have been done on raw and reacted material which were neutralized from the acid.

Figure 2.7.4 shows analytical grade alpha cellulose and reaction products. The top pictures are unreacted material. The first column is 500X magnification and the second is 2000X. The top row shows a cellulose fibers that are small as a results of the methods used to refine them. The bottom row of figure 2.7.4 are reacted material that has been crushed in a mortar with a pestle. The change in appearances shows there was a change in the material.

Figure 2.7.5 shows reacted and unreacted sugar beet pulp. The unreacted sugar beets show an open pore system which closed upon reaction. The reacted beets are fractured in

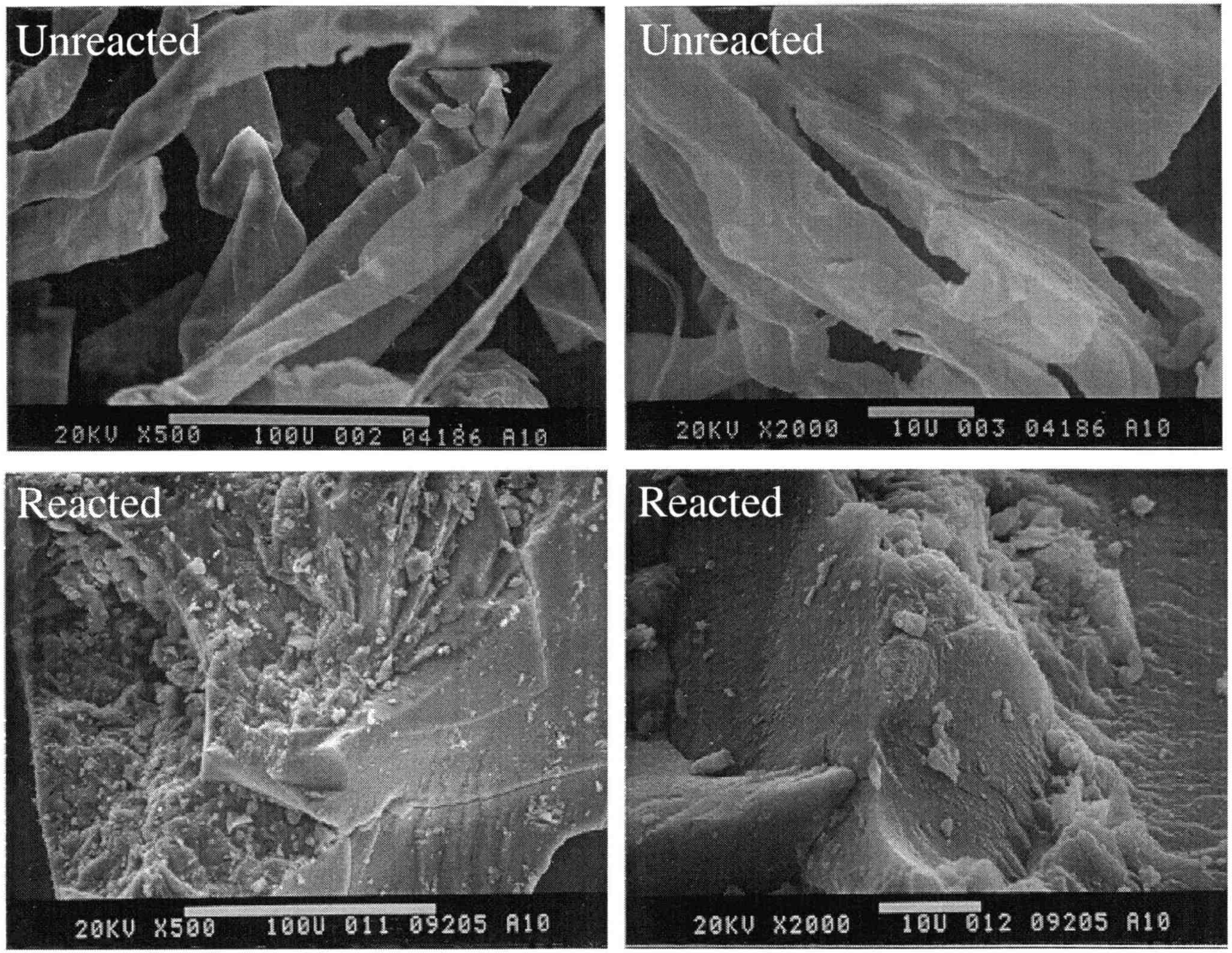


Figure 2.7.4, ESM of α Cellulose

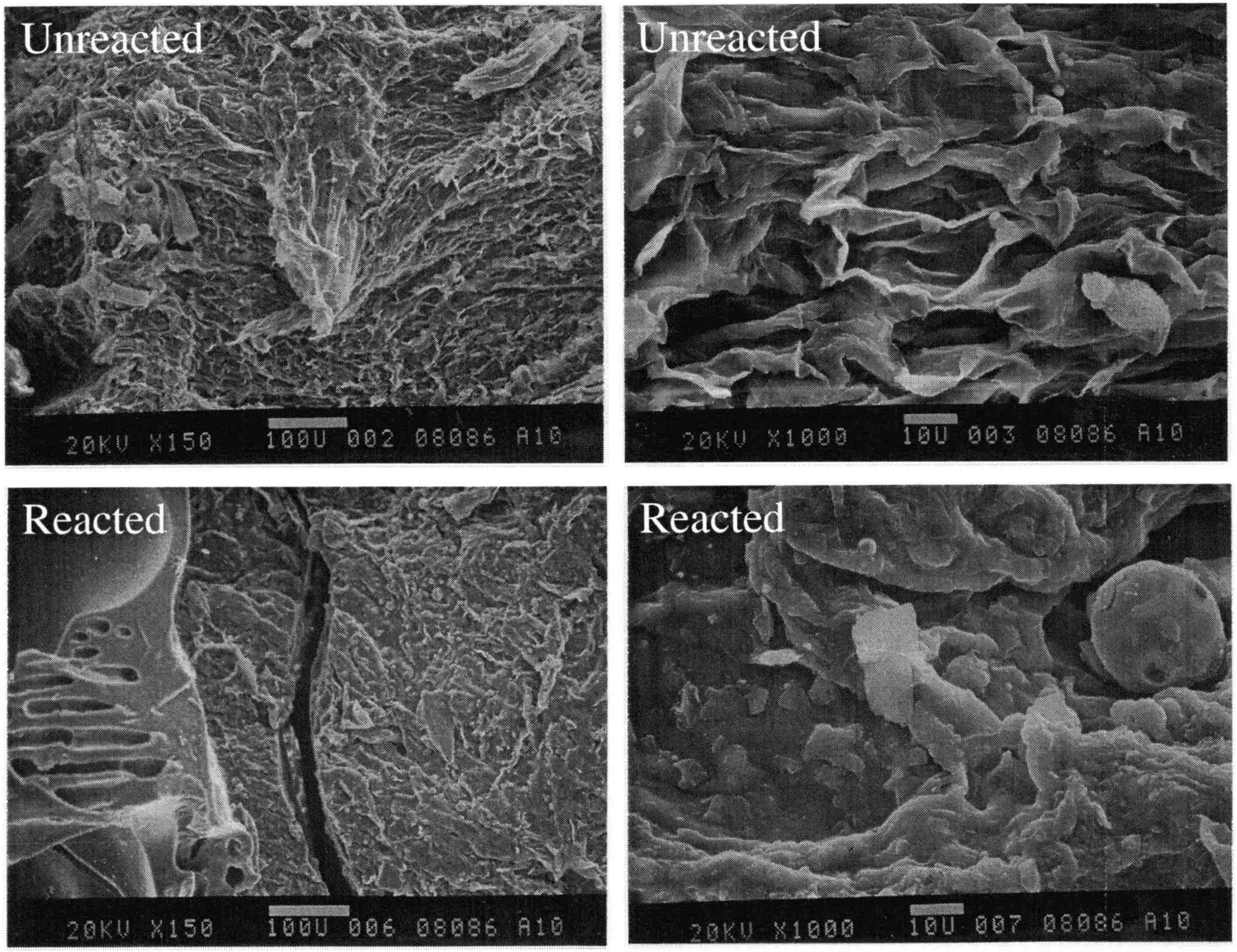


Figure 2.7.5, ESM of Sugar Beets

a few places as can be seen from the left side of the reacted 150X photograph. Further magnification is shown in figure 2.7.6.

Figure 2.7.7 shows unreacted and reacted paper pulp from a Kraft process. The unreacted pulp appears as whole fibers. The reacted material is slightly different in the fiber structure. There are small particles throughout the reacted pulp. The particles appear to be reacted material that broke off original fiber. The pulp displayed a different surface structure than the alpha cellulose or the sugar beet.

Infrared Spectroscopy

Infrared spectroscopy is a technique to study molecular structure that is based on the adsorption of infrared radiation by the vibrational modes of bonded atoms. The absorption frequency depends on the vibrational mode, bond strength, and the masses of the atoms (Bloom P. R, Leenheer A., 1989). One problem with infrared spectroscopy is the information is mainly qualitative. Another problem is the overlap of bands from multiple groups interferes with spectrums.

Figure 2.7.8 summarizes the infrared spectrum of cellulose, aged acid treated cellulose, reacted cellulose and the polycarboxyl acid product. The spectrum of the starting material shows very strong peaks at 800 cm-1 and 1250 cm-1. Treating the cellulose with acid produces a product sometimes known as hydrocellulose (Saeman J. F., Millett M. A., 1963). The hydrocellulose spectrum shows small differences in the fingerprint regime with notable less sharp peaks at 800 cm-1 and 1200 cm-1.

The reacted material yielded a much different spectrum. The biggest changes are seen in the new peaks around 1600 cm-1 and 1700 cm-1. The most notable feature of this spectra is the carbonyl and carboxyl groups at 1700 cm-1. The range of these specific peaks were 1600 to 1620 cm-1 and 1700 to 1703 cm-1 on all the reacted material. The fingerprint zone also shows significant differences compared to the starting materials. This spectrum

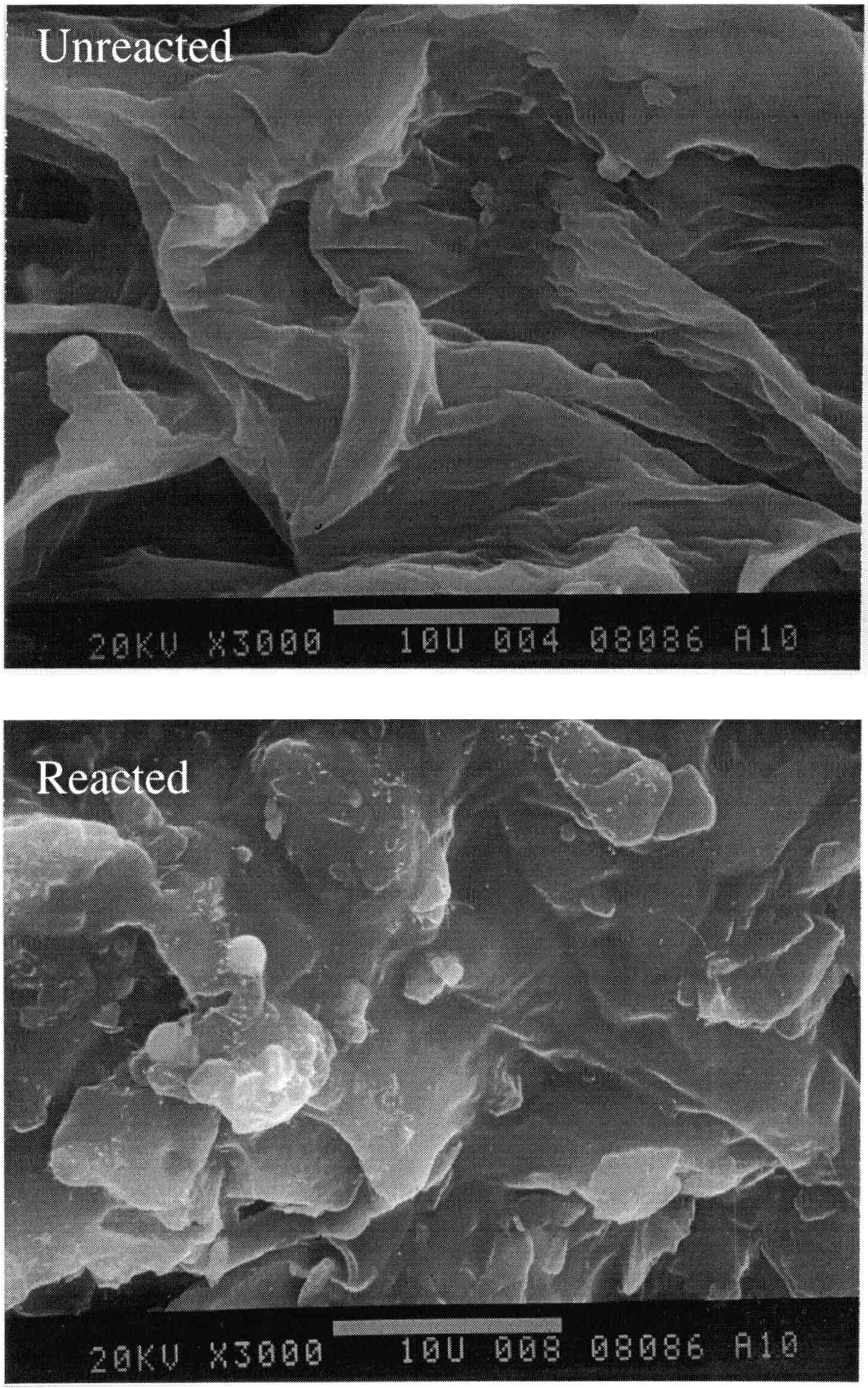


Figure 2.7.6, ESM of Sugar Beets

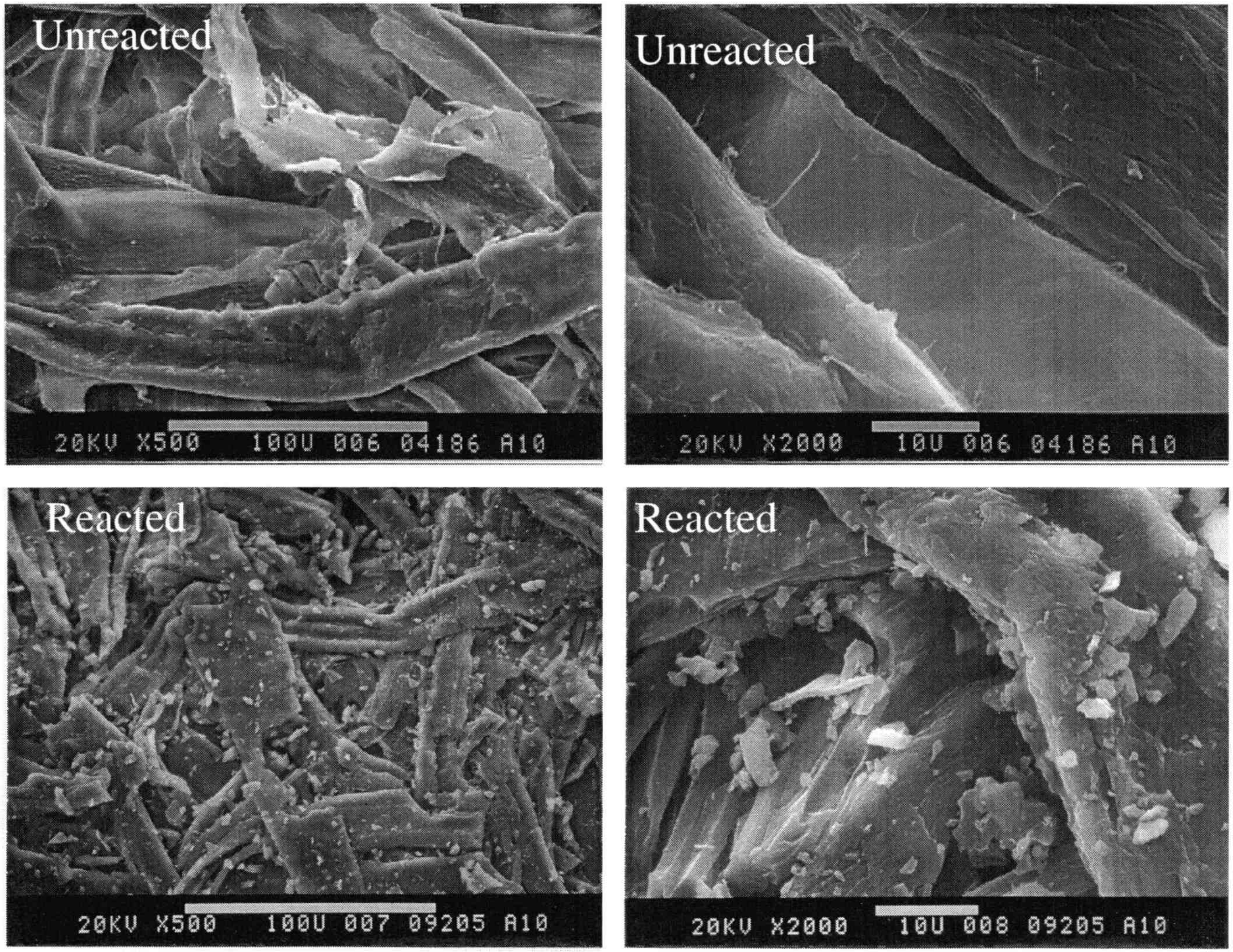


Figure 2.7.7, ESM of Pulp

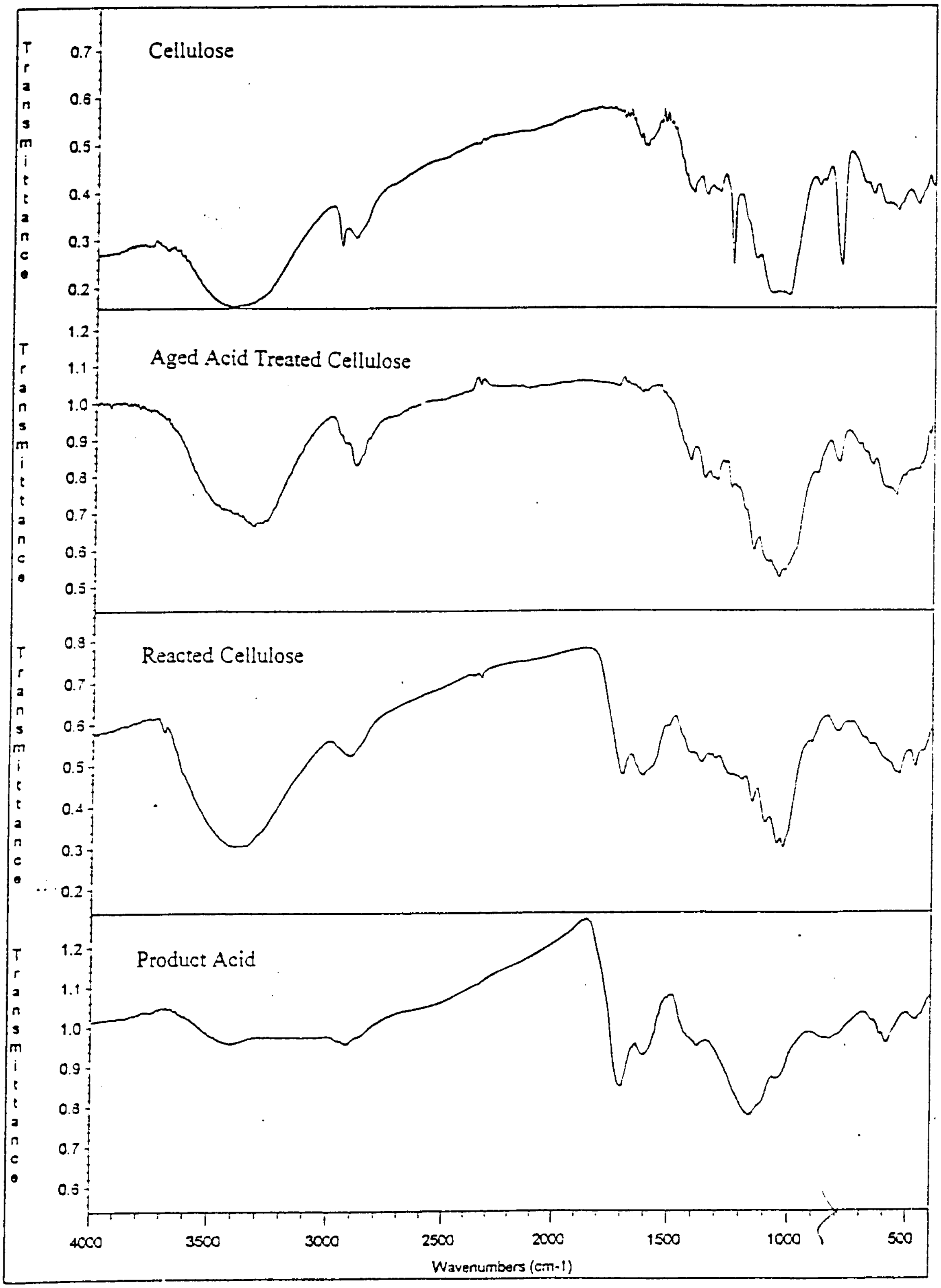


Figure 2.7.8, Infared Sectrum of Cellulose Products

is typical of the acid treated materials. Reaction of the black reacted cellulose in a sealed bomb with NaOH at 500°F produces a polycarboxylic acid. The spectrum shows significant differences at 1000 cm-1 1600 cm-1, and 1700 cm-1.

Figure 2.7.9 shows the comparison of activated materials and reacted carbohydrate. The activated carbon and charcoal are known to have functional groups like carbonyl, hydroxyl (Ishinzaki C., 1973) and ether crosslinking. The major peaks for the activated products are at 1600 cm-1 and 1050 cm-1 . The 1600 cm-1 peak is most likely carbon double bonds (C=C) and the 1050 cm-1 peak is ethers linkage (C-O). Elemental analysis of the activated carbon and charcoal are in appendix A.

The comparison of various reacted material is shown in figure 2.7.10. The materials shown are; sugar beet bagasses, corn cob, papertowel and α cellulose. The materials were reacted in the mechanical convection oven, except the alpha cellulose which was reacted in the reactor. The spectrums show very similar results for peak location. The two most significance features of these compared materials are the specific peak location (1600 cm-1 and 1700 cm-1) and the finger print zone. A missing a peak at 1700 cm-1 in sugar beet spectrum could be related to the high nitrogen content of the starting material.

The different reaction methods for paper towels are represented in figure 2.7.11. The acid equivalent per hexose ratio for these experiments is between 1.4 and 1.6. The spectrum order from top to bottom is: convection oven, vacuum drying followed by convection oven, vacuum oven, and microwave. The spectrums show that the different reaction methods produce similar products.

This type of infrared analysis shows some typical spectrum characteristic that have to be considered during interpretation. Water bands are said (Bloom, P. R, Leenheer A., 1989) to show up at 3300 cm-1 to 3500 cm-1 and 1640 cm-1 in Potassium Bromide. Heating and vacuuming were used in an effort to remove the water. Carbon dioxide, and

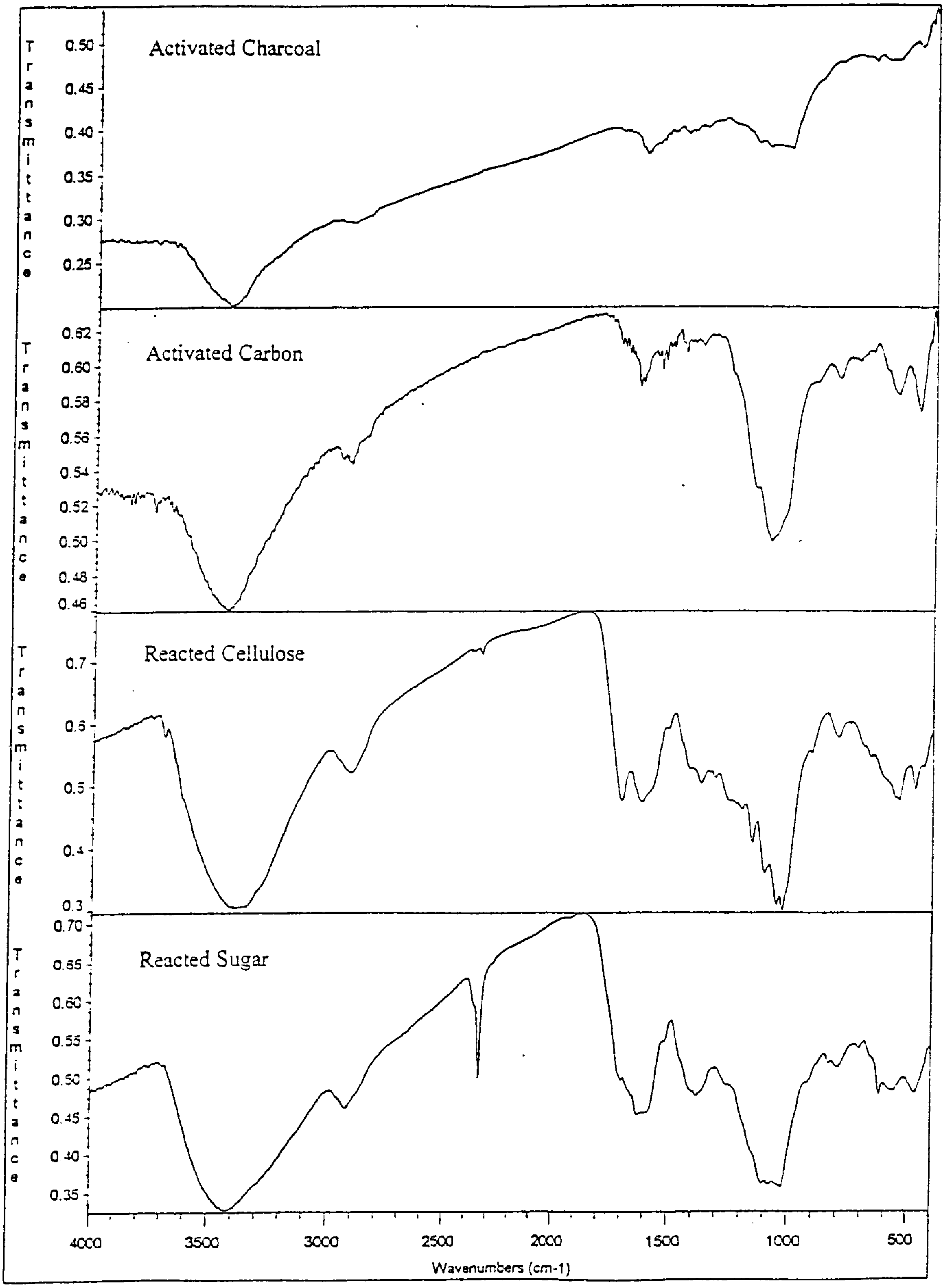


Figure 2.7.9, Infared Sectrum of comparied products

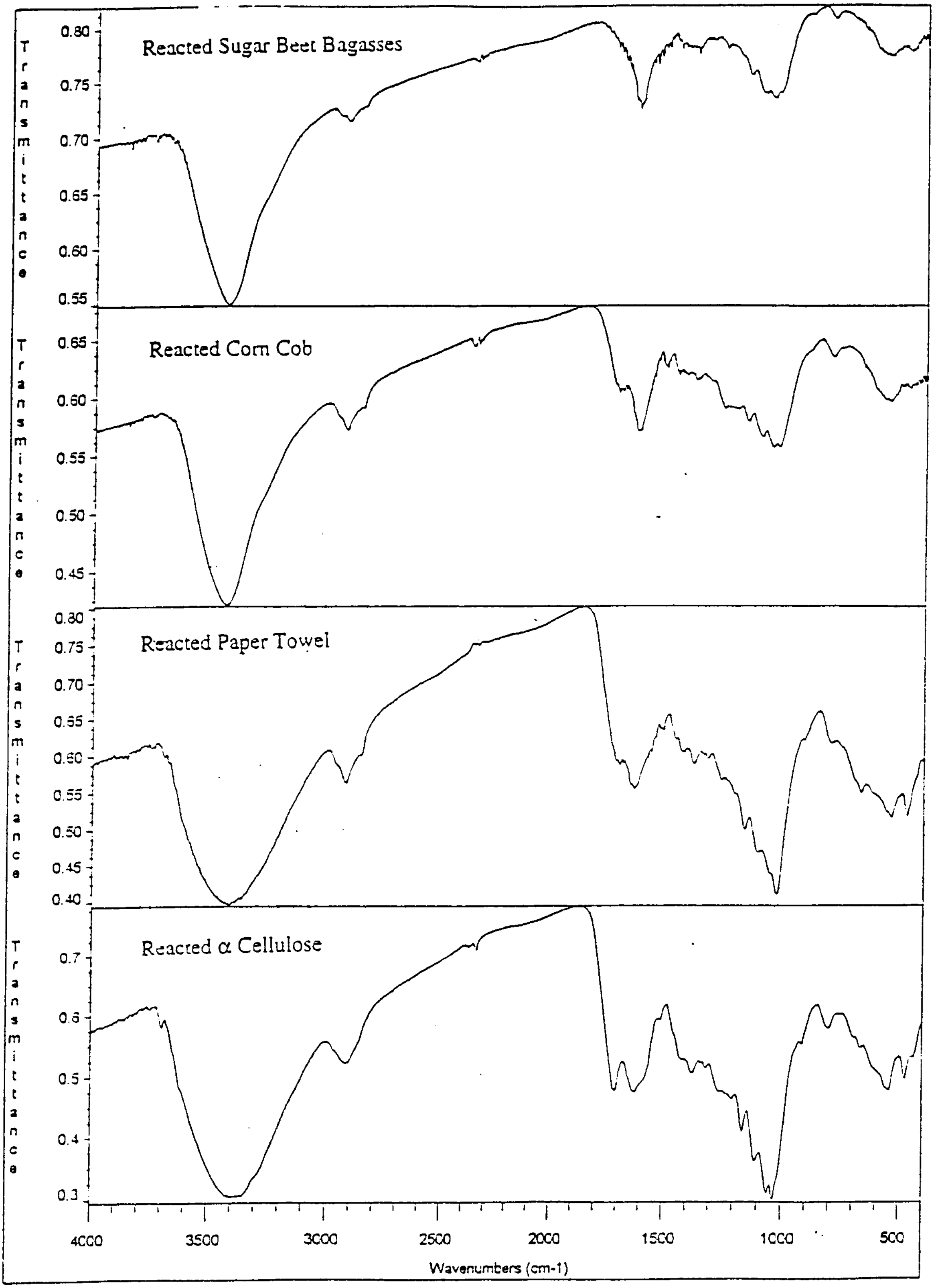


Figure 2.7.10 Infared Sectrum of Cellulostic Products

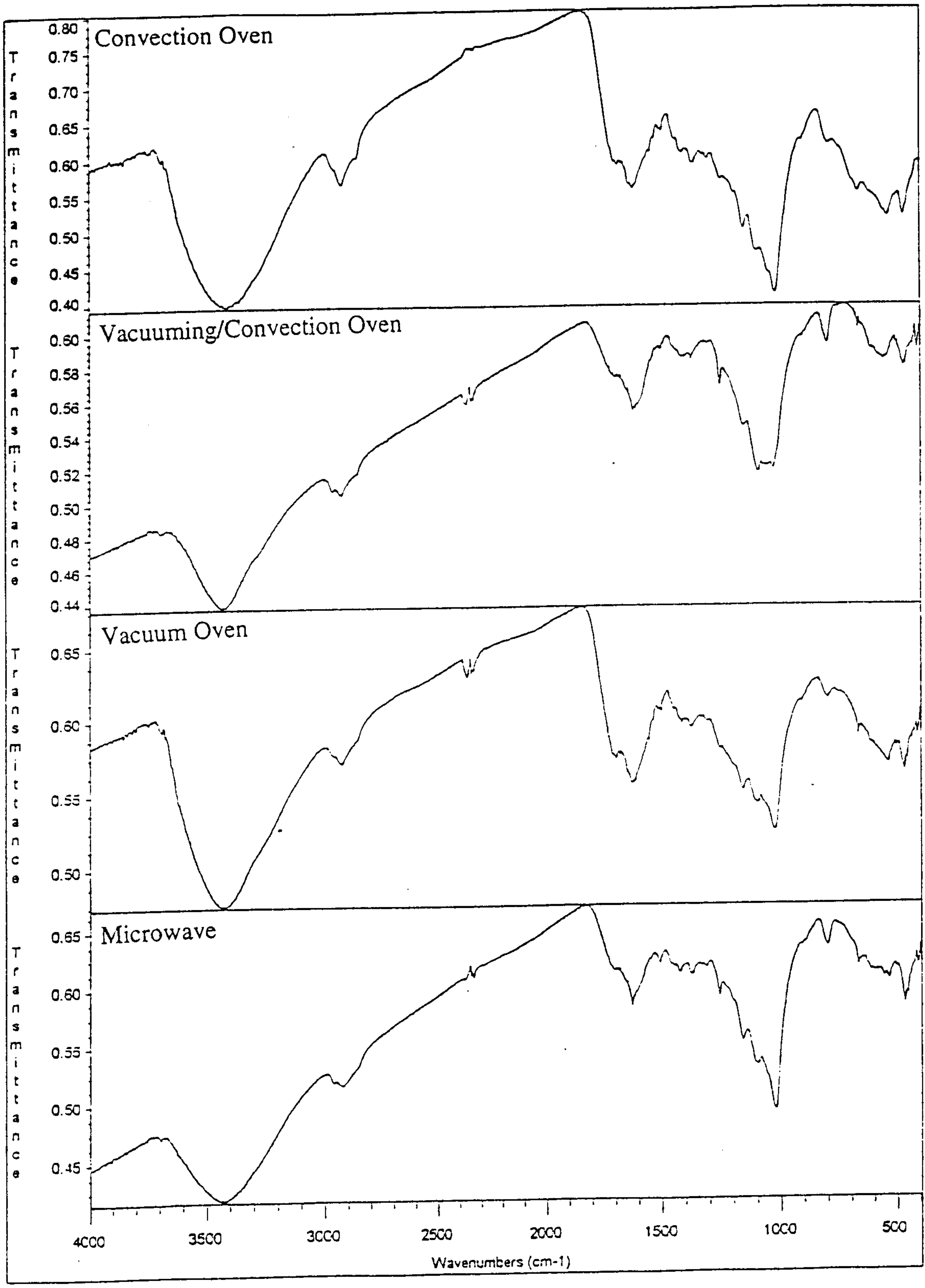


Figure 2.7.11, Infrared Spectrum of Paper Towels reacted by different methods

water were introduced into the system during the air purge, although their spectrums are subtracted out when running a background. The fingerprint zone is a very special area between 0 cm-1 to 1250 cm-1. This area is very sensitive to placement of functional groups next to the group of interpretation.

The interpretation of a spectrum can be ambiguous. The molecular groups of interest are shown in table 2.7.1. Certain groups like esters and ethers can not be distinguished in saturated hydrocarbons. One solution to this is using methods (Bloom, P. R, Leenheer A., 1989) to convert esters to other functional groups. Another example are furan rings (Bloom, P. R, Leenheer A., 1989). Furans peaks at 1370 cm-1, 1180 cm-1, 1025 cm-1 can not be distinguished from hydrocarbon alcohol's and esters in humic substances, unless specific groups are reacted.

Peak Location (cm-1)	Functional Group (Christman R. F., Gjessing E. T., 1983)
1050	CO of ethers and carbohydrates
1210	C-O stretch of ethers, esters, and phenols
1620	C=C
1710	C=O carboxyl and carbonyl
2920 and 2840	C-H aliphatic

Table 2.7.1, Functional Group Placement for Infrared Spectroscopy

2.8 Composition

Carbon Mass Balance

A carbon mass balance was done on the process to determine the fate of the lost carbon. The microwave, as described the apparatus section, was used to capture the components.

The sodium hydroxide solution and the condensate were mixed together in order to cut testing costs. The samples and backgrounds were sent out for water analysis at CH2M Hill. The tests run were: Total Organic Carbon (TOC), Total Inorganic Carbon (TIC), Sulfate, Sulfite, and Fouier Transform Infrared Gas Chromatography.

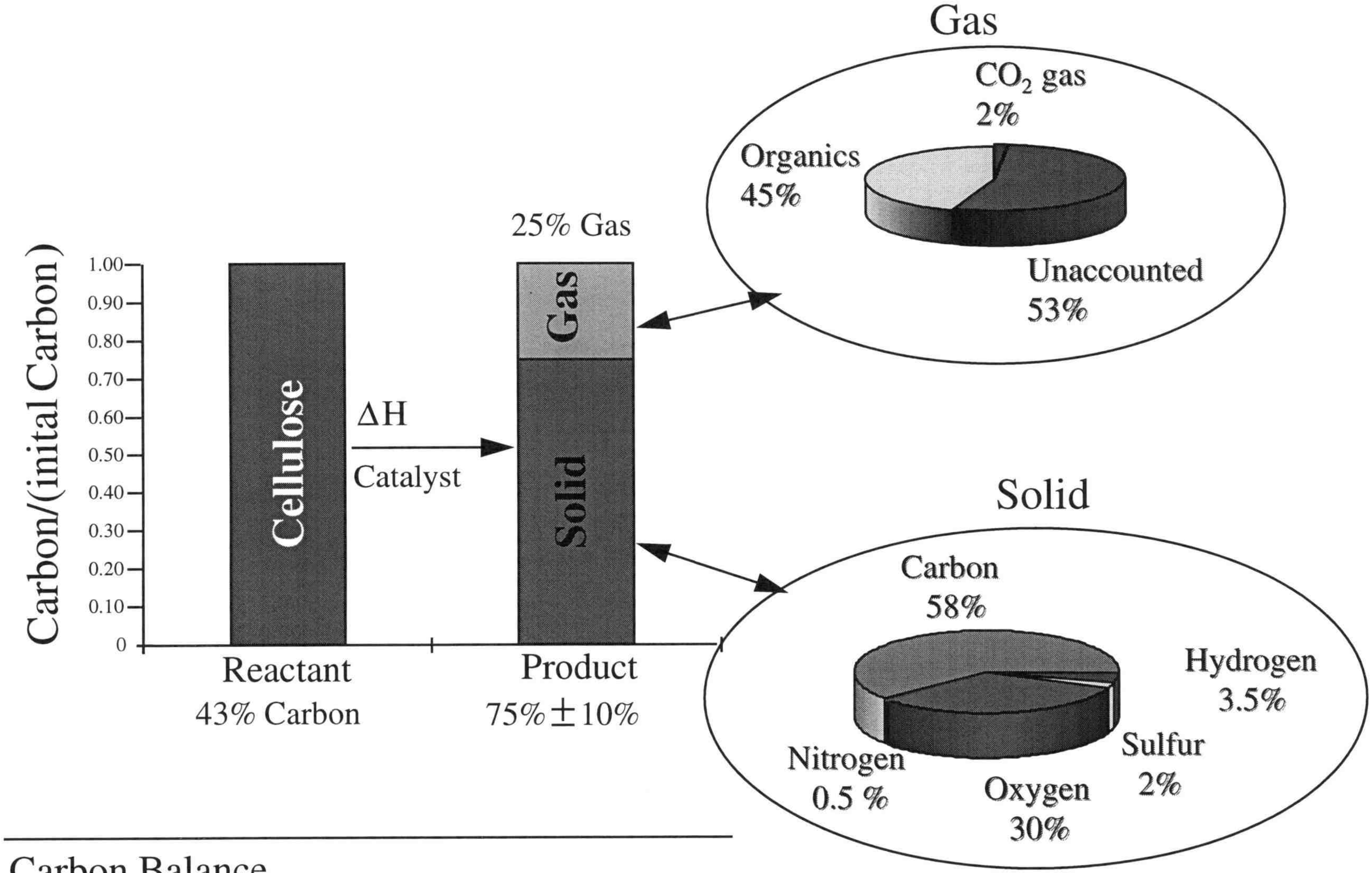
The carbon balances was based on three tests; TOC, TIC, and elemental analysis. The organics were recovered from the gas stream in the condenser or the scrubbing system. Total Organic Carbon is a measures of the organic carbon in a solution. The test does not give any information on what kind of organic materials are present. The carbon dioxide was recovered in the scrubber system. The recovery method is based on converting the gaseous CO2 to an aqueous form that will not evaporate (figure 2.8.1). Total Inorganic Carbon is a measure of the carbon in the carbonate system. Other possible gases made in the reaction that would escape the system are: carbon monoxide, methane, and hydrogen.

$$CO_2(gas) \rightleftharpoons CO_2(aq) + H_2O \rightleftharpoons H_2CO_3{}^* \rightleftharpoons HCO_3{}^+ \rightleftharpoons CO_3{}^{+2}$$

Figure 2.8.1, The Carbonate System

The solid phase carbon is accounted for by the difference in weight and carbon percent between the initial and final product. The experimental carbon loss ranged from 15% to 35% of initial carbon. The carbon balance followed the carbon species as shown by table 2.8.1. The analysis are presented in Appendix A.

By averaging the analysis, a general mass balance scheme (figure 2.8.2) can be drawn for the carbon. The distribution of carbon between the solid and gas is based on carbon loss data. The solid composition is calculated from averaged elemental analysis. The gaseous composition is calculated from the average of water analysis in table 2.8.1.



Carbon Balance

Reacted Phase	Papertowel initial carbon	α cellulose initial carbon
Solid	77 %	72 %
Organic	12 %	7 %
Inorganic	0.3 %	1 %
Unaccounted	10.5 %	19 %

Table 2.8.1, Carbon Tracing Experiment Analysis

The gas chromatography showed there were several organics in the scrubbing liquid. The paper towel experiment yielded trace amounts of furfural. The alpha cellulose showed no sign of furfural. These results are explained by the hemicellulose content typically in Kraft pulp from which paper towels are made. The hemicellulose hydrolyzes to pentoses which are further reduced to furfural in an acid environment. The other organics were unidentified.

System off Gas

The gases released from the reaction contained acidic species in addition to the organics. Analysis on the condensate from the reaction was done for sulfate and sulfite. The microwave experiments sulfate concentration ranged from 500 ppm to 1000 ppm for the undiluted condensate and 700 to 1300 mg/L for the NaOH scrubbed gas. The sulfite for these experiments was nondetectable for the condensate and ranged from 1800 to 8500 ppm for the NaOH scrubbed gas. These species result from the sulfuric acid loss. Chloride ions were also found in the condensate at 300 to 400 ppm. The pH of the condensate was in the range of 1 to 2. These concentrations depend on the reaction and reactant conditions.

Acid Leaching

Recovery of the acid from the product was done in a sequential leaching process. Pulp from Pope & Talbot was reacted in the packed bed reactor. The product was typical of the acid catalyzed reactions with the carbon composition at 56%. The newly reacted material (0.1 kg product and .05 kg sulfuric acid) were washed in 1200 ml DI water in each stage (figure 2.8.3). The leaching water temperature was changed to determine the influence on recovery of acid. After 11 stages the recovery of acid in the material was 93% for 20°C water and 95% for 70° water. The remaining acid was determined by titration of the solid with sodium hydroxide over a five day period.

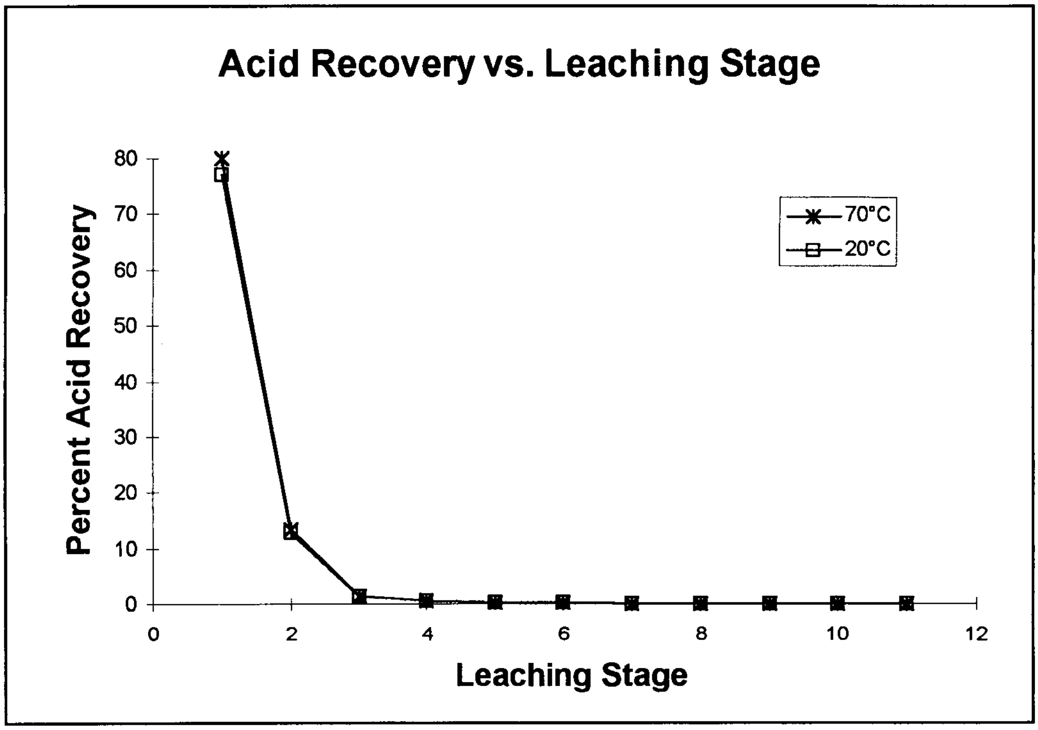


Figure 2.8.3, Acid Leaching Recovery

Soluble Product Analysis

The product that was reacted in caustic at 500°F was soluable in water. The material acted like a finely dispersed clay. When mixed in water the material did not settle very quickly even during centrifuging. When the pH was decreased incrementally the material would flocculate. Nuclear Magnetic Resonance (NMR) analysis of this material yielded a broad field of peaks which could not be analyzed. Similar results were obtained from Mass spectroscopy of the material.

2.9 Isotherms

The reacted material has several functional groups that are important in adsorption. These groups are also present in Activated Carbon. The reacted material was tested for adsorption of two contaminants. The measurement of the material was compared to activated carbon. The surface structure of the two materials is also compared.

Liquid Phase

The first compound tested was methlene blue. This testing was done in glass beakers placed on a mechanical stirrer. The mechanical stirrer was operated at 150 RPM on a 1 inch circular offset cam. The activated carbon was ground in a mortar with a pestle to a fine power. The reacted cellulose was washed in boiling DI water, dried and ground to a fine power. The contact time was determined by periodic testing of concentration. For methylene blue, equilibrium contact time of 24 hours was determined by testing the solution concentration with time.. The adsorption of methlene blue on the glass in the concentration range used was undetectable. The temperature was 25°C.

The methlene blue concentration was correlated to absorbance with a Gilson model 111B UV Detector at 254 nm wave length. A standard curve was made by sequentially diluting a 0.25g/L methylene blue solution down to 0.00024g/L and injecting in the reverse order. The detector was washed with DI water between measurements and cleaned with dilute nitric acid after decreases in concentration measurements. The nitric acid wash was used to eliminate equilibrium adsorption of the methylene blue onto the glass cell of the detector.

Initially the reacted material showed low adsorption (figure 2.9.1) compared to activated carbon. This was believed to be from contaminants attached to active sites or functional groups within the material. The material was washed 4 times in boiling DI water and rinsed. The difference can be seen in a higher adsorption data marked as humus 4X in figure 2.9.1. It was further believed that other treatments may help remove more contaminants or develop the surface. Next, the material was microwaved in one case and submerged in liquid nitrogen in another, as shown in figure 2.9.1. The treatments indicated no sign of improved adsorption.

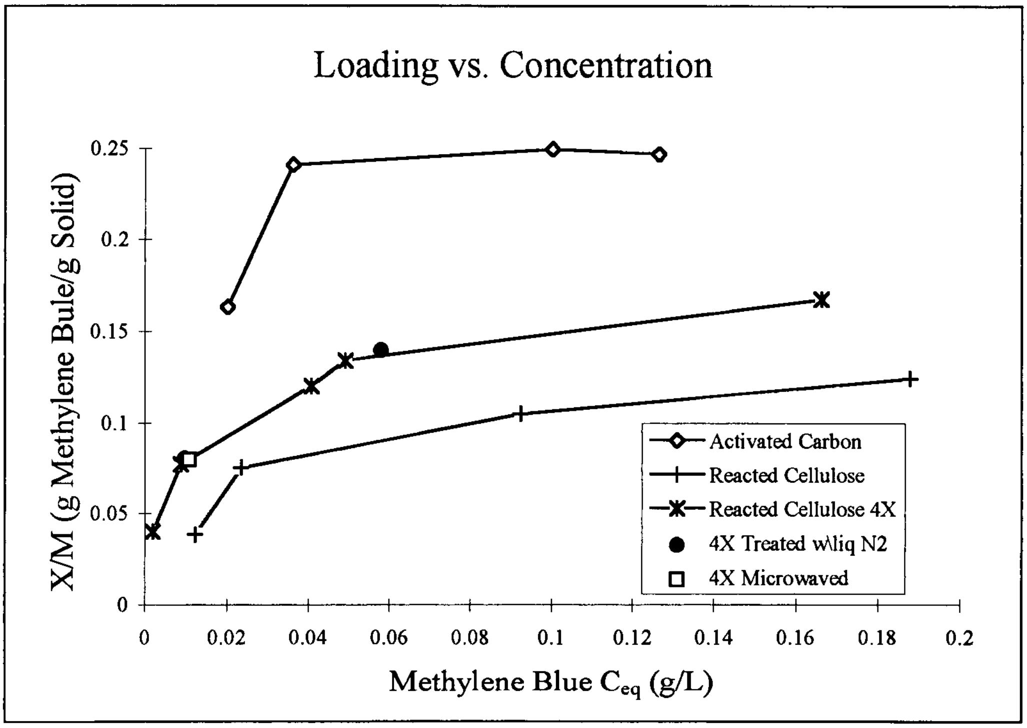


Figure 2.9.1, Methylene Blue Isotherm

Phenol adsorption testing was done in the same manor as the methlene blue testing. The reacted material was washed in boiling water 4 times and rinsed. Glass beakers were covered with para film and mixed in the same stirrer under the same conditions. A phenol standard indicated no signs of composition change or evaporation. Equilibrium contact time of 24 hours was determined by testing the solution concentration with time. The temperature was 25°C.

The Phenol concentration was correlated to the UV Detector at 254 nm wavelength. The standard curve was made by sequentially diluting a 5 g/L phenol solution down to 0.32 g/L and injecting the standards. The detector was washed with DI water between measurements.

The phenol isotherm (figure 2.9.2) reveals similar results to the methylene blue isotherm. In this case, the loading of the reacted cellulose was an order of magnitude lower that the activated carbon.

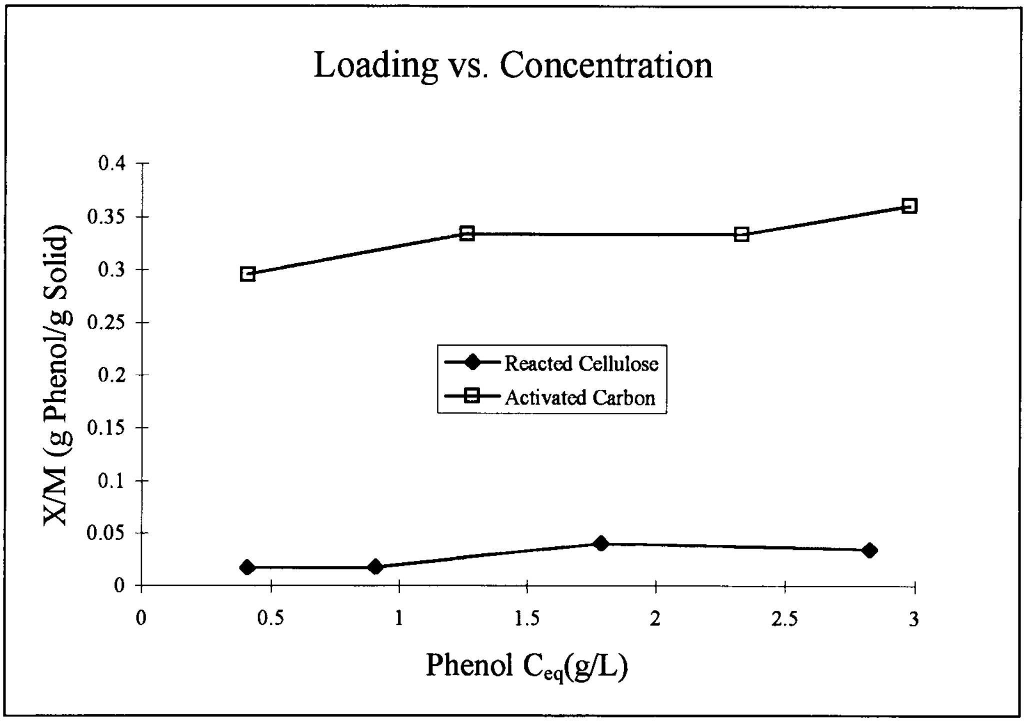


Figure 2.9.2, Phenol Isotherm

Gas Phase

The adsorption of SO2 in the gas phase was suggested to be a good test of this material. The 4 times washed material was placed in a chamber and purged with SO2 gas at atmosphere pressure for 15 minutes. When the material was removed, the weight increased by 10%. The sample was then allowed to come to equilibrium with the atmosphere over a 6 hour period. The equilibrium weight gain was 4%.

Surface Analysis

Due to oxygen functional group the reacted material was expected to adsorb as much or more than the activated carbon. Some adsorption takes place on the particle surface. Therefore, surface areas can influence loading of materials. The surface area of the activated carbon and the reacted material were compared. Surface areas for activated carbon range up to 1600 m^2 per gram. BET adsorption to determine the surface area of the reacted material was attempted, but proved unsuccessful.

The surface of the activated carbon and reacted cellulose were then profiled by Scanning Electron Microscopy (figure 2.9.3). The surface of the reacted material is not developed like the activated carbon, and appears to be a function of the particle size. The surface area per weight of this material is probably an order on magnitude smaller than the activated carbon. If there is surface adsorption, this suggests that if the reacted cellulose surface was activated, it may be a better adsorbent than activated carbon.

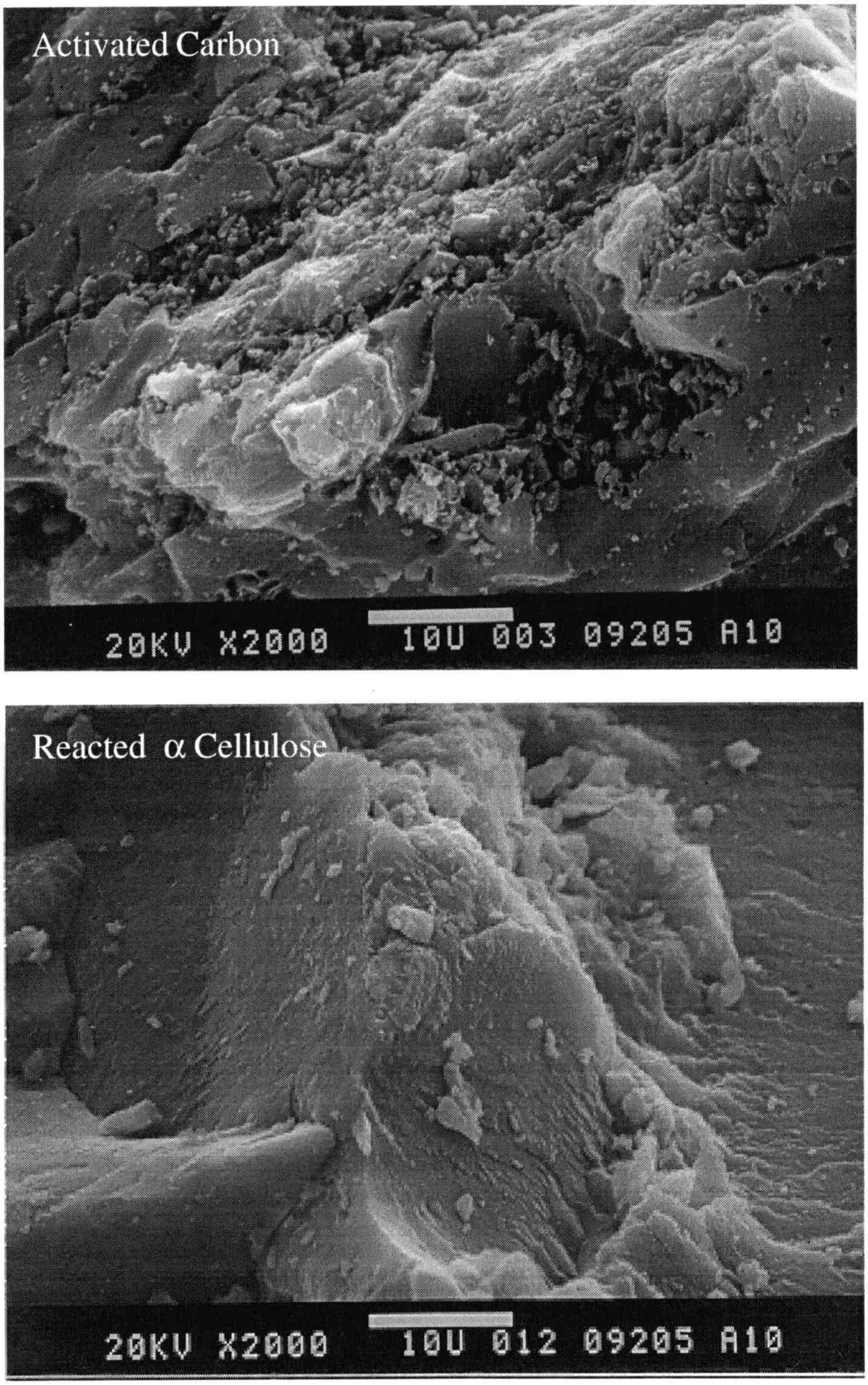


Figure 2.9.3, ESM of Activated Carbon and Reacted α Cellulose

2.10 Discussion

Reaction Methods

Five different reaction methods are discussed in section 2.5. Natural convection was excluded from this study. The first experiments were done in a natural convection oven. The reactions were slow and often incomplete. During several experiments in a closed vessel the reaction stopped when water started to reflux on the container wall. These results indicated that water inhibited the reaction, and a method to remove the water should be used. The different reaction methods outlined in section 2.5 produce similar products. The similarities are illustrated in the infrared study of paper towels (figure 2.7.11) with the exception of the packed bed method. This indicates that specific reaction methods could be chosen based on the available resources. Each method has advantages and disadvantages as outlined in table 2.10.1. All the reaction methods can be batch or continuous.

Method	Major advantage	Major disadvantage
Reactor	Easy setup	Energy and Equipment cost, Slow Reaction
Packed Bed	Easy to scale up Use of waste heat	Pressure drop, Condensation of water
Vacuum Oven	Fast reaction Low temperature	Equipment and Energy cost
Radiation	Fast reaction	Energy cost and scale up
Convection Oven	Off the shelf technology Use of waste heat	Scale up

Table 2.10.1, Reaction Method Advantages and Disadvantages

Reaction Materials

Different starting materials appear to have the same product characteristics. The materials tested produce a close chemical similarity after the reaction. The structural similarity is shown by infrared spectrometry (section 2.7). An example is the product similarity (figure 2.7.10) of sugar beet bagasses, corn cob, papertowel, and α cellulose. The structural similarity is also illustrated in reformation of structure by SEM (section 2.7). The closed structure of the reacted sugar beets bagasses and the alpha cellulose is depicted in figures 2.7.4 and 2.7.5. The elemental analysis shows further resemblance in composition (Appendix A). Table 2.10.2 briefly overviews the results. This indicates that materials with similar composition, not tested here, will produce results close to those presented here.

Material	C%	N%	S%
α Cellulose	54 to 62	0 to 0.15	1.9 to 3.0
Corn Cob	52 to 57	0.4 to 1.0	NA
Sugar Beet	53 to 58	1.4-1.8	NA
Pulp	55 to 61	0 to .14	1.4 to 1.8
Paper Towel	53 to 59	0 to .35	1.5 to 1.8
Sucrose	55 to 56	<0.1	.52 to .85

Table 2.10.2, Elemental Analysis of Reacted Materials (weight %)

Chemical Structure

The reaction taking place in this material is described by literature (section 2.2) on hydrolysis, pyrolysis, dehydration, polymerization, thermal crosslinking, and decomposition. The chemical structure for this material is complex. It is similar to humus. The structure is a polymeric mixture of compounds connected by ether and ester linkages.

The polymer is expected to be made from furans, carbonyl compounds, pentoses, hexoses, cellulose, and expoxides. The functional groups are expected to be aldehydes, ketones, hydroxyl, and carboxyl. Crosslinking between polymers is also expected.

Recommendations

One topic for further research should include better analytical analysis. One recommendation would be complete elemental analysis on all the samples. This would give more precise results. Another recommendation would be to use equipment like Pyrolysis/mass spectrum. This method can yield kinetic information as well as specific chemical species evolved from the reaction. Another area that could be improved is the determination of the type of functional groups that are present. A reaction to isolate the groups could be used in conjunction with infrared analysis. For instance, reduction of carboxyl groups by special salts removes the carboxyl from the infrared spectrum. Several methods for this are mentioned in Bloom, P. R, and Leenheer A. (1989). A final recommendation in this topic is a study for the form of the sulfur in the solid.

Another topic that deserves attention is the investigation of acid in this reaction. First, the different types of acids for this reaction should be studied. Second, the acid concentrations should be investigated. The acid concentration influences the products. The initial belief was that one acid equivalent should be used for each hexose group. The use of less acid results in unreacted areas in the material. The use of excess acid yields a product with high carbon losses that appears to have liquefied and resolidified.

A further topic should focus on contaminant removal. Activation of this material may prove it a better adsorbent than activated carbon. This material is similar to humus in infrared spectrums and composition. Humus has good chelation and adsorbent proprieties. Based on this similarity, chelation of metals on the activated and unactivated material would be worthwhile study.

A final topic is Liquefaction of this material. This reacted material is similar to coal which undergoes liquefaction. The possibility of high boiling point organics given off from catalytic cracking has been suggested as an alternative fuel to gasoline or potential chemicals. This possibility could change the future of the earth's fuel and chemical supply.

Chapter 3, Technology Development

3.1 Properties of the Reacted Material

The reacted carbohydrates are similar to humus. Humus is degraded products of plant material. Humus is degraded by microbes and decomposition processes. The humus products are a mixture of many types of functional groups on polymer structures. The elemental analysis (table 3.1.1) of the humus and reacted cellulose are very close.

Component	Humus (Schnitzer M., Khan S. U., 1972)	Reacted Cellulose	Peat Coal (Van Krevelen D. W., 1993)
Carbon	50 to 60	43 to 62	60
Hydrogen	4 to 6	3 to 4	4.9
Oxygen	30 to 35	28 to 31	33
Nitrogen	2 to 4	0 to 2	0.9
Sulfur	1 to 2	1.4 to 3	.05

Table 3.1.1, Compared Ultimate Analysis (in weight %)

Reported functional groups for humus are: Carboxyl, Carbonyl, Phenolic, Esters, Ethers, Alcohol, and Methoxyl groups. The different groups have specific characteristics; chelation of metals and adsorption of organics. The chelation of metals on humus is well documented (Snoeyink V. L. Jenkins P., 1980; and John J., et al., 1988). Humus adsorption of organics (Christman R. F., Gjessing E.T., 1983;) is also well documented. Carbonyl, phenolic, and hydroxyl are among some of the groups presently believed (Ishinzaki C., 1973) to play a role in adsorption. These groups typically are seen in an infrared spectrum. The comparison of the infrared spectrums of the reacted carbohydrates (section 2.7) and humus (Gadel F., Bruchet A., 1987) yields similar results.

The solubility of the reacted cellulose is similar to humus. Most humus is insoluble in acid solution and slightly soluble in hot caustic. The reacted carbohydrate shows little solubility in hot caustic solution and none in acid solution. Several unsuccessful solvents have been tried on the material such as: DMSO, Amines, and Chloroform.

Another comparison of the reacted carbohydrates are peat coals. The elemental analysis between peat coal and the synthetic material (table 3.1.2) are close. The heating value for the reacted cellulose material were calculated at 9340 Btu's/LB (Desert analytical lab) and 9298 Btu's/LB (Perrys [1], R. H., Chilton C. H., 1973). These values fall in the coal heating values range of 6,300 to 14,000 Btu's/LB (Perrys [2], R. H., Chilton C. H., 1973).

Coal is known to undergo gasification or liquefaction. One method of gasification of coal is pyrolysis. A method of coal liquefaction is accomplished with a catalysts and pressurized hydrogen gas. This method transforms the solid into a liquid which can be further processes to chemicals or fuels. Currently, we believe this conversion is possible with the reacted cellulose material.

One of the objectives of this thesis is to identify some uses of this material. Current research of acid catalyzed reactions of cellulose focuses on production of chemicals, and fertilizer. The adsorbent properties of the reacted material are briefly investigated in this thesis.

One of the new research topics under this category is conversion of cellulose and lignin's into a slow release fertilizer. The process is similar to the technology in this thesis, but it differs in the extent and sophistication. First, nutrients are added to the waste. Second, the acid remains in the product. Initial testing shows results comparable to commercial fertilizers. This product is currently is being tested by the Penn State University agriculture science department and the Texas A&M University Agriculture Research department.

Another new research topic for cellulose is the acid catalysts conversion to chemicals. One application of this (Stinson S. C., 1996) has been to react recycled paper in acid at 300°C. One of the products is levoglucosenose. This product is an exopoxide that is further used to produce nucleoside antiviriral drugs.

An application studied in this thesis is the adsorption capacity. The reacted material shows potential for better adsorption than activated carbon. Isotherms for the two materials show the reacted material to be lower, but on the same order of magnitude as the activated carbon. The isotherms are shown in section 2.9. The difference can be attributed to contact surface area. The carbon has been activated to increase the surface area 500 to 1600 m^2/gram. The reacted material surface area is expected to be orders of magnitude smaller. Other characteristics of the reacted cellulose are outlined in section 2.1.

3.2 Process Description

The following process is designed based on the experimental information described in chapter 2. Conceptually the process would follow a scheme similar presented in figure 3.2.1. The equipment list is outlined in table 3.2.1. The three main sections of this technology process solids, acid and gases. The solids processing are the necessary steps to react the carbohydrates. The gas processing equipment recycles the acidic vapors onto the incoming material as a pretreatment. The acid processing recycles the acid. A system like this could be run as a continuous or as a batch process. In the case that this will be operated in a continuous flow the solids would have to be moved by conveyers and augers that are not listed. A case study process flow sheet is illustrated in appendix C.

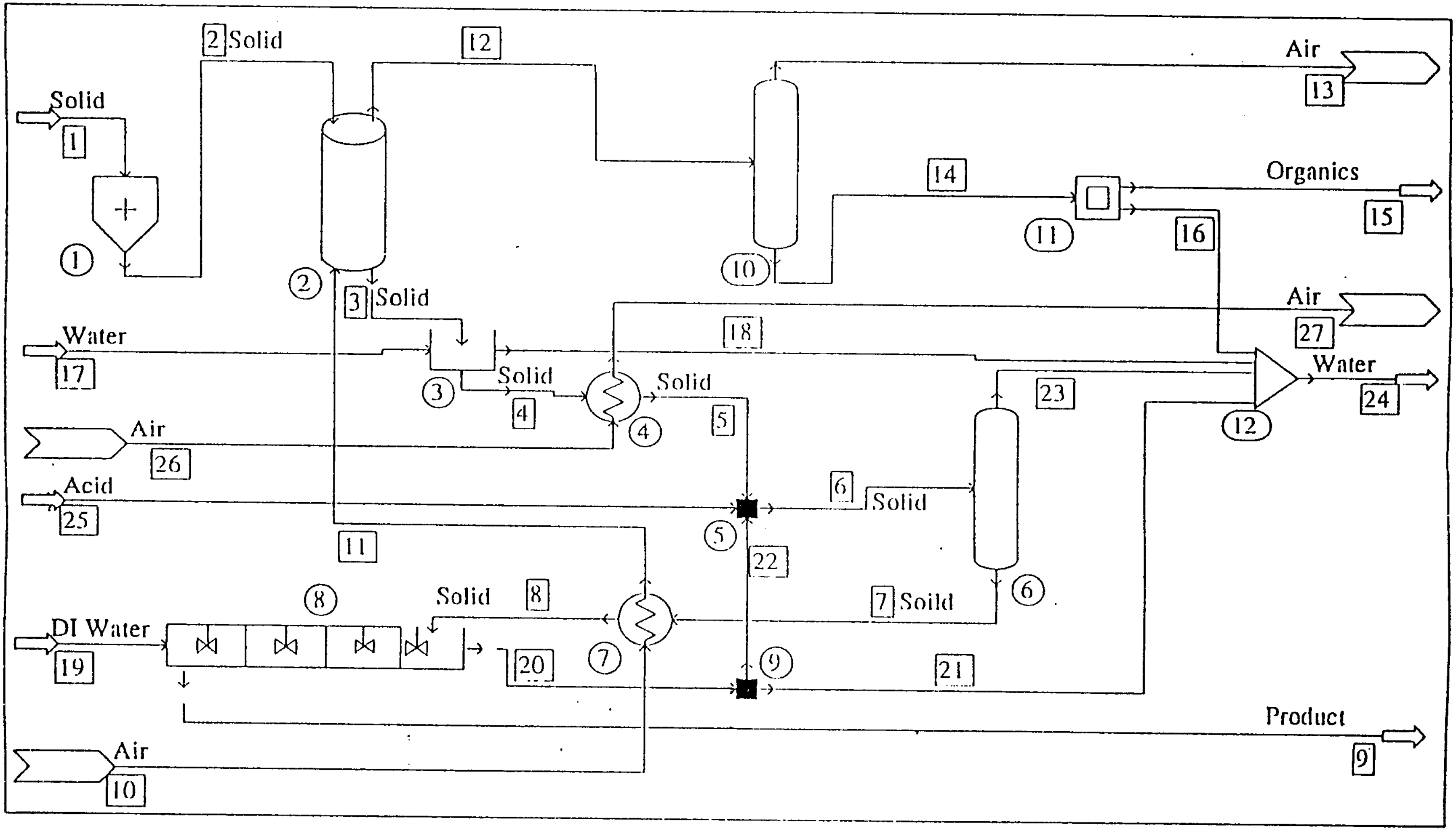


Figure 3.2.1, Process Flow Diagram

Solid Processing Pretreatment

The solid processing starts with size reduction. This step compensate for material differences in size, type and physical structure. Second the material is contacted with the acidic air from the reaction. This process has two purposes. One is the removal of some of the acid from the air stream. It also serves as acid pretreatment of the material. Acid pretreatment removes complexed contaminants like salts and metals. This process can be

Equipment	Operation Description	Equipment List
1	Size Reduction	Hopper, Attrition Mill, or Rotary Knife Cutter
2	Gas Solid Contactor	Acid resistant Pipe (1 to 3 ft Dia)
3	Solid\Liquid Washer	Stage 1: Acid resistant Tank , Mixer Stage 2: Mechanical water removal Process: I.E. Roll Crusher
4	Moisture Removal	Acid Resistant Pipe (1 to 3 ft Dia)
5	Solid/Acid Addition	Stage 1: Acid Resistant Tank, Mixer Stage 2: Mechanical Water Removal
6	Evaporation Moisture Removal	Acid Resistant Tank, Vacuum Pump
7	Reactor	Acid Resistant Pipe (1 to 3 ft Dia)
8	Acid Recovery	Liquid Pump, Each Stage: Acid Resistant Tank , Mixer, Mechanical Water Removal Process
9	Acid Recycle\Bleed	Valve
10	Acid and Organic Recovery	Fiber Filter and Activated Carbon
11	Phase Separation System	Settling Tank
12	Mixing Point	Fitting Adapter

Table 3.2.1, Process Equipment

achieved by methods like fluidized beds, or moving packed beds. Third, the solid are washed. Washing the material removes some of the contaminants. This step washes the contaminants and some of the prewash acid from the solids. Next the water content in the solid is decreased to accommodate the acid addition step.

Solid Processing Acid Addition

The fifth piece of equipment is the acid addition tank. This is where the sulfuric acid is added to the solid. This step removes the excess moisture from the solids. The contact and mixing time in this step would vary bases on the material characteristics. Next, the material could be delivered to the evaporative moisture reduction process. This step is optional. This process removes water using evaporation processes. The evaporation could be done by exposing the material to ambient air or in a vacuum. At low temperatures most of water could be evaporated leaving the acid on the solid. Acid losses could be as in the range of 0 to 5 %.

Solid Processing Reaction

Seventh, the material is reacted. Several reactors types could be used for this step: Convection, Radiation, Vacuum assisted, and solar assisted. The choices can be made based on the available infrastructure and resources. The convection method could be any of the following, a packed bed, a fluidized bed, a moving packed bed, or a convection oven. The radiation method could use the same type of apparatus as the convection method with the aid of radiation like microwaves. The vacuum assisted process could be implemented to cut the reaction temperature or time. The solar aided process could be implemented to utilize solar energy. In this case forced convection contactor would be used. Acid loses for 40 to 60 minutes at 110°C in a convection reactor is 5 to 15% of the original acid (figure 2.6.1).

Acid Processing

The final step of the solid material is acid extraction. Counter current leaching would be ideal for this process. This method recovers the most concentrated acid from the process with the least amount of water. The recovered acid solution can then be recycled to the process. An experimentally determined amount of the acid would have to be bleed from the system to control accumulation of contaminants. The bleed acid could be mixed with the other acid waste streams and sent to a water treatment plant. Another option for the bleed acid would be to use it in the preacid treatment step. The leaching process would recycle 90 to 95% of the acid in the reacted material (figure 2.8.3). Fresh acid would be added to compensate for acid losses. Acid would also be recovered from the air onto the material in the preacid treatment.

Gas Processing

The reaction produces organics and acidic species. The acid species made in this process are identified as sulfate and sulfite. Sulfite in a gas stream scavenges water and forms sulfuric acid in drop sizes of .1 to 8 micrometer diameter. Next the gas is pumped through the gas solid contactor as described above. The gas solid contactor will remove some of the acid species from the stream. The final step is the organic and acid recovery step. The acidic mist can be removed by several methods. Two methods are Horizontal Flow Mesh, and Fiber Bed. The organics species are another concern. They were several organics that were not identified. This leaves the options for recovery undefined. One method that would remove both the acid and most of the organics would be a scrubbing system. Other methods for organic recovery could be, adsorption, absorption, condensation, or membrane separation. The trade off between pressure drop and scrubbing cost would have to be part of the considerations for this choice.

Distribution of Products

The typical distribution of products is represented in figure 3.2.2. The starting material is cellulose. The gaseous products were determined by experiment described in the composition section 2.8. They were identified as carbon gases. Water was a product based on experiment and the lost mass. The solid fraction is based on an average value from figure 2.6.4.

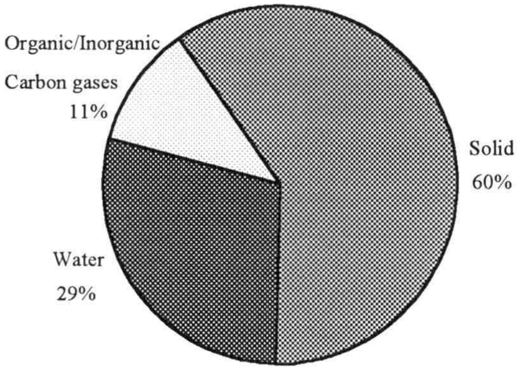


Figure 3.2.2, Process Products Distribution

Energy

An order of magnitude energy usage for this process is 14,366 KJ/Kg. This calculation is based on assumptions covered in appendix C. One assumptions is that waste heat would be available for this process. Different methods could be used decrease the energy needed. The heating values for the reactant and product are summarized in table 3.2.3. There are about 11 kg of unidentified organic and inorganic carbon gas species produced from this process that are not included.

The energy consumption and product yield estimates are based in initial investigation of this process. Optimization of the process could easily reduce losses and boost yields. For instance the acid losses could be reduced by lowering the reaction temperature. Lower temperature could possible reduce carbon losses as organics. Much work is needed here.

	Cellulose	Reacted Cellulose Product
Higher heating value	15,035 KJ/Kg[1]	21,724 KJ/Kg[2]

Table 3.2.2, Heating Values of Cellulose and Reacted Cellulose ([1] Table A2, [2] Perrys[1] R. H., Chilton C. H., 1973)

3.3 Evaluation of Sustainability

This technology fits in with most of the sustainable technology goals defined in Chapter 1. The source is natural, renewable and abundant. It can fit in with industrialized society in large and small scale operation. The ecosystem is stable and maintainable. Resource usage and impact on the environment are minimal. The areas to be investigated are the minimum impact on the earth and maximum yields of resources. The objectives are also investigated.

Business Practices

Pulp and paper plants around the world have waste pulp they disposed. Some of the fiber is too small, or has been recycled to many times. A situation like this is ideal for production of the acid reacted product. The production could use the infrastructure of the mill. Waste heat is abundant for the reaction. Plant personnel is trained in equipment setup, operation and maintenance for similar operations. The waste material is on site which cuts shipping, and waste removal costs. A useful product with potential for profit is made from the waste. There would most likely be equipment on site to accommodate part of the process.

Another possibility for this could be smaller operation of this at a farm or food packaging place. The waste material would serve as the reactant. This type of operation could be done as a batch process carried out in the same reaction vessel throughout the process. In this case the reaction could be solar assisted. The operation would be done on the waste that is generated at the site or several sites could form a cooperation. The material could be used on site as a fertilizer or an absorbent.

Ecosystem

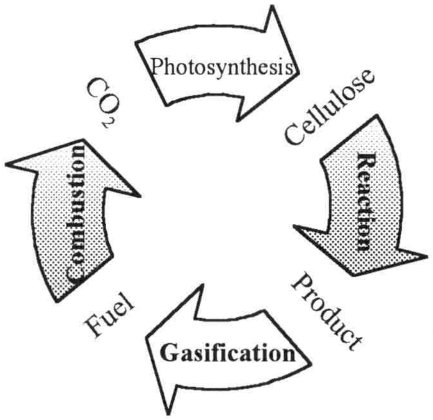


Figure 3.3.1, Carbon Cycle

This technology fits in with the earth's ecosystem in two ways. First, this is a naturally renewable resource. Second, if the products are combusted then the carbon is recycled through the ecosystem. Plants remove the carbon dioxide and convert it into solid forms like cellulose. After the plant has been harvested the cellulose is converted to products like chemicals and fuel. Combusted of the products release carbon dioxide to the atmosphere for plants to use. The cycle can now be repeated.

Resource Usage

This technology uses a minimal amount of resources. Currently the sources that can be used are waste: wood, grasses, and other agriculture waste. The use of this resource is actually a waste reduction because these materials are disposed of in many cases. The development of this technology may change these wastes into resources. The other resources used in this technology are acid, and energy. The acid loss in this process is estimated to be 5 to 15% which. Currently the price for sulfuric acid 40$/ton of 93% assay. The energy cost would depend how the process is integrated into an existing production system. If the process was setup at a paper plant the energy cost would be minimal because the excess waste heat from the plant could be utilized. Again if the process was solar assisted then energy use could be small.

Impact on the Environment

The impact on the environment needs to be studied. The type of waste streams that are released to the ambient can be treated. The liquid streams exiting the system result in a salt solution. The exiting air contains acid species, organics and water. The technology recommended can remove most of the acid and some of the organics. Additional equipment may be necessary to remove all the gaseous organics. A detailed pilot plant study would provide better information.

The natural fate of carbohydrates is another consideration for the impact of this technology. Methane and carbon dioxide are greenhouse gases. Carbohydrates are decomposed to products like methane and carbon dioxide by natural processes. Graedel T. E., and Crutzen P. T., (1993) estimates the release rates of 0.5 grams methane per gram of carbohydrate disposed of on land. The carbon dioxide is of little concern here for two reasons. First, it is an end product if this technology is used to make a fuel. Second, it will be recycled to the plants. The suggested technology produces approximately 11% of the carbon as a gas. The experiments indicated that one half of that could easily be recovered. In this case, the gas emission would be reduced from 50% methane to 6.5% unidentified gas. This area needs more study to determine: exactly the types of gases given off, their effect on the atmosphere, and possible recovery methods.

Maximum yield of Resources

The maximum use of resources is another area that needs to be researched. If the desired product is a liquid fuel then pyrolysis or fermentation are current options. The conversion efficiencies for these methods are low. Pyrolysis produces low Btu gas, oil and a char. The oil would have to be further processed to a liquid fuel suitable for combustion. The efficiency for this process will be lower than 45%. The second option is fermentation. The first step is done with hydrolysis or an enzyme. This step breaks the carbohydrate down into sugars suitable for fermentation. Next a microorganism converts the sugar into an alcohol and carbon dioxide. The efficiency of this around 30%. This sets the stage for developing new technologies to make liquid fuels made from cellulose. If a new technology can be developed that increases the efficiencies to 50% or more then it should be investigated.

Objectives

The next step is to evaluate how the objectives for sustainable technology can be met. The objectives for society and business are have to be addressed on a level different than here. These objectives are possible, but they depend on the entities present in society or business.

The objectives for this technology illustrated in the previous discussion are summarized in table 3.3.1. This technology is a waste minimization process. The paper mill example illustrate how this technology could fit in with business practices. The farm example shows how this technology can be done on small scale. The paper mill also has elements of closed loop technology and minimum infrastructure. The closed loop technology is heat recovered for processing the material from existing operations. The use of existing facilities and personnel reduces the infrastructure. The objectives that remain to be seen are the economic performance and decentralization of investment. The deficiency of this technology is acid and organic recovery systems that are an end of pipe treatment.

Objective	Meets Objective
Closed loop technology(waste minimization/cogeneration)	yes
Fits in with business practices	yes
Small or large operation	yes
Minimum infrastructures	yes
Economic performance	possible
Decentralization of investment	possible
Clean technology instead of end of pipe treatments	no

Table 3.3.1, Evaluation of Objectives

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Appendix A, Analysis Section

Elemental Analysis

In each case the carbon and nitrogen composition were determined on a Carol Erba NA 1500 analyzer. At the Oregon State University Department of Forest Science(table A.1) the samples were dried first and then analyzed. At Tucson's Desert Analytical lab (table A.2): the samples were dried first. Sulfur was determined using a Control Equipment Corporation 240XA Elemental Analyzer, Oxygen was determined using a Perkin Elmer 240A Analyzer, Ash was determined by combustion of 0.5 to 1g sample muffled at 900°C to 1000°C to a constant weight. In house Ash residual was determined by combustion of 0.25 to 1g sample at 500°C to 600°C to a constant weight. Heating values were calculated by elemental analysis using a program by D.M. Mason and K. Ghendi, "Formulas for Calculating Heating values of Coal and char..." IGT publications, 1980. At Weyerhaeuser Technology Center Analytical Laboratory (table A.3), oxygen was determined by difference, and ash percentage at 750°C.

The carbon and nitrogen content I from the Oregon State University Forest Science were measured on a Carlo-Erba NA 1500 Series II CNS Analyzer. This analytical method is based on the complete and instantaneous oxidation of the sample by "flash combustion" which converts all organic and inorganic substances into combustion products. The resulting combustion gases pass through a reduction furnace and are swept into the chromatographic column by the carrier gas (helium). The gases are separated in the column and detected by the thermal conductivity detector, which give an output signal proportional to the concentration of the individual components of the mixture.

The carbon, nitrogen and sulfur in Oregon State University Crop & Soil Science were measured on a LECO® CNS-2000 Analyzer. The method is based on combustion in an oxygen medium. The combustion product are CO_2, SO_2, N_2, and NO_x (NO_x is passed through a catalysts and reduced to N_2). An infrared detector measures the carbon and sulfur content and a thermal conductivity cell measures the N_2.

Description	Reaction Method	Experiment	Carbon %	Nitrogen %	Sulfur %
A Charcoal	None		86.28	0.51	NA
A Carbon	None		95.18	0.24	NA
α Cellulose	None		43.30	0.20	NA
α Cellulose	Reactor	150	58.06	0.16	NA
α Cellulose	Reactor	151	47.96	0.18	NA
α Cellulose	Reactor	152	60.05	0.14	NA
α Cellulose	Microwave	308	61.87	0	NA
α Cellulose	Microwave	308	62.72	.034	3.0
α Cellulose	Microwave	315	58.36	0.15	NA
α Cellulose	Microwave 2	354	54.8	<0.1	2.5
α Cellulose	Vacuum Dried Convection Oven	250	59.6	<0.1	1.9
α Cellulose	Beaker/Conc H_2SO_4	321	56.10	0.07	NA
Old Cob	None		47.61	0.28	NA
Fresh Cob, 1x	None		48.65	1.09	NA
Fresh Cob, 5x	None		48.12	0.48	NA
Fresh Cob	Reactor	10	56.49	0.57	NA
Fresh Cob	Reactor	11	51.96	0.93	NA
Fresh Cob	Convection Oven	101	57.04	0.45	NA
Fresh Cob	Convection Oven	102	52.55	0.39	NA
P&T Pulp	None		43.85	0	NA
P&T Pulp	Packed bed	200	55.6	<0.1	1.4
P&T Pulp	Packed bed	222	56.6	<0.1	1.8
P&T Pulp	Microwave	303	61.59	0	NA

Table A.1, OSU Forest Science, Crop & Soil Science Analysis (in weight %)

Description	Reaction Method	Experiment	Carbon %	Nitrogen %	Sulfur %
P&T Fibers	Convection Oven	160	58.71	0.13	NA
P&T Pulp	Convection Oven	161	59.51	0.13	NA
P&T Pulp	Convection Oven	161, Washed	61.37	0.14	NA
P&T Pulp	Vacuum Dried Convection Oven	256	51.2	<0.1	1.8
Paper Towel	None		42.97	0	NA
Paper Towel	Microwave	301	56.64	0	NA
Paper Towel	Microwave	309	58.75	0.16	NA
Paper Towel	Microwave	310	59.21	0	NA
Paper Towel	Microwave 2	355	54.4	<0.1	1.5
Paper Towel	Convection Oven	T2D	56.60	0.11	NA
Paper Towel	Convection Oven	IR spectra 1	52.52	0.25	NA
Paper Towel	Convection Oven	111	57.59	0.12	NA
Paper Towel	Convection Oven	113	47.48	0.10	NA
Paper Towel	Convection Oven	113	55.52	0.17	NA
Paper Towel	Convection Oven	114	49.91	0.14	NA
Paper Towel	Convection Oven	114	57.99	0.12	NA
Paper Towel	Convection Oven	115	55.78	0.10	NA
Paper Towel	Convection Oven	116	54.34	0.18	NA
Paper Towel	Convection Oven	361	54.7	<0.1	1.6
Paper Towel	Convection Oven	360	54.1	<0.1	1.5
Paper Towel	Vacuum Dried Convection Oven	251	53.4	<0.1	1.6
Paper Towel	Vacuum Oven	271	54.5	<0.1	2.1
Paper Towel	Vacuum Oven	272	54.7	<0.1	1.4

Table A.1, OSU Forest Science, Crop & Soil Science Analysis (in weight %)

Description	Reaction Method	Experiment	Carbon %	Nitrogen %	Sulfur %
Paper Towel	Sperry	Sperry A	45.4	0.24	NA
Paper Towel	Sperry	Sperry B	46.9	0.12	NA
Paper Towel	Sperry	Sperry C	50.37	0.12	NA
Sugar beet	None		43.84	1.8	NA
Sugar beet, 2x	None		44.60	1.8	NA
Sugar beet	Convection Oven	130	53.87	1.76	NA
Sugar beet	Convection Oven	131	56.80	1.70	NA
Sugar beet	Convection Oven	132	58.31	1.46	NA
Sucrose	Beaker/Conc H_2SO_4	340	56.3	<0.1	.85
Sucrose	Beaker/Conc H_2SO_4	341	55.2	<0.1	.52

Table A.1, OSU Forest Science, Crop & Soil Science Analysis (in weight %)

Carbon	Nitrogen	Hydrogen	Sulfur	Oxygen	Residue	BTU/lb.
60.95	.03	3.44	1.65	31.33	3.36	9340

Table A.2, Desert Analytics Analysis (Sample 199 in weight %)

Sample	Carbon	Nitrogen	Hydrogen	Oxygen	Residual
021	56.1	.36	3.1	28.3	12.2
022	56	.34	4	28.1	11.6

Table A.3, Weyerhaeuser Technology Center Analysis (in weight %)

Capillary Electrophoresis

Ions were measured on an electrophoresis system in the Oregon State University Chemical Engineering Department. Aqueous Ion analysis (table A.4) were measured on a CES-1A Dionex Capillary Anion PMA Electrolyte buffer (Dionex P/N 044138) was used in a 50 μm ID x 50 cm length capillary. The separation voltage was -30 KV (240 V/cm). Indirect UV detection at 210 nm was measured at the anode. The injection method was Hydrostatic, 100 mm for 30 seconds. The run duration was 5 minutes. The samples were undiluted condensate from the microwave experiments.

Sample	SO_4 (ppm)	CL (ppm)
300	494	263
302	1051	407

Table A.4, OSU Chemical Engineering Analysis

Scanning Electron Microscopy (SEM)

The Microscopy was performed on an AmRAY 1000A SEM operated at 20 KV, in the Electron Microscopy Facility, Oregon State University Department of Botany and Plant Pathology. The images were recorded on Polaroid Type 55 P/N positive/negative 4x5 format film. The specimens were mounted on aluminum planchettes using adhesive tabs (Avery Commercial Products, Azusa, Ca). They were coated with 20 nm of 60/40 wt % Au/Pd alloy in an EDWARD'S S150B sputter coater operating at $1x10^{-2}$, 5 mbar Argon pressure, 1.2 KV, 40 milliampere plasma current, for 60 seconds.

Water Analysis

The water analysis (table A.5) was performed at CH2M HILL Corvallis Applied Science Laboratory. The analysis methods are: Sulfate - EPA300, Sulfite - EPA.377.1, TOC - EPA415.1/2, TIC - EPA415.1/2M, and Furfural - GC-FID.

Analyte	Papertowel	Papertowel background	α Cellulose	α Cellulose background
Sulfate (mg/L)	735	1	1330	1.2
Sulfite (mg/L)	8450	0	1820	0 (estimated at 418)
TOC (mg/L)	1790	14.9	314	3.5
TIC (mg/L)	157	107	134	20
Furfural (mg/L)	18	16.5	16.5	not available

Table A.5, **CH2M** HILL Analysis

Infrared (IR) Spectrum

The Infrared analysis were prepared according to the following procedure. Baker Instra-analayzed Potassium Bromide (for infrared analysis, 2961-03)was used to suspend the sample. The die used was a Barnes Vacuum Die (model 129) with a 13 mm diameter die. A Carver Labs hydraulic press with a pressure gauge in 200 lb. increments up to 20,000 lb. was used to compress the pellet. The Infrared instrumentation was a Nicolet 5PC FT-IR Spectrometer interfaced through a Microsoft Windows program.

The Potassium Bromide was initially placed in a 105°C oven for 12 hours to drive off foreign material. In a clean mortar with a pestle, 0.3 grams of the KBr were ground smooth with 0.001 grams of the sample. The mixture was then put in a 105°C oven for 10 to 40 minutes. The die contact surfaces were cleaned with pure ethanol and placed in the oven to drive off residuals. Next, the powered mixture was places in the die. The die was then placed in the hydraulic press, connected to a vacuum source, and allowed to reach 29 PSIG of vacuum for 5 minutes. Then the press was loaded to 10,000 lb. force (50,929 psi) for 1 hour under a vacuum. In the case of a cloudy pellet, the pressing was repeated. The product pellet was typically 1 mm thick. The infrared equipment was immediately purged with clean dry air for 3 minutes and a background spectrum was run. The pellet was then placed in the He Ne laser marker and purged with clean dry air for 3 minutes. Then the final spectrum was run.

pH Measurements

The pH was tested with a BECKMAN Φ 10 pH meter (serial NO. 0213786). The meter was calibrated using two buffer solutions, a Gel-filled Electrode (VWR Cat. NO. 34105-023) and a BECKMAN Temperature Sensor (598115 S609A) The buffers were Metrepak pHydrion buffers pH 10.00 (Cat NO. 270-10.00) and pH 4.00 (Cat NO. 270-4.00). Deionized water was used to make solutions and for rinsing. When not in use the Gel-filled electrode was stored in pH electrode storage solution (VRW CAT. NO. 34105-042).

The procedure to calibrate the meter started by rinsing the probe in DI water. Then the probes were placed in the 4.00 pH buffer and stirred momentarily. The first standardization point was achieved by pressing the "pH" key followed by "STD" key and allowing the meter to lock in. Next, the probes were rinsed with DI water and stirred into the 10.00 pH buffer. The second standardization point was achieved by pressing the "STD" key, and allowing the meter to lock in. The meter was ready to use after rinsing the probes.

Differential Scanning Calorimeter (DSC)

DSC measurements were made with a Shimadzu Model DSC-50 in the Oregon State University Chemistry Department. The materials were placed in a 120°C drying oven for 2 or more hours to drive off residual water. The samples were quickly weighted on a mettler model AE100 analytical balance and hermetically sealed in 0.24 in diameter aluminum boats. A reference boat with air was sealed at the same time. In order to avoid inaccuracies from skin oils, the boats were handled with tweezers.

The sample and reference were placed on the electric heating element in the DSC. During operation 35 ml/s nitrogen was run through the system. The two containers were heated at a constant rate of 8°C/min. The system temperature started at ambient and was heated up to 320°C or higher. The cooling cycle or repeated cycle analysis were ignored because the reactions that took place changed the material.

Appendix B, Definitions and Chemical Group Structures

Definitions

Carbonyl	The carbon oxygen pair in a ketone or aldehyde
Hemicellulose	A polymeric substance similar to cellulose in structure, except the sugars mers are hexoses and pentoses compared to glucose sugars in cellulose.
Hexoses	A 6 carbon sugar
Melanoids	A black pigment substance
Monosacchrides	A 4, 5, or 6 carbon sugar
Murorotation	Conversion of a sugar to an aldehyde or a ketone by removal of a blocking group, particularly with an acid or base.
Oligosacchrides	A molecule more than 3 and typically less than 12 monosacchride units long
Pentoses	A 5 carbon sugar
Polysacchrides	A molecule many monosacchride units long

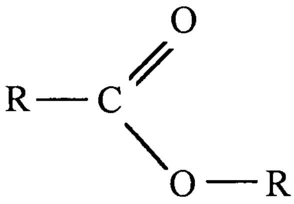
Chemical Group Structures


Aldehydes

Ketones

Figure B.1, Chemical group structures

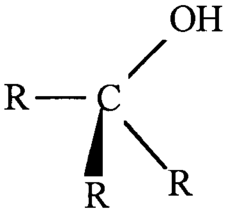
Ester linkage



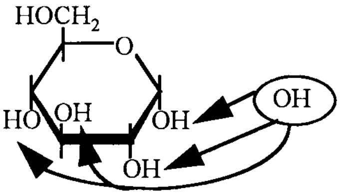
Ether linkage

R — O — R

Alcohol

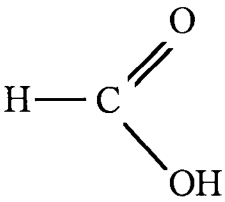


Glycoside hydroxyl group



Carboxylic acids

Formic acid



Levulinic acid

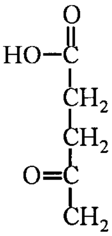
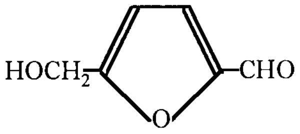


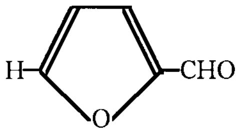
Figure B.1, Chemical group structures (Continued)

Furans

Hydroxyl Methyl Furfural (HMF),

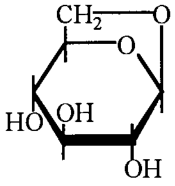


Furfural



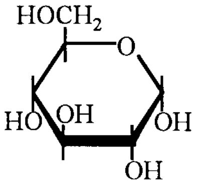
Expoxides

Levoglucosan, (anhydro-β-D-glucopyranose)



Monosacchrides

Glucose



Polysacchrides

Cellulose

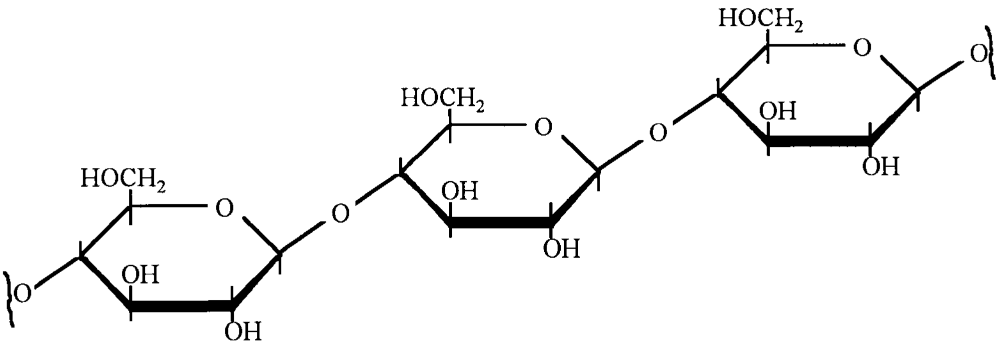


Figure B.1, Chemical group structures (Continued)

Appendix C, Process Mass Balance

A process flow sheet is shown in figure 2.2.1. This process has been fabricated to utilize the resources of a fictitious paper plant. The reactant is assumed to be rejected fiber reduced to 150% water. Waste heat was assumed available to heat ambient air to 110°C. Different assumptions could be made to adapted this process for other various situations. The equipment is listed in table 2.2.1. Possible stream flow rates are listed in table C.1.

Ambient air was taken as 50% humid air at 20°C. The reactor was taken to run as a counter current forced convection moving packed bed. Adiabatic saturation to 50% relative humidity was assumed for the reaction. The same assumptions were made for the solid drier. The air mass and energy consumption were calculated from these assumptions. The flow composition were calculated from experimental data.

The equipment selection is as follows. The evaporative moisture removal and the size reduction equipment was not used for this case. The acid/organic recovery and the phase separation systems were not considered here due to insufficient information. Data like the types of organics and acid mist size are necessary information for this design. The acid bleed was assumed zero because this will depend on the quality of the starting material, the acid, and the water. Counter current moving packed bed designs are a possibility for the gas solid contactor, the reactor and the moisture removal equipment. The solid acid addition step would include a mechanical device that would physically remove excess moisture. The acid recovery system is a counter current leaching process.

Stream	Temperature	Carbohydrate	Product	Water	Acid	Organic/Inorgani	Air
1	20	100	0	150	0	0	0
2	20	100	0	150	0	0	0
3	20	100	0	170	3	0	0
4	20	100	0	100	0	0	0
5	28	100	0	13	0	0	0
6	20	100	0	70	30	0	0
7	20	100	0	70	30	0	0
8	110	0	60	0	27	0	0
9	20	0	60	60	1.3	0	0
10	110	0	0	29.4	0	0	3674
11	47	0	0	128.7	3	11	3674
12	47	0	0	108.7	0	11	3674
13	47	0	0	108.7	0	0	3674
14	20	0	0	0	0	11	0
15	20	0	0	0	0	11	0
16	20	0	0	0	0	0	0
17	20	0	0	500	0	0	0
18	20	0	0	570	3	0	0
19	20	0	0	117	0	0	0
20	20	0	0	57	25.	0	0
21	20 to 40	0	0	0	0	0	0
22	NA	0	0	57	25.	0	0
23	NA	0	0	0	0	0	0
24	20	0	0	570	3	0	0
25	20	0	0	0.33	4.6	0	0
26	110	0	0	25.7	0	0	3222
27	47	0	0	112.7	0	0	3222

Table C.1, Process Mass Balance

Appendix D, Experimental Data

The data in table D.3 is composed of many different experiments from different materials and different reaction methods. The materials for each experiment are identified my a material code defined in table D.1. The reaction methods are identified by a reaction method code in table D.2.

Material Code	Material
1	Paper Towel
2	Old Corn Cob
3	Fresh Corn Cob
4	Sugar Beets
5	α Cellulose
6	Pulp, Short Fiber
7	Pulp, Bleached Chip Paper
8	Cotton Paper
9	Sucrose

Table D.1, Material Code Identification

Reaction Method Code	Reactor Place
1	Natural Convection Oven
2	Reactor
3	Forced Convection Oven
4	Packed Bed
5	Vacuum Oven
6	Vacuum followed by Forced Convection Oven
7	Microwave
8	Beaker

Table D.2, Reaction Method Code Identification

Exp #	Material Code	Reaction Method Code	Material Weight (g)	Ageing Time (hrs)	H_2SO_4 Concentration (w fraction)	Damp Weight (g)	Weight at time of Reaction (g)	Rxn Temp (°C)	Rxn Time (min)	Final Weight (g)	H_2SO_4 Equ. Spent (% inital)	Weight Change (% inital)	Acid eq/ Hexose
1	1	1	2.84	0	0.27	6.73	6.73	102	165	na	na		1.24
2	1	1	2.85	0	0.27	6.72	6.72	102	240	na	29.04	na	1.23
3	1	1	2.89	0	0.27	7.11	7.11	102	360	na	na	na	1.32
4	1	1	2.87	0	0.27	6.82	6.82	102	1560	na	19.66	na	1.24
5	1	1	2.92	0	0.27	6.83	6.83	97	50	na	21.27	na	1.21
6	1	1	2.93	0	0.27	6.76	6.76	97	70	na	10.24	na	1.18
7	1	1	2.88	0	0.27	6.81	6.81	97	90	na	14.43	na	1.23
8	1	1	2.90	0	0.27	6.76	6.76	97	50	na	10.21	na	1.20
9	1	1	2.88	0	0.27	6.74	6.74	97	70	na	9.90	na	1.21
10	1	1	2.88	0	0.27	6.51	6.51	97	90	na	na	na	1.14
11	2	1	6.10	0	0.27	8.44	8.44	100	60	na	53.06	na	1.15
12	2	1	6.29	0	0.27	10.04	10.04	100	90	na	69.08	na	1.79
13	2	1	7.46	0	0.27	10.58	10.58	100	120	na	55.01	na	1.26
14	2	1	3.50	0	0.27	13.50	13.50	90	30	na	na	na	8.60
15	2	1	3.79	0	0.27	14.43	14.43	90	60	na	18.56	na	8.45
30	2	1	6.84	0	0.07	14.55	14.55	100	105	na	7.58	na	0.38
32	2	1	5.92	0	0.07	12.84	12.84	100	205	na	15.18	na	0.39
25	3	1	3.95	0	0.07	8.81	8.81	100	105	na	10.35	na	0.41
26	3	1	4.10	0	0.07	9.38	9.38	100	205	na	10.20	na	0.43
28	3	1	4.08	0	0.07	10.85	10.85	100	205	na	18.22	na	0.55
29	3	1	4.03	0	0.07	8.24	8.24	100	105	na	na	na	0.35
30	3	1	4.11	0	0.07	7.74	7.74	100	205	na	na	na	0.29
33	3	2	11.61	0	0.07	49.55	49.55	108	240	na	na	na	na

Table D.3, Experimental Data

Exp #	Material Code	Reaction Method Code	Material Weight (g)	Ageing Time (hrs)	H_2SO_4 Concentration (w fraction)	Damp Weight (g)	Weight at time of Reaction (g)	Rxn Temp (°C)	Rxn Time (min)	Final Weight (g)	H_2SO_4 Equ. Spent (% inital)	Weight Change (% inital)	Acid eq/ Hexose
35	3	2	5.04	0	0.12	19.62	19.62	102	150	3.78	na	25.00	1.78
36	3	2	5.00	0	0.06	19.20	19.20	102	120	4	na	20.00	0.87
118	3	2	5.01	0	0.27	14.70	14.70	102	150	na	na	na	2.70
150	5	2	8.08	0	0.27	31.16	31.16	102	180	4.06	na	49.75	2.59
151	5	2	8.10	0	0.12	31.82	31.82	102	120	5.61	na	na	1.17
152	5	2	8.02	0	0.50	33.28	33.28	102	120	3.54	na	55.86	5.23
51	1	3	2.87	1032	0.28	6.48	4.57	100	330	1.91	na	33.45	1.16
53	1	3	2.92	864	0.28	6.93	4.82	100	330	1.87	na	35.96	1.27
111	1	3	2.98	0	0.28	9.92	9.92	100	60	1.698	na	43.02	2.18
112	1	3	2.86	0	0.28	8.18	8.18	100	30	1.82	na	36.36	1.74
113	1	3	2.97	0	0.28	10.38	10.38	100	70	1.766	na	40.54	2.33
114	1	3	2.91	0	0.28	9.91	9.91	100	80	1.652	na	43.23	2.25
115	1	3	2.90	0	0.28	9.43	9.43	100	90	1.779	na	38.66	2.11
116	1	3	2.92	0	0.28	9.46	9.46	100	120	1.805	na	38.18	2.10
210	1	3	2.91	12	0.29	6.39	5.53	110	15	2.03	na	30.24	1.15
211	1	3	2.88	12	0.29	6.80	5.44	110	25	1.83	na	36.46	1.31
212	1	3	2.94	12	0.29	7.19	5.75	110	48	1.86	na	36.73	1.39
213	1	3	2.96	12	0.29	6.74	5.38	110	75	1.93	na	34.80	1.22
214	1	3	2.91	12	0.29	7.01	5.52	110	130	1.89	na	35.05	1.35
215	1	3	2.95	40	0.29	6.85	5.86	110	45	1.83	na	37.97	1.27
216	1	3	2.92	40	0.29	7.08	6	110	60	1.84	na	36.99	1.37
217	1	3	2.90	40	0.29	6.77	5.78	110	75	1.84	na	36.55	1.28
218	1	3	2.87	40	0.29	6.96	5.93	110	90	1.84	na	35.89	1.37

Table D.3, Experimental Data (Continued)

Exp #	Material Code	Reaction Method Code	Material Weight (g)	Ageing Time (hrs)	H_2SO_4 Concentration (w fraction)	Damp Weight (g)	Weight at time of Reaction (g)	Rxn Temp (°C)	Rxn Time (min)	Final Weight (g)	H_2SO_4 Equ. Spent (% inital)	Weight Change (% inital)	Acid eq/ Hexose
219	1	3	2.95	40	0.29	6.82	5.83	110	120	1.82	na	38.31	1.26
225	1	3	2.99	135	0.29	6.92	5.7	110	23	1.95	0.60	34.78	1.26
226	1	3	2.93	135	0.29	6.71	5.64	110	35	1.81	2.73	38.23	1.24
227	1	3	2.91	135	0.29	6.65	5.56	110	51	1.83	12.45	37.11	1.23
228	1	3	2.93	135	0.29	6.73	5.58	110	75	1.81	19.87	38.23	1.24
229	1	3	2.94	135	0.29	6.66	5.64	110	120	1.83	27.42	37.76	1.21
230	1	3	2.98	0	0.29	6.76	6.76	110	45	1.95	na	34.56	1.22
231	1	3	2.92	0	0.29	6.62	6.62	110	65	1.87	na	35.96	1.21
232	1	3	2.95	0	0.29	6.71	6.71	110	85	1.85	na	37.29	1.22
233	1	3	2.91	0	0.29	6.42	6.42	110	120	1.84	na	36.77	1.16
234	1	3	2.95	0	0.29	6.58	6.58	110	180	1.83	na	37.97	1.18
235	1	3	2.84	18	0.29	6.87	5.73	200	15	1.7	75.77	40.14	1.36
236	1	3	2.88	18	0.29	6.82	5.67	200	30	1.65	92.71	42.71	1.31
237	1	3	2.87	18	0.29	6.86	5.73	200	47	1.61	95.68	43.90	1.33
238	1	3	2.87	18	0.29	7.02	5.9	200	61	1.61	95.85	43.90	1.39
239	1	3	2.86	18	0.29	6.77	5.72	200	104	1.58	95.59	44.76	1.31
240	1	3	2.81	66	0.29	8.97	8.97	110	20	1.59	na	43.42	2.10
241	1	3	2.80	66	0.29	9.02	9.02	110	35	1.58	1.17	43.57	2.13
242	1	3	2.85	66	0.29	8.92	8.92	110	55	1.69	11.98	40.70	2.04
243	1	3	2.84	66	0.29	9.03	9.03	110	80	1.73	19.26	39.08	2.09
244	1	3	2.86	66	0.29	8.96	8.96	110	95	1.71	24.66	40.21	2.04
245	1	3	2.82	68	0.29	9.07	6.85	160	20	1.65	30.14	41.49	2.12
246	1	3	2.86	68	0.29	9.02	6.95	160	30	1.71	67.36	40.21	2.07

Table D.3, Experimental Data (Continued)

Exp #	Material Code	Reaction Method Code	Material Weight (g)	Ageing Time (hrs)	H_2SO_4 Concentration (w fraction)	Damp Weight (g)	Weight at time of Reaction (g)	Rxn Temp (°C)	Rxn Time (min)	Final Weight (g)	H_2SO_4 Equ. Spent (% inital)	Weight Change (% inital)	Acid eq/ Hexose
247	1	3	2.84	68	0.29	9.01	6.86	160	50	1.66	82.31	41.55	2.08
248	1	3	2.85	68	0.29	8.97	6.92	160	65	1.68	84.98	41.05	2.06
249	1	3	2.84	68	0.29	9.03	6.94	160	95	1.63	87.93	42.61	2.09
280	1	3	3.02	0	0.29	7.53	7.53	110	32	na	0.64	na	1.43
281	1	3	3.03	0	0.29	7.53	7.53	110	42	na	10.64	na	1.42
282	1	3	3.04	0	0.29	7.05	7.05	110	57	na	14.04	na	1.26
283	1	3	3.01	0	0.29	7.62	7.62	110	77	na	26.48	na	1.47
284	1	3	3.02	0	0.29	7.50	7.5	110	122	na	30.75	na	1.42
360	1	3	2.81	0	0.32	5.60	5.6	110	1440	na	na	na	1.05
361	1	3	2.82	0	0.32	5.60	5.6	110	1440	na	na	na	1.04
101	3	3	2.05	336	0.12	7.87	3.68	100	120	1.758	na	14.24	1.75
102	3	3	1.71	336	0.12	4.99	2.339	100	120	1.27	na	25.73	1.18
120	4	3	3.01	0	0.07	13.08	13.08	110	105	2.22	na	26.25	0.92
121	4	3	2.99	0	0.12	12.85	12.85	110	105	2.12	na	29.10	1.68
122	4	3	3.00	0	0.27	12.86	12.86	110	105	1.89	na	37.00	3.79
130	4	3	4.99	528	0.07	22.19	22.19	110	120	3.37	20.28	32.46	0.95
131	4	3	5.01	528	0.12	20.94	20.94	110	120	3.24	73.33	35.33	1.62
132	4	3	5.01	528	0.27	20.02	20.02	110	120	2.93	61.84	41.52	3.47
133	4	3	7.52	0	0.07	27.28	27.28	110	120	na	16.34	na	0.72
134	4	3	5.47	0	0.12	21.34	21.34	110	120	3.98	70.85	27.24	1.48
135	4	3	5.57	0	0.27	25.55	25.55	110	120	2.89	6.82	48.11	4.15
160	6	3	7.24	0	0.27	19.13	19.13	110	120	4.93	5.79	31.91	1.98
161	7	3	9.43	0	0.27	28.13	28.13	110	120	5.67	na	39.87	1.80

Table D.3, Experimental Data (Continued)

Exp #	Material Code	Reaction Method Code	Material Weight (g)	Ageing Time (hrs)	H_2SO_4 Concentration (w fraction)	Damp Weight (g)	Weight at time of Reaction (g)	Rxn Temp (°C)	Rxn Time (min)	Final Weight (g)	H_2SO_4 Equ. Spent (% inital)	Weight Change (% inital)	Acid eq/ Hexose
199	7	3	45.60	0	0.27	136.76	136.76	110	120	26.35	na	42.21	1.80
290	8	3	5.24	0	0.29	14.18	14.18	110	65	3.31	19.68	36.83	1.64
200	7	4	48.66	0	0.29	113.12	113.12	110	120	26.31	3.66	45.93	1.30
201	7	4	46.39	408	0.29	114.87	91.49	115	92	27.96	28.03	39.73	1.44
220	7	4	173.00	432	0.23	408.07	282.94	115	130	111.19	na	35.73	1.01
221	7	4	178.49	456	0.23	437.20	290.62	115	180	111.49	15.59	37.54	1.08
222	7	4	182.32	384	0.22	456.95	289	115	155	92	33.19	49.54	1.11
223	7	4	178.77	408	0.22	464.51	280.3	115	na	99.54	25.81	44.32	1.18
271	1	5	2.84	0	0.50	7.41	7.41	160	30	1.69	31.46	40.49	2.66
272	1	5	2.89	0	0.29	7.15	7.15	160	30	1.73	11.00	40.14	1.41
251	1	6	2.82	0	0.29	7.08	4.35	110	15	1.86	2.90	34.04	1.45
252	1	6	2.84	0	0.29	7.11	4.37	110	34	1.83	16.59	35.56	1.44
256	5	6	3.00	0	0.12	13.00	4.93	110	25	2.07	na	31.00	1.32
250	7	6	31.14	240	0.23	86.79	43.37	110	80	15.54	15.57	50.10	1.33
253	7	6	4.55	0	0.22	11.53	6.55	110	104	2.94	13.30	35.38	1.13
355-35	1	7	8.47	0				high		5.15	na	39.20	0.00
300	1	7	2.85	0	0.29	7.87	7.87	high	2	1.7	61.09	40.35	1.69
301	1	7	2.83	0	0.29	7.78	7.78	high	3.5	1.67	65.18	40.99	1.68
302	1	7	2.83	0	0.29	7.79	7.79	high	3.5	1.66	64.09	41.34	1.68
309	1	7	2.83	0	0.34	7.97	7.97	high	3.5	1.6	74.18	43.46	2.04
310	1	7	2.80	0	0.50	8.62	8.62	high	3.5	1.52	87.98	45.71	3.44
311	1	7	2.82	0	0.50	7.44	7.44	high	3	1.56	89.18	44.68	2.71
317	1	7	2.87	72	0.50	9.36	8.17	high	3.5	1.53	65.09	46.69	3.74

Table D.3, Experimental Data (Continued)

Exp #	Material Code	Reaction Method Code	Material Weight (g)	Ageing Time (hrs)	H_2SO_4 Concentration (w fraction)	Damp Weight (g)	Weight at time of Reaction (g)	Rxn Temp (°C)	Rxn Time (min)	Final Weight (g)	H_2SO_4 Equ. Spent (% inital)	Weight Change (% inital)	Acid eq/ Hexose
318	1	7	2.84	72	0.50	8.97	7.69	high	3.5	1.51	37.49	46.83	3.57
319	1	7	2.88	72	0.50	9.14	7.19	high	3.5	na	na	na	3.59
351	1	7	1.81	0	0.27	4.00	4	high	na	na	na	na	1.08
355	1	7	2.81	0	0.29	5.81	5.81	high	2	na	na	na	1.01
356	1	7	2.84	0	0.29	5.86	5.86	high	2	na	na	na	1.00
357	1	7	2.82	0	0.29	5.90	5.9	high	2	na	na	na	1.03
307	5	7	3.52	0	0.29	15.74	15.74	high	3.5	1.76	71.32	46.58	3.57
308	5	7	6.45	0	0.29	26.56	26.56	high	4.75	3.31	78.29	45.17	3.21
315	5	7	1.81	0	0.50	5.94	5.94	high	3.5	1	40.30	44.75	3.79
316	5	7	1.87	72	0.50	5.53	4.78	high	7	0.91	33.54	51.34	3.25
353	5	7	1.00	0	0.12	3.75	3.75	high	3	na	na	na	1.10
354	5	7	2.00	0	0.18	9.20	9.2	high	4	1.14	na	43.00	2.17
303	7	7	5.68	0	0.29	14.09	14.09	high	3	2.99	71.31	43.15	1.53
304	7	7	5.91	0	0.50	17.19	17.19	high	2.5	2.97	80.80	45.73	3.41
306	7	7	9.30	0	0.29	30.75	30.75	high	4	4.7	79.11	44.55	2.43
320	5	8	3.31	0	0.93	na	na	15°C	1440	0.64	na	80.49	na
321	5	8	6.01	0	0.93	na	na	70°C	20	3.13	na	47.92	na
340	9	8	na	0	0.97	na	na	20°C	30	na	na	na	na
341	9	8	na	0	0.97	na	na	70°C	15	na	na	na	na

Table D.3, Experimental Data (Continued)