# Acid Catalyzed Conversion of Lignocellulosic Biomass into Biofuels and Biochemicals

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# ABSTRACT

## Acid Catalyzed Conversion of Lignocellulosic Biomass into Biofuels and Biochemicals

Dora Petraccone

Lignocellulosic biomass shows great potential as a candidate for replacing fossil fuels as an energy source. Research is currently investigating conversion processes for production of fuels and chemicals derived from renewable energy sources such as lignocellulose. However, high product yields are difficult to attain. The structural and chemical complexity of the plant cell wall make it quite resistant to chemical attack. Thus, in order to gain a more fundamental understanding of its reactivity, various biomass feedstock are subjected to reactions within a one-pot system while varying parameters including temperature, reaction time, and catalyst acidity.

The current study is focused on the development and optimization of the acid-catalyzed conversion of lignocellulosic biomass; AC3B process. Addition of an oxidizing agent along with an acid catalyst indicated evident change in the degradation of the lignocellulosic materials. Such oxidative cracking resulted in significant increases in yield of the main products: ethyl levulinate, ethyl formate, and ethyl acetate. In fact, an overall yield of 70 wt% has been achieved. This conversion level can be attained because our process has been shown to derive products from all the structural constituents (cellulose, hemicellulose, and lignin). This will allow future efforts to focus on further refining of the AC3B process in an attempt to obtain optimal yields of these desired products.

# Acknowledgements

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# Chapter 1. Introduction and Literature Review

The aim of this work is to develop and partially optimize the acid-catalyzed conversion of lignocellulosic biomass (AC3B) process in order to propose it as an alternative to current energy sources in the medium to long term. This section provides a general overview of the supply and demand of energy within industrialized societies. A relatively small portion of our current energy supply arises from renewable sources [1, 2]. Generally, the majority of our sources of energy is used in one of two ways, first, as a source of fuel or to give rise to an energy carrier and, second, as a means of producing chemicals. That is, while primary energy sources such as a coal is often used to produce electricity, the petrochemical industry produces large amounts of chemicals that are used in a large variety of products [3].

According to the U.S. Energy Information Administration (EIA), as of 2008 the global demand for energy stands at approximately 504.7 quadrillion British thermal units (Btu), a figure that is projected to increase to 769.8 quadrillion Btu by 2035. By consequence, it is almost certain that this increased demand will lead to greater consumption of all current sources of energy. Figure 1-1 [1] illustrates the projected increase in terms of it's constituent energy sources.

Currently, renewable energy is a rapid growing source of energy and this trend is poised to continue for the coming decades. In light of issues such as global warming and energy security from the use of fossil fuels, many governments have started to work towards formulating policy and invest in research in order to facilitate the developments and implementation of renewable energy technologies [2, 4].

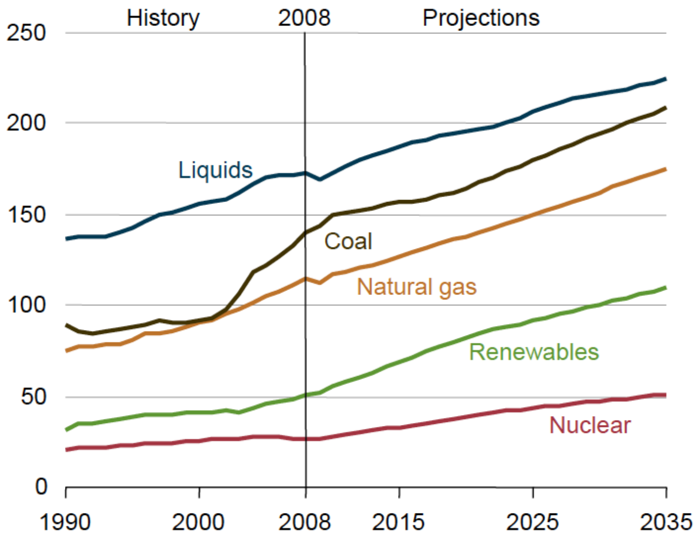


**Figure 1-1. World energy consumption by fuel types, 1990 to 2035 (quadrillion Btu)**

## *1.1. The Problems with Fossil Fuels as an Energy Source*

Recently, the severity of societal dependency on fossil fuels as a principal energy source has been increasingly recognized. According to the International Energy Agency [5], more than 80% of the current global energy supply comes from fossil fuels or, more precisely, from natural gas, coal, and crude oil. As shown in figure 1-2, only a relatively small percentage of the current energy supply originates from renewable resources.

While fossil fuels make up the dominant share of energy consumption, the use of fossil fuels is entwined with important drawbacks. Namely, a finite supply, complex geopolitical concerns, as well as known environmental issues. Though understood for some time, most nations are becoming increasingly aware of the depleting availability and decreasing reserves of fossil fuels. This fuel source is considered non-renewable since its consumption is significantly more rapid compared to the rate of formation and thus cannot be readily renewed. Research by Demirbas [6], predicts that peak oil production will be reached by the year 2015 and will continue to decrease as a function of oil supply. While this peak is illustrated in figure 1-3, if this prediction is accurate, it would imply that oil production would be exhausted within less than one century.

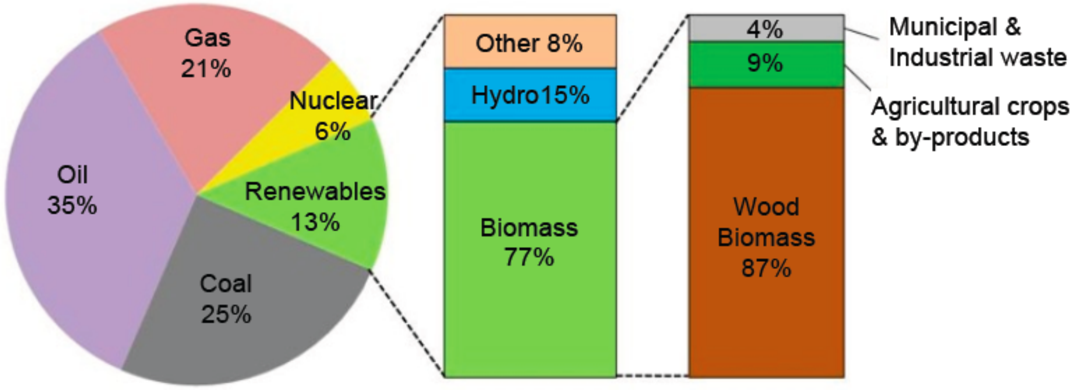


**Figure 1-2. Status of current global energy supply [5]**

It is worth briefly mentioning that decreasing oil reserves will increase carbon dioxide emissions in at least two ways. First, as underground oil reservoirs are being depleted, oil producers will come to rely more heavily on other sources such as tar sands or oil shale. Processing these energy sources requires a greater energy investment and therefore results in greater carbon dioxide emissions [7]. Second, as the supply of oil decreases, alternate sources of energy, such as coal, will step in to fill the void. This will likely be the case in countries such as the United States, Russia and China, which hold the largest recoverable coal reserves [1].

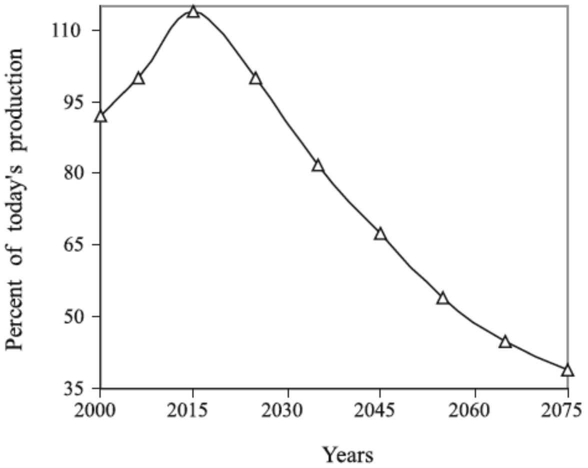


**Figure 1-3. Projected oil production**

Geopolitical concerns are yet another important facet of our current energy supply. Given that the study of how energy supply and infrastructure is related to politics and political systems is beyond the scope of this work, only a brief treatment of this issue is given here. Interruptions to oil supply can arise from a number of factors including political instability of oil producing nations, natural disasters or trade embargos. On a related but separate note, the Organization of the Petroleum Exporting Countries (OPEC) professes holding more than 80% of crude oil reserves [8]. These disproportionate holdings, as well as their coordinated rate of their extraction and supply to the market, form the basis of this oligopoly. While there are certainly significant socio-economic and political factors to consider, the geographic localization of fossil fuels in certain regions have caused many governments to become preoccupied with energy security.

Global warming may very well become one of the central issues that result in defining our current generation. The anthropogenic emissions of GHGs have a significant impact on global temperature [9]. The build up of gases such as carbon dioxide and methane in the earth's atmosphere leads to the capture of increasing amounts of heat. In other words, as sun light warms up the earth's surface, some of the build up of thermal energy is reemitted into the atmosphere. Instead of being emitted back out into space an increasing proportion of this radiation is absorbed by GHGs, thus causing an increase in global temperature. As will be seen, over time, this increase has a variety of important negative impacts. The past decades have seen increasing levels of carbon dioxide emissions. In fact, according to figure 1-4, the years between 1970 and 2004 have shown a 70% increase in GHG emissions. For example, during this time the level of carbon dioxide, as opposed to GHG in general, has increased from approximately 21 to 38 gigatonnes respectively; an increase of approximately 80% [9].

Though these increased emissions are alarming, what Figure 1-4 does not convey is the increased rate of emissions during recent years. That is, the average increase of carbon dioxide equivalent ($CO_2$-equ) emissions stood at 0.43 gigatonnes (Gt) of $CO_2$-equ per year between the 1970's and 1994. However, during the following decade, 1995 to 2004, this rate increased more than two fold to approximately 0.92 $GtCO_2$ per year [9]. Clearly, with increased industrialization in many countries around the world, and specifically in Asia, this trend seems unlikely to abate in the near future.

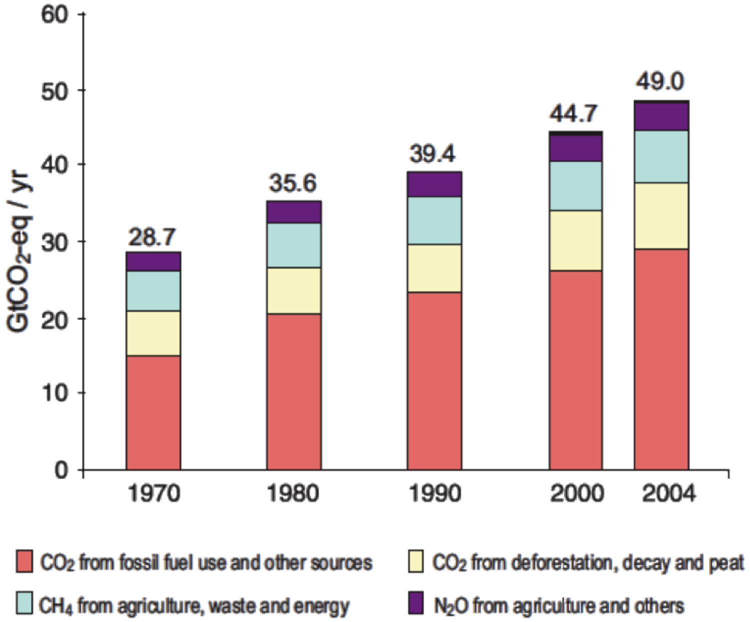


**Figure 1-4. World-wide human related GHG emissions – 1970 to 2004 [modified from 9]**

A variety of impacts are projected to arise due to the increasing levels of green house gases. The severity of most of these consequences will be proportional to the increase in global temperature. Figure 1-5 [9], provides a brief overview of the categories and extent of a variety of impacts that are expected to arise as global temperature progressively rises. Among others, changes within the water cycle will have a significant influence on ecosystems as well as the availability of freshwater. For example, rising temperatures will melt mountain glaciers and ultimately decrease the availability of fresh water, a resource that is increasing in demand. The extent to which these consequences will be manifested remains uncertain as it is difficult to know the degree to which global temperature will increase.

Clearly, gaining insight into the severity of how future generations will be impacted by increased temperatures is no easy task. Presently, in so far as the use of fossil fuels is poised to increase, the challenge of managing global GHG emissions seems to be an uphill battle. Considering the negative outcomes mentioned, i.e., depleting reserves, geopolitical issues, and environmental factors, it becomes evident that the compromises associated with the use of fossil fuels are rising incrementally. This situation underscores the pressing need for technological innovation that aims to reduce our dependency on fossil fuels, such as the AC3B process or other renewable technologies.

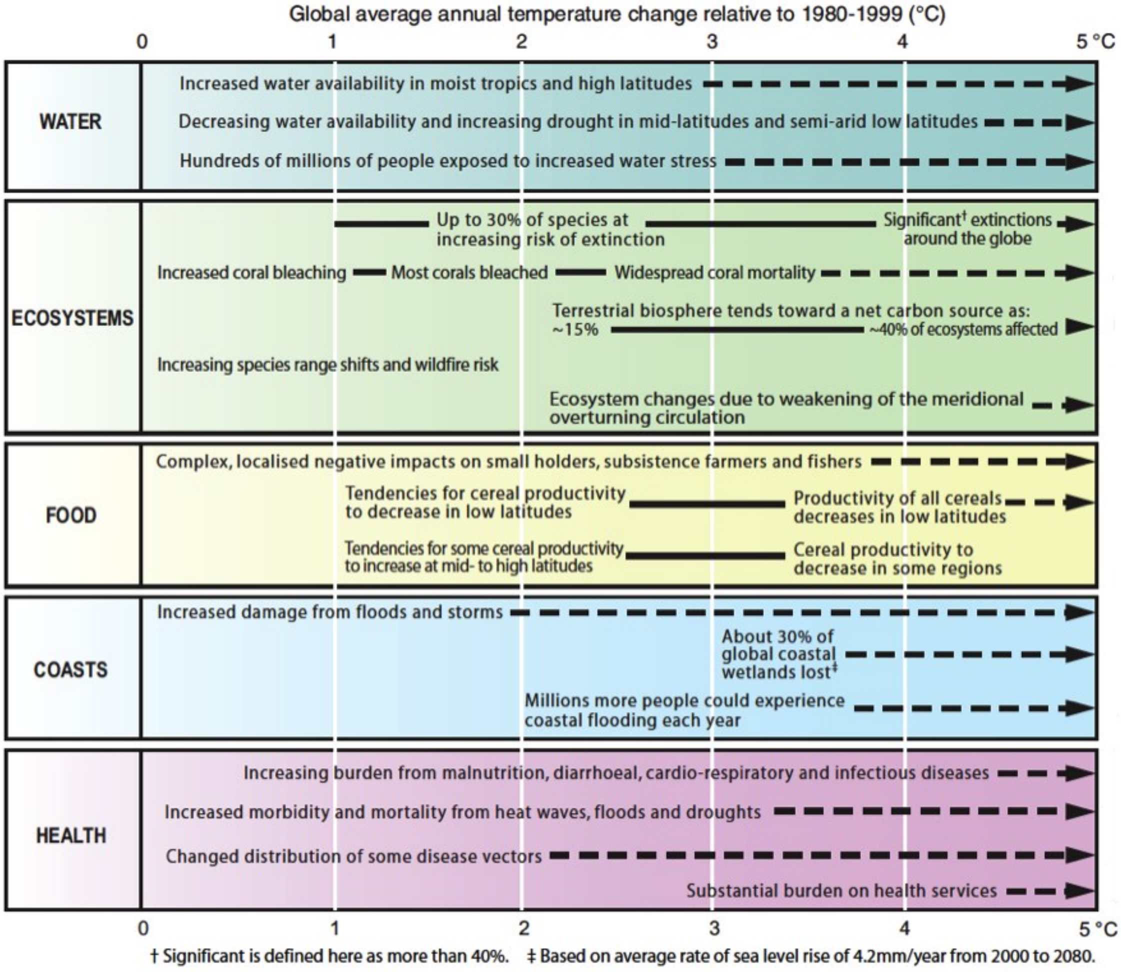


**Figure 1-5. Global average temperature change**

## 1.2. The Advantages of Biomass as an Energy Source

The problems previously presented have motivated many researchers to exert considerable effort and dedication to finding lasting solutions to energy demand that avoid, or at least minimize, the impacts previously discussed. In this light, biomass holds great potential and has spurred on a substantial research effort in the production of fuels and chemicals [10-12]. Biomass is organic material that can be used as a source of fuel, this includes forestry and agricultural crops as well as sewage and municipal waste. Examples of the various types of biomass are illustrated in figure 1-6 [13].

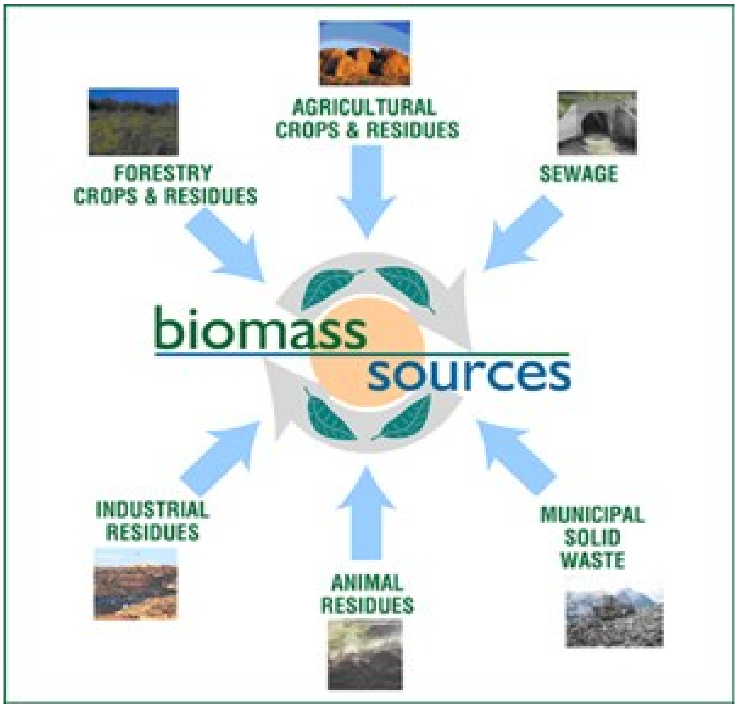


**Figure 1-6. The various types of biomass [13]**

Research into the development of biomass as an alternative to, and potential replacement for, non-renewable energy sources is justified by numerous considerations [6]. First, biomass is considered to exist in abundance and can be renewed within a relatively short time period. Thus, it is reasonable to presume that this resource could be exploited at sustainable rates at some point in the future, thus providing a stable and lasting energy source. Second, biomass can provide important environmental advantages over many non-renewables. If used sustainably, net GHG emissions could be significantly reduced as the carbon dioxide produced by processing or combusting biomass can be re-sequestered by new plant growth.

Biomass and fossil fuels also differ in their chemical properties and composition. Fossil fuels are composed of complex mixtures of mainly alkane and aromatic compounds [6]. Though biomass is often, if not always, characterized by a functional biological structure, it also differs in its typical chemical composition. The oxygen content of biomass ranges from 10-44% [6], while fossil fuels essentially do not contain any. In terms of fuel consumption, an advantage of this increased oxygen content is a ‘cleaner burning’ of fuels derived from this source. An important drawback of using fossil fuels is that carbon monoxide is produced through incomplete combustion. Therefore having more oxygen in the fuel would lead to the production of more carbon dioxide and a corresponding decrease of carbon monoxide. Furthermore, replacing fossil fuels with biomass as a fuel source can reduce the production of detrimental gases such as sulfur oxides and nitrogen oxides which are important contributors to the occurrence of acid rain [14].

While research is ongoing, processes under development are required to be economically feasible, i.e. be a viable competitor to other energy sources currently on the market. Another criteria that should be considered is the versatility of the technology with respect to the variety of feedstocks that can be processed. As will be seen, biomass exists in a wide variety of chemical forms that often react differently under similar conditions.

## *1.3. Literature Review*

### 1.3.1. Evolution of Biofuel Generations

Biomass can be classified into various 'generations' of biofuels according to the feedstock used. First generation biofuels are made from agricultural crops using conventional production techniques. Bioethanol is obtained by the fermentation of corn (starch), sugarcane, and sugar beet (sucrose) crops. Unlike cellulose (see section 1.3.2.1), starch possesses $\alpha$-linkages which produces branching of the chains that does not allow for a high degree of H-bonding [15]. Thus this nature of starch facilitates its reactivity and can be easily hydrolysable. Presently, the USA is the largest producer of bioethanol from corn with a production of 19.8 billion L/year [16]. Unfortunately much wastewater is produced at about four times the amount of bioethanol [17]. Soybean, rapeseed, sunflower and other vegetable oils can also be converted to their methyl esters for biodiesel production via transesterification process. The use of first generation biofuels give rise to some major disadvantages. First, important ethical issues arise from the fact that the feedstock used is also used to nourish humans and livestock. Thus, competition for food sources raises their relative prices making it more difficult for poorer demographics to obtain. Also, the fertile soil available to grow many of these crops is limited. The marginal reduction of carbon dioxide emissions is another important limitation, this is due to the high energy input needed for crop maintenance, such as the addition of fertilizers, pesticides, harvesting, etc. [16]. Produced by the US Department of Energy, the histogram below (figure 1-7 [18]) depicts the reduction of GHGs in relation to gasoline from fossil fuels. Taking into account the complete life cycle, bioethanol from corn does not offer such a great advantage in terms of GHG emissions, with a reduction ranging between 19% and 52% [18].

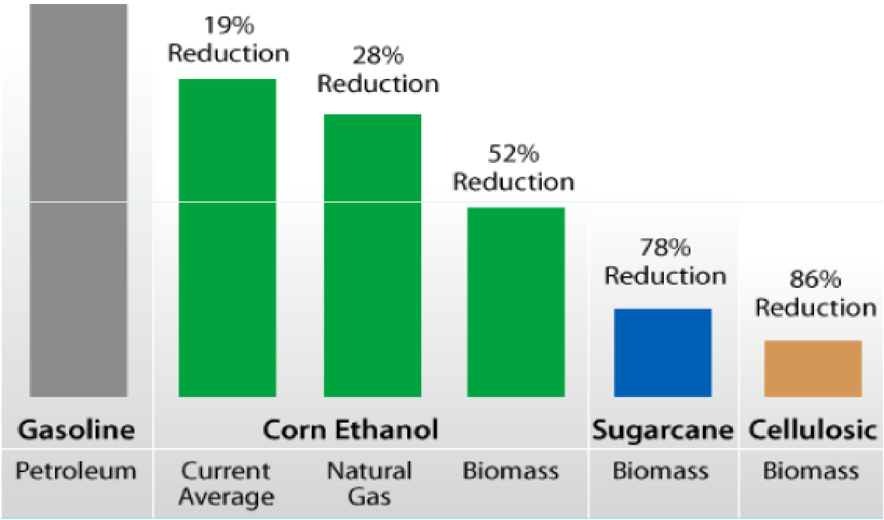


**Figure 1-7. GHG emissions using various energy sources**

Second generation biofuels utilize lignocellulosic biomass for ethanol production thus avoiding the ethical issues presented by the first generation, i.e. competing with food supply. The conversion process uses an intermediate process known as pretreatment before subjecting the material to fermentation. An example of this pretreatment step involves hydrolyzing the biomass with an acid in order to facilitate the fermentation process. This additional step is required due to the rigidity of the cellulose structure as well as the presence of undesired lignin. A limitation of lignocellulosic materials is that lignin is considered non-fermentable and, thus, constitutes a major byproduct when biological approaches are employed. The wastewater produced through fermentation of lignocellulosic biomass ranges from nine to ten times the amount of ethanol produced [17]. However, referring to figure 1-7, relative to gasoline, lignocellulosic biomass can emit approximately 86% less of green house gases, this constitutes an important advantage over first generation biofuels. In terms of the conversion processes, third generation biofuels are similar to that of second generation. What differs is that algae is used as the fuel source. Algae is a fast growing plant, where harvesting can occur multiple times in a year, the fuel produced from algae is 15-300 times higher of oil than previous crops mentioned [19]. The difficulty arises in trying to find a strain of algae with high lipid content that is easily grown and harvested in a cost-effective manner [17]. Finally, fourth generation biofuels are distinct from previous generations in that the processes used are novel [20]. This includes processes such as thermo-chemical and chemo-catalytical processes, the later is used in our laboratory and is discussed further in section 1.3.3. Briefly, there are three main thermo-chemical processes; combustion, gasification, and pyrolysis. Thermo-chemical processes require more energy relative to chemo-catalytic processes since the biomass is exposed to extremely high temperatures (above 500°C) [21]. The advancement of these fuel generations has allowed for significant breakthroughs, however, much work is needed to further develop a process which is both environmentally and economically sustainable.

### 1.3.2. Components and Structure of Lignocellulosic Biomass

During photosynthesis of biomass, the energy from sunlight is stored as chemical bonds between the carbon, hydrogen and oxygen molecules. When these chemical bonds are broken by various chemical or biological processes, the stored chemical energy can be released [22]. In order to improve energy sustainability, current research is investigating how to harness the energy stored within these bonds in the most efficient and economic way.

This section conveys information pertaining to both the chemical nature of the three main constituents of biomass as well as the overall structure of the cell wall. More specifically, the structural components of biomass, cellulose, hemicellulose and lignin, are the primary compounds of interest. Due to their composition and abundance, these three components contain the bulk of the chemical energy available for conversion. Although the relative quantities of each vary depending on the source being used, figure 1-8 [23, 24] relates the range in which these materials are typically found. These constituents are bound through covalent and non-covalent bonds forming the structure known as the plant cell wall [25].

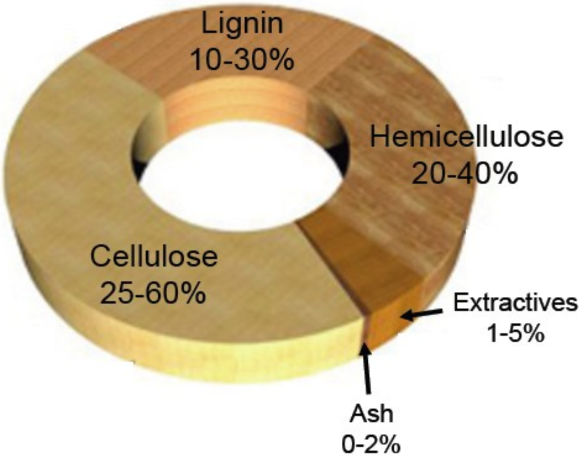


**Figure 1-8. Varying amounts of the constituents of lignocellulosic biomass**

For the purpose of this study, it is important to have some rudimentary insight into the structure of the plant cell wall. Figure 1-9 [26] provides a cross-sectional view of a typical plant cell. The cell wall can be divided into the primary and secondary walls. Woody tissues are created when multiple layers of lignin and cellulose microfibrils build up over time. While there is no lignin found in the primary cell wall, cellulose is found at lower degrees of polymerization. For example, the cellulose in cotton typically ranges from 5 000 - 7 500 glucose monomers in the primary cell wall, whereas this range increases to 10 000 - 15 000 monomer units in the secondary wall [27].

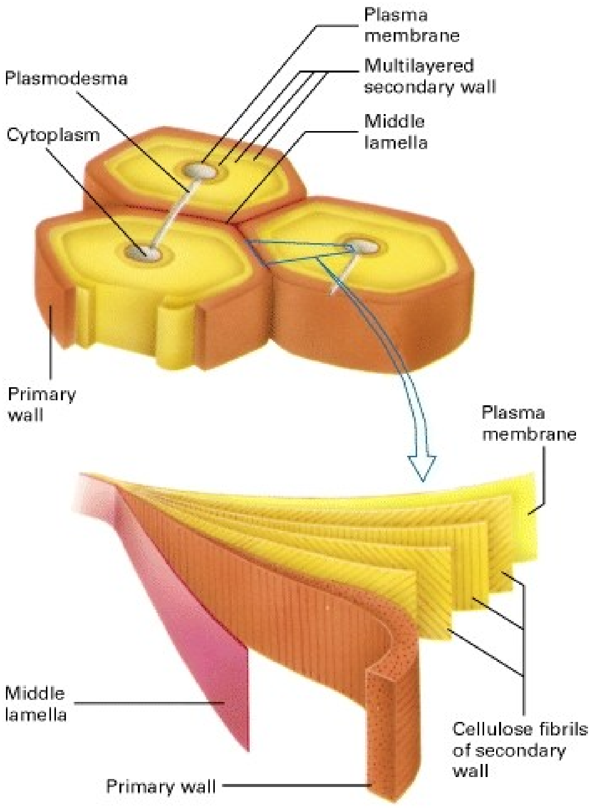


**Figure 1-9. Overview of the plant cell overall structure**

Furthermore, it is important to note that the three constituents previously mentioned intertwine to form a complex structure. Figure 1-10 [28] below provides some basic understanding of how these constituents associate with each other rendering the reactivity of the complex, as a whole, more difficult to understand. Hemicellulose ties the structure together by binding covalently to lignin and non-covalently to cellulose [22, 27]. This added complexity must be taken into account when deriving biofuels and biochemicals from biomass.

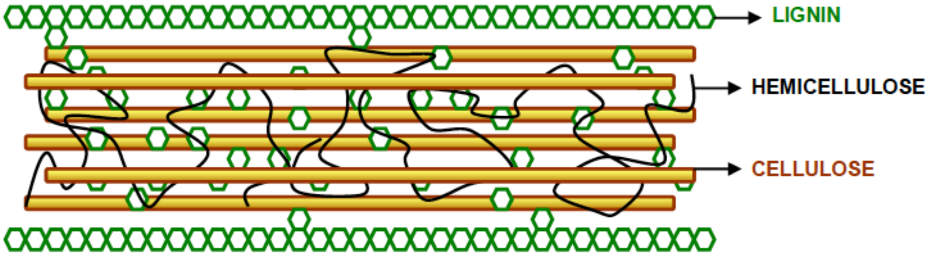


**Figure 1-10. Plant cell wall structure**

While this subsection has provided an overview of the structure of lignocellulosic biomass, the next subsections describe the chemical nature of each component. This is necessary in order to understand its reactivity and some of the current problems that research faces.

## 1.3.2.1. Cellulose

Considerable research has been exerted so as to understand the nature of cellulose, the most abundant macromolecule on earth [24, 25]. Thus, it is a reasonable candidate for producing biofuels and biochemicals. Despite its great potential as an energy source, substantial challenges remain. As will be seen, cellulose exhibits a high degree of hydrogen bonding thus forming a crystalline structure that is very stable. In order to optimally extract the energy from this molecule it is necessary to first depolymerize the cellulose fibrils. This remains a major obstacle for current research.

Cellulose has an average molecular weight of approximately 100 000 [22] and is composed solely of linear chains of D-glucopyranose monomers linked via β-(1-4)-glycosidic linkages shown in figure 1-11(a).

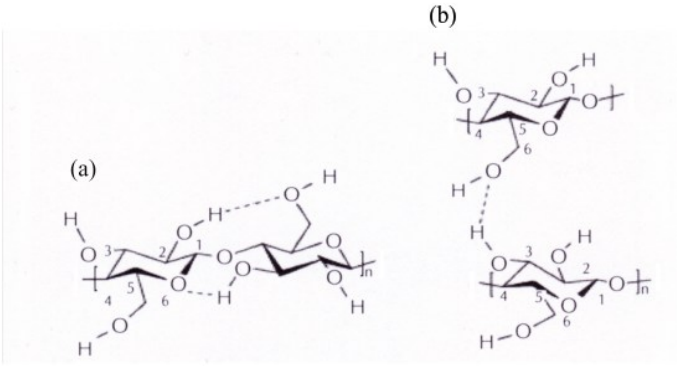


**Figure 1-11. Cellulose (a) intramolecular hydrogen bonding and (b) intermolecular hydrogen bonding [24]**

These glycosidic linkages allow for intramolecular hydrogen bonding between C2-OH, C6-OH and C3-OH with endocyclic oxygen, illustrated in figure 1-11(a). Intermolecular hydrogen bonding in Figure 1-11(b), is also illustrated between C3-OH and C6-OH. These specific bonds are key in producing a network of intermolecular hydrogen bonding of a cellulose chain within a sheet and intermolecular hydrogen bonding of the chains between sheets, in figure 1-12 below [24]. This nature of cellulose creates a highly crystalline structure resulting in fibrous arrangements. The rigid nature of cellulose makes it very resistant to enzymatic and chemical attack.

Depicted in figure 1-12, these sheets of cellulose form a crystalline net. Stacking of these sheets form elementary fibrils and, in turn, when these are combined together microfibril are formed [24]. Thus, this macromolecule exists in a vast array of sheets that ultimately forms the crystalline macromolecule. Because of this rigidity, it is well known that the major obstacles of converting lignocellulosic biomass into biofuels and biochemicals is the depolymerization of cellulose. The difficulty noticed in the literature is based on two main concepts (1) accessibility of the cellulose in relation to it being bound to the other constituents of biomass and (2) the depolymerization of the crystalline structure of cellulose [29, 30].

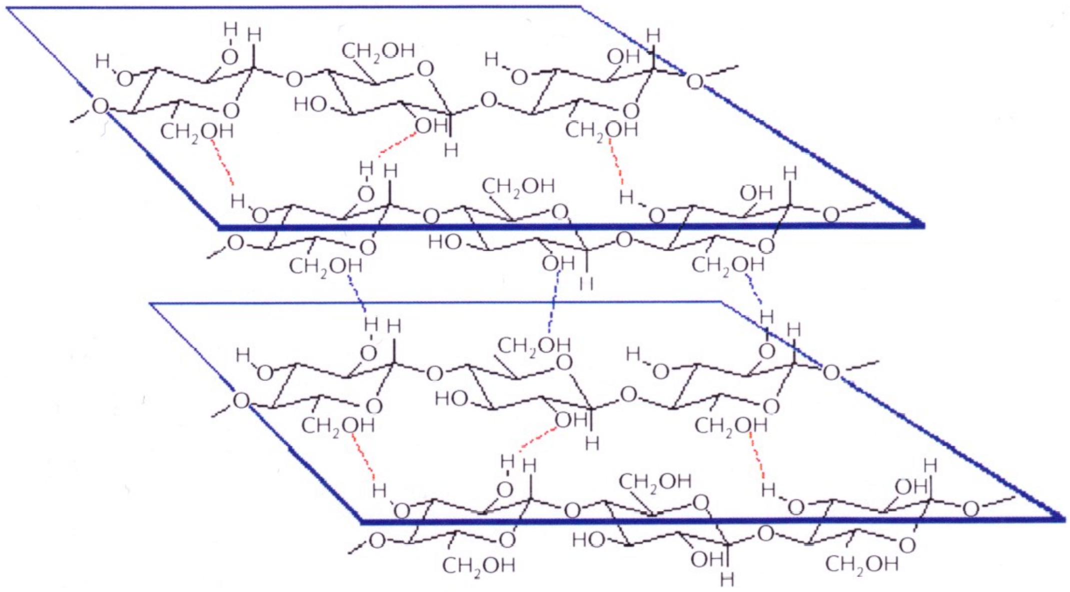


**Figure 1-12. Hydrogen bonding within and between cellulose sheets [24]**

#### 1.3.2.2. Hemicellulose

Unlike cellulose, hemicellulose is a heterogeneous polymer composed mainly of xylose but also contains other pentose (arabinose) and hexose (galactose, glucose, mannose) monosaccharides [24]. Hemicellulose has an average molecular weight of 30 000 [22] and is highly substituted with acetyl groups giving rise to monomer branching off the main chain. Figure 1-13 illustrates a representative portion of the structure of hemicellulose. This random branching results in amorphous regions that allow it to tightly bind with cellulose via hydrogen bonding [27]. Hemicellulose is also soluble in aqueous solutions, again due to its branched construction. Thus, hemicellulose is much more susceptible to chemical or enzymatic attack in comparison with cellulose.

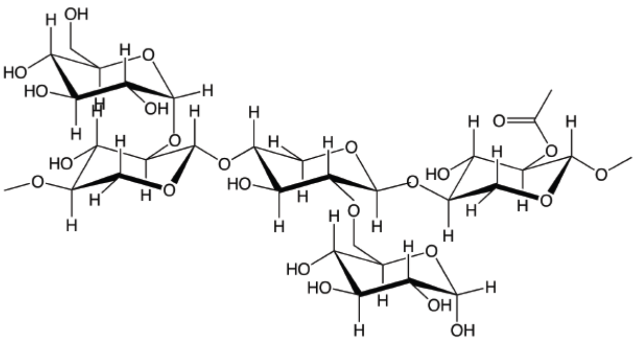


**Figure 1-13. Hemicellulose structure**

## 1.3.2.3. Lignin

The production of lignin by the plant, like cellulose, requires a large energy investment and is important in providing structural support. Furthermore, it is also an abundant molecule that is found in woody tissues [25] and the most abundant non-polysaccharide macromolecule found in nature.

It is a highly cross-linked polymer composed of phenylpropane units as shown in figure 1-14. The exact structure of lignin is unknown; literature suggests that these phenylpropane units appear in a random manner [31]. However, it is well accepted that there are three main repeating units, these are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, shown in figure 1.15 [24, 31].

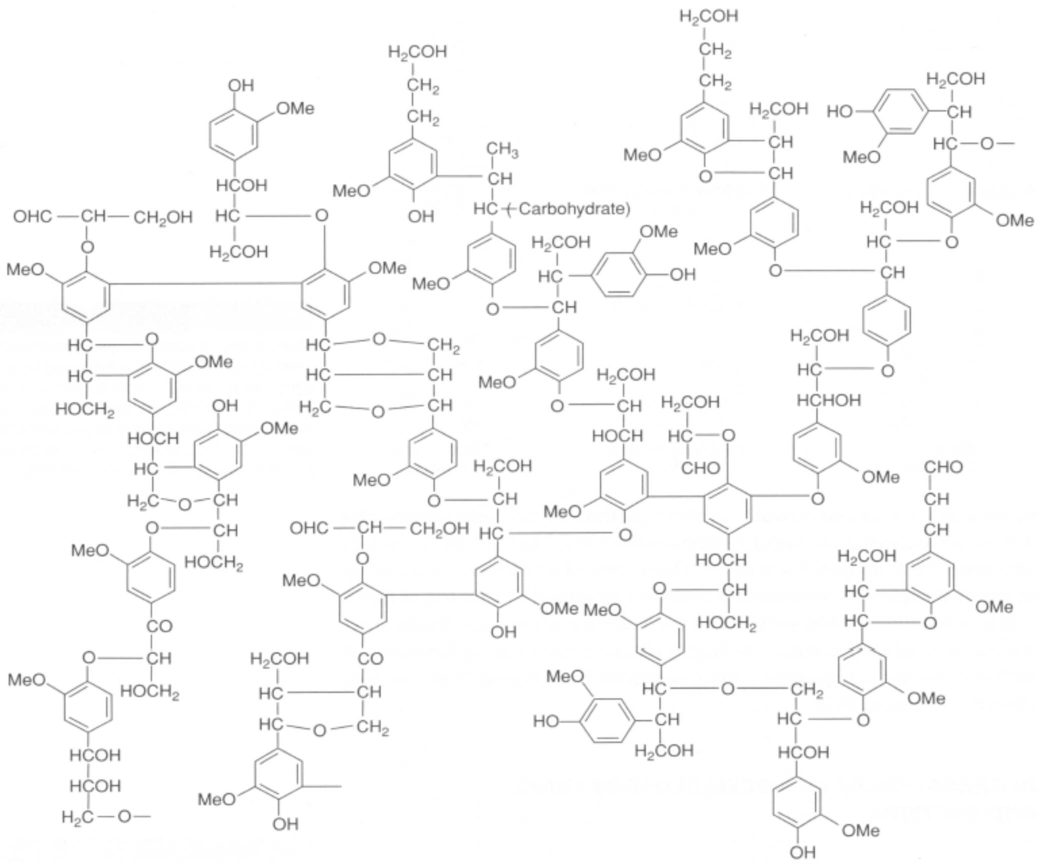
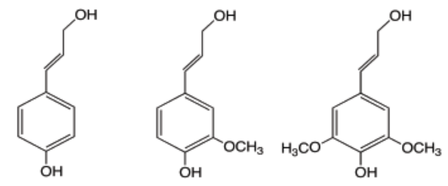


Figure 1-14. Structure of lignin [modified from 32]

At present, research focused on producing biofuels and biochemicals has primarily focused on deriving products from the holocellulose constituents, that is, cellulose and hemicellulose. Lignin is a major by-product that is mainly used in order to fuel the process.



p- Coumaryl alcohol

Coniferyl alcohol

Sinapyl alcohol

Figure 1-15. Main repeating units of lignin [24]

### 1.3.2.4. Non-Structural Components of Biomass

A small percentage, less than 5%, of the plant cell does not confer any structural strength to the plant, these are extractives and ash. Extractives is a general term used to describe a range of compounds that can be extracted using polar and weakly polar solvents such as acetone and dichloromethane [24]. Among others, extractives are composed of phenolic compounds, wood resins, triglycerides, and steryl esters [24]. The ash content is essentially inorganic compounds present in the biomass. This can be in the form of minerals required for the function of organic substances. Another source of ash is as extraneous inorganic compounds which are obtained from contaminated soil around the plant [24].

### 1.3.3. Current Chemo-Catalytic Processes

Current chemo-catalytic processes essentially involve subjecting the lignocellulosic biomass to catalytic hydrolysis by using an acid catalyst; either a liquid or a solid catalyst can be used. This allows for the production of various biochemicals as well as biofuels [11, 17].

Much of the literature focuses on using solid acid catalysts in biomass depolymerization [for example, 33, 34 and references therein]. However, in terms of industrial applicability, there are two major shortcomings associated with the use of solid catalysts. The first issue is that both the solid catalyst and the biomass are in solid form, therefore only the surface of the biomass will be depolymerized [35]. This results in having a considerable amount of the biomass un-reacted, thus lowering the yield of final products. Second, the restricted pore size of the solid catalyst places geometric constraints on the biomass [35]. This results in the requirement of longer reaction times thus making the process less favourable.

The most common approaches for chemo-catalytic processes involve utilizing mineral acids. Sulfuric acid is the most commonly used, other mineral acids such as hydrochloric acid and hydrobromic acid have limited applications due to their negative environmental impacts. There are two main research techniques for the chemo-catalytic process which involve varying the acidity and reaction temperature [36]. The first approach employs high concentrations of mineral acid (31-70 wt%) with low operating temperatures (20-50°C) [37, 38]. The downfall of this technique is that concentrated acids are highly toxic and corrosive thus necessitating expensive construction material. The second approach, which is more widely used, employs a low concentration of mineral acids (1.0-3.0 wt%) in conjunction with high operating temperatures (150-220°C) [39-41]. Generally, the goal of these chemo-catalytic approaches is to effectively depolymerize the biomass feedstock in order to facilitate production for biofuels and biochemicals.

In terms of finding application in the industrial sector, two particular processes exist that have made significant breakthroughs in the production of biofuels from biomass, both are discussed in detail. First, the Biofine process is used in a plant that is presently operational in South Glen Falls in the United States of America [15]. Using cellulosic biomass alone the authors claim to have obtained approximately 50 wt% of levulinic acid from cellulose. As shown in figure 1-16, the process first involves pretreating the biomass feedstock, that is paper sludge, with dilute sulfuric acid at concentrations between 1.5-3%. The feed is then transferred to a plug flow reactor where there is a continuous flow of material, at this point, the polysaccharides undergo acid hydrolysis to form aldehyde intermediates. This reaction is carried out at temperatures of 210-220ºC at pressures of 25 bar for a few seconds. The material is then transferred to a considerably larger back mix reactor in order to subsequently form the final desired products, one of which is levulinic acid. The conditions for this reaction used are at temperatures of 190-200ºC at pressures of 14 bar for approximately 20 minutes.

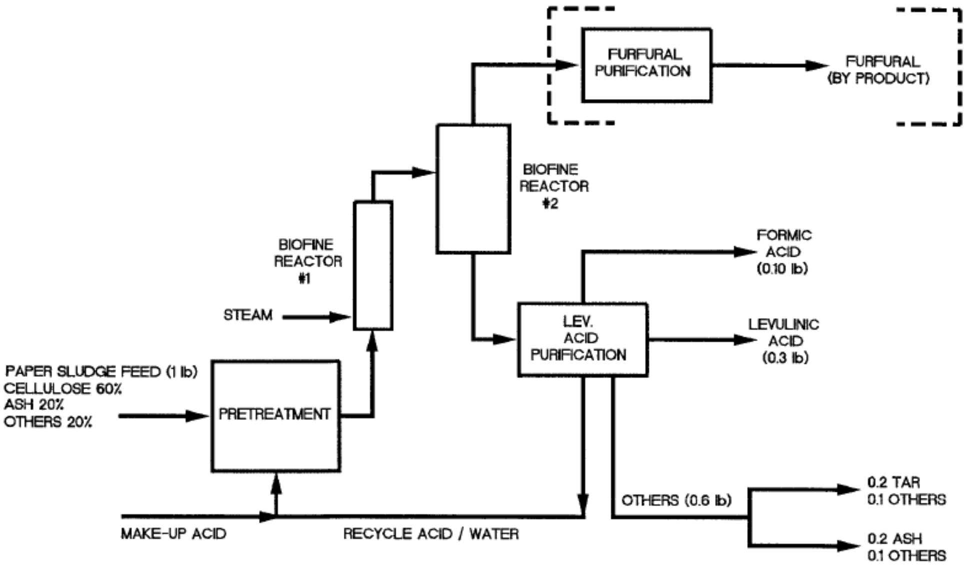


**Figure 1-16. The Biofine process [42]**

The levulinic acid yield is 30 wt% from paper sludge, after having gone through several purification and extraction steps. Given that the subsequent esterification of levulinic acid will result in maximum yield of up to 85% [43], the final yield for ethyl levulinate would become 25.5%. This translates to about 61% of the theoretical maximum obtained from cellulose content.

Bianchi et al. have invented another similar process for synthesizing the esters of levulinic acid directly from biomass [44]. However, instead of using mineral acids, organic acid catalysts are employed. The feedstock undergoes an initial mechanical treatment to ensure that the resulting wood particles have a diameter of less than 1mm. The preferential catalyst used is 2-naphthalenesulfonic acid at a concentration of 0.5-2.0 wt%. The reaction is carried out in an autoclave with required temperature of 200ºC for 4 hours. The resulting liquid phase is separated from the solid residue by filtration. Generally, for 10 g of wood used, the final yield of ethyl levulinate is 50 wt%, corresponding to 95% yield based on the cellulose. However, Mascal et al. [45] provided a critique of this patent, where the authors attempted to reproduce the same results with no success. The experiments were carried out with the same reaction conditions as described by Bianchi et al. and a final yield obtained is 22-23% of the theoretical maximum.

### 1.3.4. The Primary Research Idea

The research methods adopted by Dr. Le Van Mao in order to produce biofuels and biochemicals from lignocellulosic materials involve two main procedures. The first is named sequential procedure (SEQ) and involves hydrolyzing the lignocellulosic biomass in dilute acid media and, subsequently, adding ethanol for esterification. The second idea is the direct procedure requiring one step in which the lignocellulosic biomass undergoes ethanolysis only, utilizing dilute acid directly in ethanol. The ethanol used for these procedures can be obtained from the fermentation of biomass therefore the entire process would solely use renewable resources.

## 1.3.4.1. General Scheme of Reactions

### *1.3.4.1.1 Sequential Procedure*

The acid-catalyzed conversion of the polysaccharides has been investigated for the production of fuels and chemicals. There is little known in the literature concerning the reaction mechanisms [46]. The gathered information is shown in the following reaction schemes of figure 1-17 and 1-18, which indicates that the polysaccharides i.e. cellulose and hemicellulose are deconstructed to their monomer sugar units, glucose and xylose. These are then dehydrated to form aldehyde intermediates 5-hydroxymethyl-2-furaldehyde (HMF) and 2-furaldehyde, respectively. The HMF is subsequently hydrated to yield formic acid and levulinic acid. Ethyl formate and ethyl levulinate are produced via the esterification of the acids in the presence of ethanol. Our laboratory demonstrated that the 2-furaldehyde also undergoes esterification to form ethyl formate. Acetic acid is also formed from the hydrolysis of the hemicellulose, which is then converted to ethyl acetate. [47]

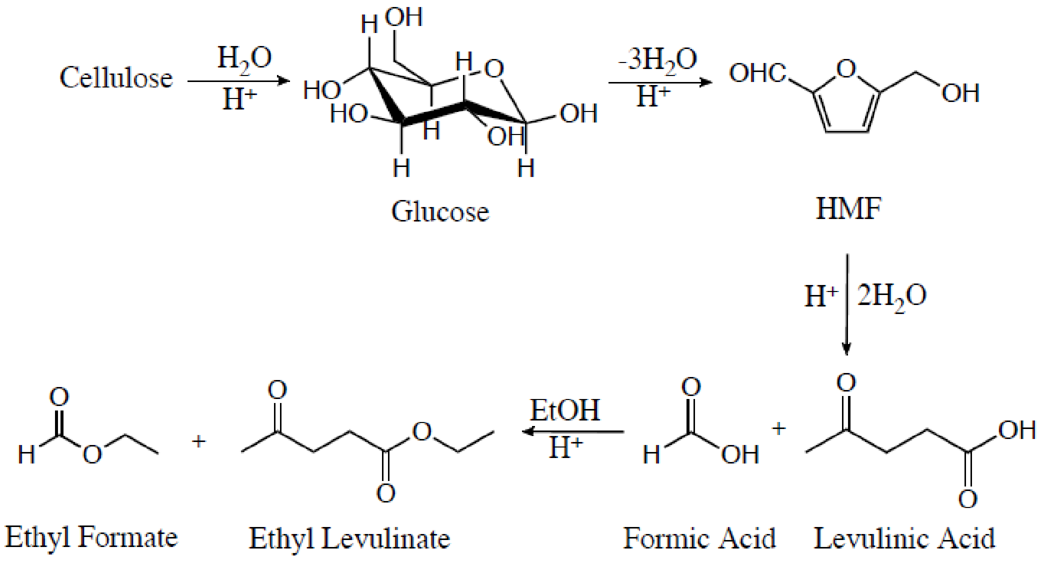


**Figure 1-17. Cellulose degradation reactions in the sequential procedure**

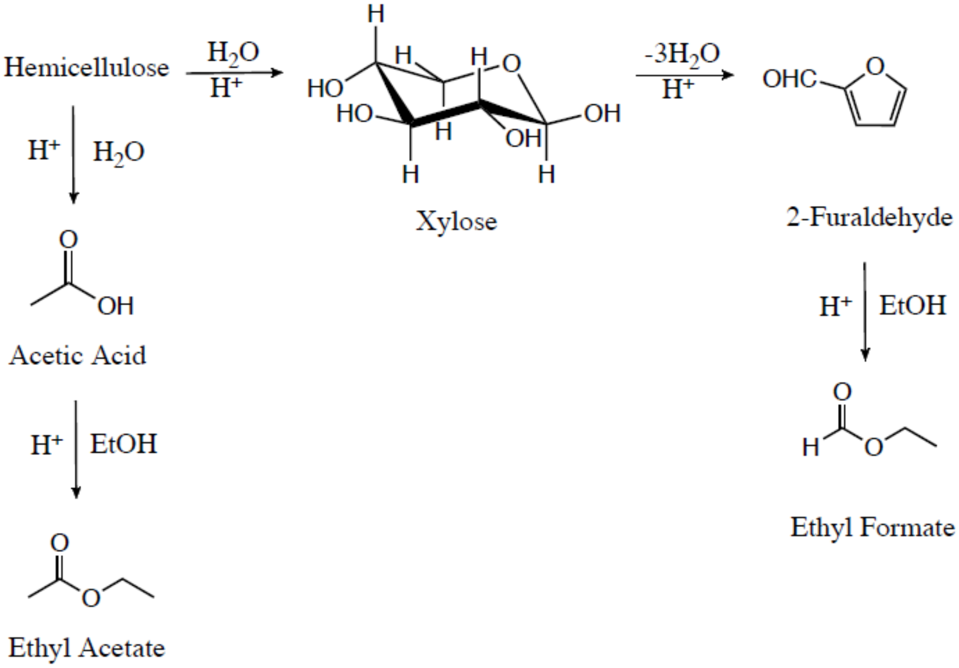


**Figure 1-18. Hemicellulose degradation reactions in the sequential procedure**

### *1.3.4.1.2 Direct Procedure*

The products from the direct procedure are the same as those obtained for the sequential procedure, i.e. ethyl levulinate, ethyl formate, and ethyl acetate. The main difference is that the reaction is carried out in ethanol medium therefore ethanol acts as the nucleophile as opposed to water as in the sequential procedure [33]. The reaction schemes are illustrated in figures 1-19 and 1-20. The ethanolysis of cellulose and hemicellulose produces ethyl glucoside and ethyl xyloside, respectively. These intermediates are then dehydrated to form 5-ethoxymethyl-2-furaldehyde (EMF) and 5-ethyl-2-furaldehyde which in turn are converted to the final desired products. Ethyl acetate is also formed from the ethanolysis of hemicellulose.

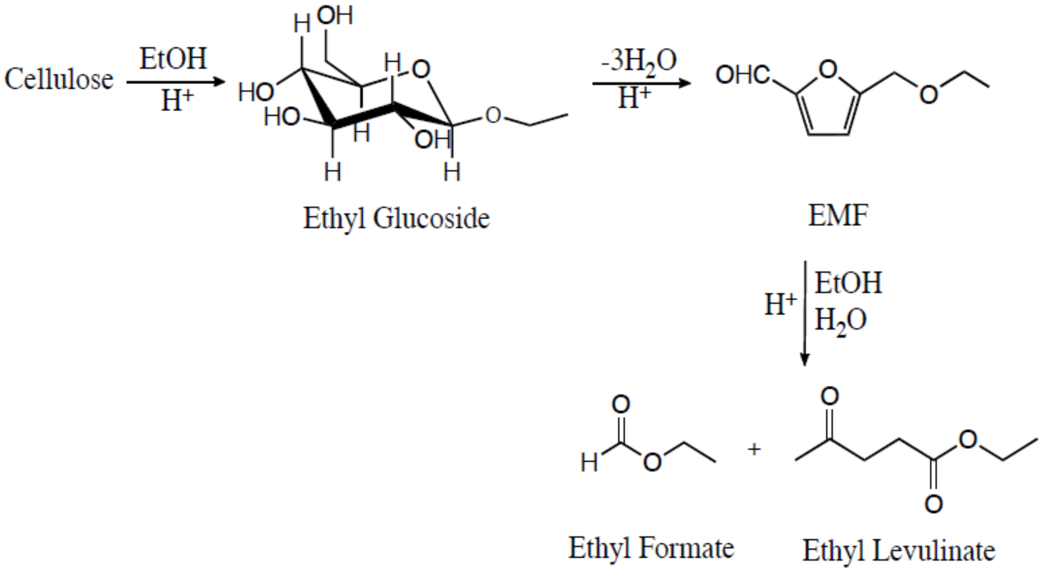


**Figure 1-19. Cellulose degradation reactions in the direct procedure**

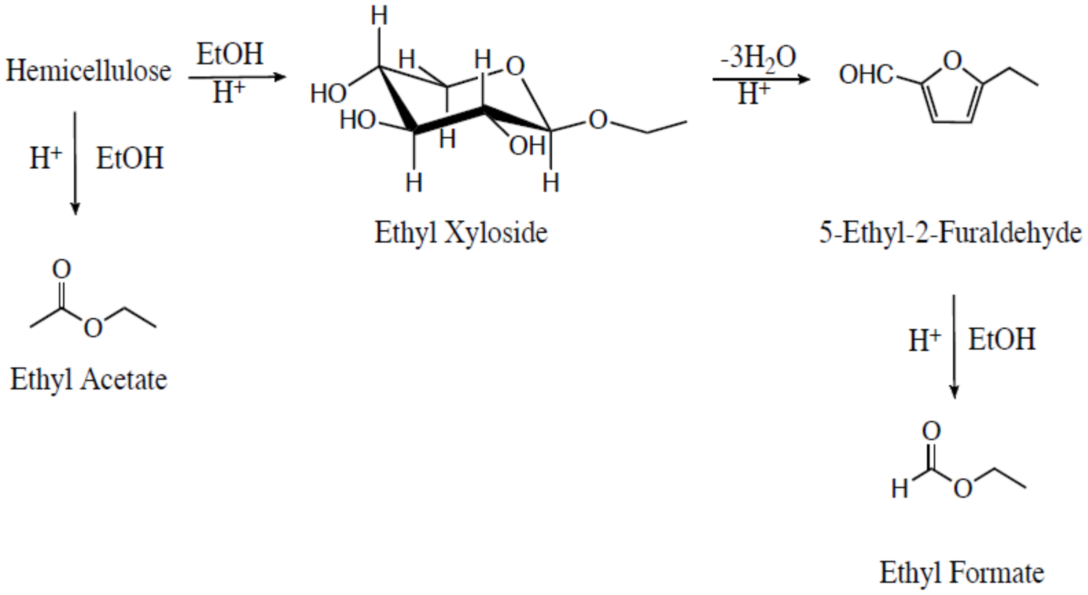


**Figure 1-20. Hemicellulose degradation reactions in the direct procedure**

### *1.3.4.1.3 Production of Tars*

A major byproduct of the chemo-catalytic process is the production of solid residues known as tars. Lignin is not included in the general reaction schemes since it is well known in the literature and generally accepted that lignin is insoluble in dilute acid medium [17] and, thus, remains unconverted. Another source of tar formation can arise from the decomposition and condensation reactions from the cellulose and hemicellulose polymers and their intermediates [48]. Research estimates that there is a possibility of over one hundred intermediates which can be formed in this process [15]. However, the pathways are not clearly understood, these intermediates are formed through polymerization reactions producing black insoluble polymeric material known as tars [15, 46, 49] shown in figure 1-21.

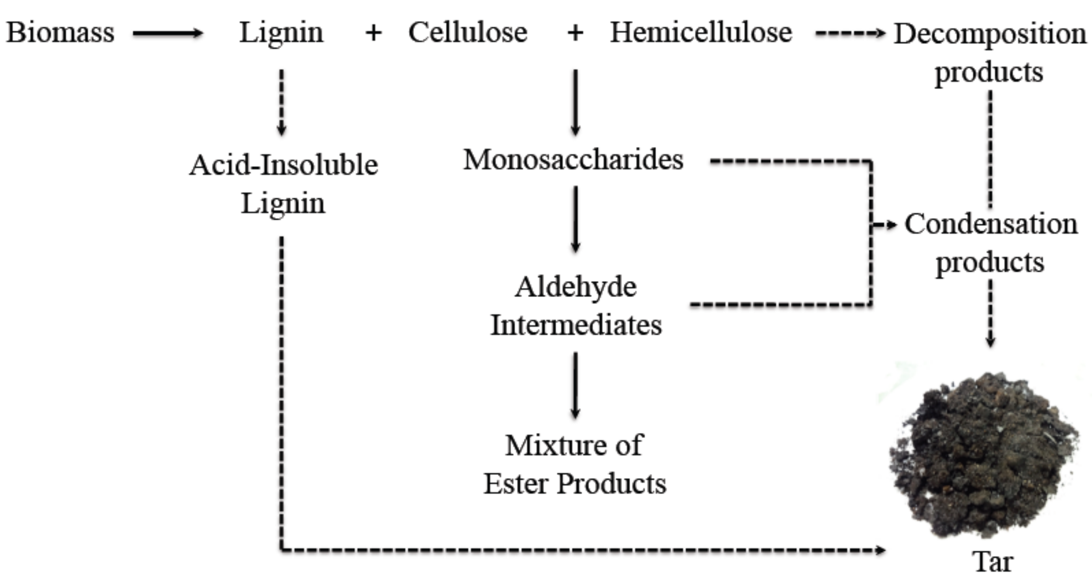


**Figure 1-21. Production of tars**

It is important to note that these reactions are mutually exclusive, i.e. either the reaction conditions are favouring formation of tars or promoting the pathway towards the production of desired ester products. Therefore, decreasing the production of the tars would lead to an increase in production of ethyl acetate, ethyl formate, and/or ethyl levulinate.

## *1.4. Potential Commercial Applications of the Ester Products*

The commercial applications for ethyl acetate, ethyl formate, and ethyl levulinate are many. Ethyl levulinate can be used as a biochemical product as a flavouring agent, and also as a general solvent, and plasticizers. However, the major use for ethyl levulinate is as an oxygenate additive in fuels to improve fuel combustion and as an octane and cetane number enhancing agent [50]. Ethyl acetate is a general organic solvent, also used to make glue, and nail polish remover [51]. Ethyl formate is also a general usage solvent. A potential application for ethyl formate is also as a fumigant against stored grain insects [52].

## *1.5. Research Objectives*

The overall objective of this research was to investigate the means of producing biofuels and biochemicals so as to reduce, or eventually replace, the use of fossil fuels. The present work is focused on the development of the acid-catalyzed conversion of lignocellulosic biomass (AC3B) process. This process will be discussed in a latter section. This is done in order to produce and also optimize the yield of ethyl acetate, ethyl formate, and ethyl levulinate which can be used as biofuels and biochemicals. The AC3B process is a chemo-catalytic process where acid-catalyzed depolymerization of the polysaccharides take place at moderate temperatures to directly produce a mixture of ester products. Two procedures have been developed (1) sequential (acid hydrolysis followed by esterification) and (2) direct (direct acid- catalyzed conversion in alcohol medium). Once the process is established, the second objective involved determining the relation between the chemical composition of the biomass feedstock and the product yields. Since different feedstocks contain varying amounts of the structural constituents, the yields obtained can offer an indication to which reaction conditions are favourable. Finally, further optimization was carried out through modification of the reaction conditions in order to increase the yields of desired products. This in turn would lead to a decrease in side reactions. With the addition of an oxidizing agent to the complex conversion medium, the yields of desired products increased significantly. A new reaction pathway involving the chemically robust lignin has been identified. A fundamental study of the cellulose and hemicellulose acid degradation pathway was also performed. This offers a deeper understanding of the underlying reactions of the chemo-catalytic process. Finally, the final objective was to reduce the production of undesired side reactions. The first effort is through semi-optimization with the addition of polymerization inhibitors. This was done to potentially reduce the formation of tars which would in turn result in an increase in desired products. The second aim was focused on the reduction of undesired diethyl ether production. The final products are obtained as a liquid mixture where the yields are quantified using gas chromatography with a flame ionization detector (GC-FID).

# Chapter 2. Experimental

## 2.1. Materials and Chemicals

This section provides a list of the materials and chemicals needed as well as a summary of the preparations required in order to carry out the experiments. Jack pine wood chips, paper pulp, and switch grass are each used as raw materials and were dried overnight in an oven at 120ºC. The structural composition of the raw materials are shown below in table 1. Also, absolute ethanol, n-dodecane, hydrogen peroxide, sodium sulphite, ferrous sulfate and sulphuric acid were purchased from Aldrich. The reactor used is a 1L Parr stirred-tank reactor which is connected to a vacuum device Model 2028 from Welch.

| Starting Materials (%wt) | Jack Pine | Paper Pulp | Switch Grass |
|---|---|---|---|
| Cellulose | 42 | 78 | 35 |
| Hemicellulose | 26 | 20 | 34 |
| Lignin | 31 | 0 | 30 |

**Table 1. Structural composition of the biomass raw materials**

## 2.2. Experimental Design

The design of the AC3B process, as shown in figure 2-1, contains two main elements; a reactor as well as the vacuum system that is connected via a series of condensers. The acid-catalyzed conversion of the biomass occurs in the reactor, the reaction products can then be extracted using a mild vacuum. Having the highest boiling point of the reaction mixture, n-dodecane is used as a reference and extracting agent to assure recovery of all the products.

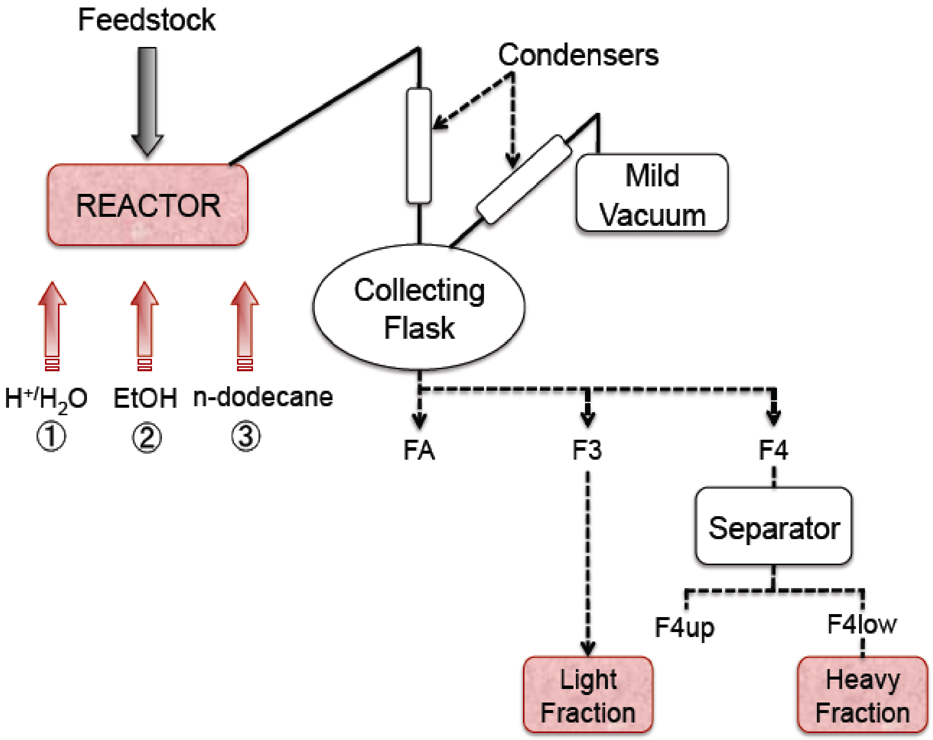


**Figure 2-1. The AC3B reactor design**

## 2.3. Experimental Procedures

The first procedure adopted by our laboratory is the sequential procedure. The reactor is loaded with 80 g of feedstock along with 300 g of an aqueous solution of dilute sulfuric acid (2.6 wt%). The hydrolysis reaction is then performed for 2 h at 192°C and a fraction of the liquid is then collected at 95°C with a vacuum up to 100 torr, which is named FA containing essentially only water. With the mineral acid still present in the reactor, 150 g of ethanol is added for esterification. This reaction is carried out for another 2 h at 145°C.

The direct procedure is based on a similar concept, although when loading the reactor, the sulfuric acid (2.6 wt%) is diluted in ethanol for a total of 250 g. Only one reaction is performed i.e. esterification, for 3 h at 157°C therefore collection of FA (removal of water) is not required.

For the experiments performed using hydrogen peroxide, the reactor contained the feedstock along with dilute sulfuric acid in ethanol medium. Also, hydrogen peroxide was added at 3.57 wt%, i.e., 30 g of 30% hydrogen peroxide in aqueous solution. Furthermore, varying amounts of the Fenton reagent were used in the subsequent reactions. These amounts are 0.0, 0.6, 1.2, and 2.4 g of ferrous sulfate diluted slowly with 10 g of 50% aq. hydrogen peroxide and added to the reactor. Experiments performed using increasing amounts of sodium sulphite required 1.0, 1.3, and 1.8 g of sodium sulphite which was then added to the reactor already containing the feedstock and the reaction mixture. The investigation of diethyl ether formation involved the addition of increasing amounts of water, 0.0, 12.5, and 25.0 g to the reactor along with the feedstock and reaction mixture. Subsequently, reactions with the use of H-USY zeolites required the addition of the reaction mixture then increasing amounts of zeolites 0.0, 5.0, 7.5, 10.0 g and finally the feedstock to the reactor.

Once the reactions reach completion, the following recovery of reaction products is the same for both sequential and direct procedures. Extraction is performed at 93°C and 200 torr, this is called F3, this collection is the light fraction where the low boiling point compounds are obtained. That is, the F3 is composed of ethyl acetate, ethyl formate, diethyl ether, ethanol, and a small amount of water. For the final collection, F4, a long chain, high boiling point n-paraffin is added into the reactor and used as a reference and extracting agent. The n-dodecane possesses the highest boiling point of all the components, therefore a high recovery of n-dodecane would signify an efficient extraction of the remaining components. This is because the presence of n-dodecane vapours during the phase of product extraction contributes to lowering the partial pressure of the products (e.g., ethyl levulinate), thus increases its extractability. Physical properties of the products are found in table 2. At this point, a vacuum is applied to the system reaching a negative pressure of about 4-5 torr and a temperature of 250°C is reached, this was performed using a temperature programmed heating at 2°C/min. Since the distillate obtained formed two dichotomous phases, the use of a separatory funnel was in order. The F4up contains n-dodecane which can be recycled for use in future extractions, and F4low or heavy fraction containing the high boiling point compounds; ethyl levulinate, levulinic acid, water, and ethanol. The remaining solid residue in the reactor can be burned as a direct fuel source.

**Table 2. Physical properties of the products in the reaction mixture [53] [54]**

| Product | Molecular Formula | Boiling Point (°C) |
|---|---|---|
| diethyl ether | $C_4H_{10}O$ | 34.6 |
| ethyl formate | $C_3H_6O_2$ | 53-54 |
| ethyl acetate | $C_4H_8O_2$ | 77 |
| ethanol | $C_2H_6O$ | 78.5 |
| ethyl levulinate | $C_7H_{12}O_3$ | 205-206 |
| n-dodecane | $C_{12}H_{26}$ | 216.3 |

## *2.4. Gas Chromatographic Analysis*

The reaction mixtures are analyzed using gas chromatography equipped with a flame ionization detector with a DB-WAX column. An internal standard (IS), isopropanol, is used as a reference where the ratio of peak area of the IS is compared to the other peaks of interest providing quantitative information. Another motivation for using an IS is also for correcting variability in injection volume. A typical chromatogram of the reaction products obtained is illustrated in figure 2-2.

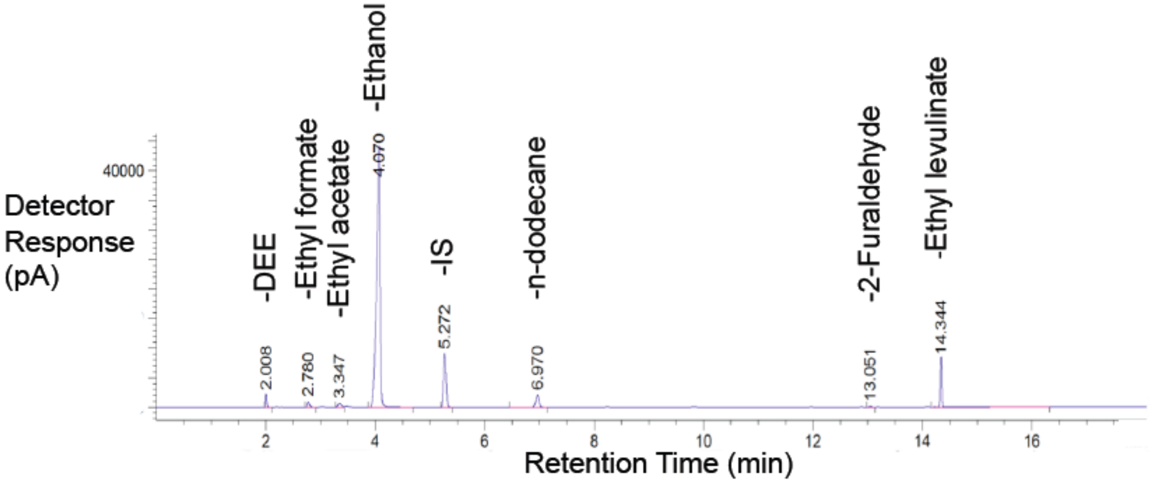


**Figure 2-2. Typical GC chromatogram of a reaction mixture**

Relative response factors (RRF) are used since the flame ionization detector is mass sensitive thus does not respond to the concentration of analyte in the mixture [55]. The relative response factors for each compound is determined using standards of known composition and concentrations. Therefore quantification of unknown mixtures can be obtained by multiplying the respective peak area by the corresponding RRF.

### 2.4.1. Product Yields

The product yields obtained are given in wt%, signifying the weight in grams of product obtained per 100 g of raw material. The total liquid products obtained are reported as reaction products (RP). A note that the diethyl ether produced is not a product of biomass conversion but of ethanol dehydration in acidic medium. Therefore diethyl ether should not be accounted for as a reaction product.

# Chapter 3. Results and Discussion

This chapter is composed of four main goals each of which, however, shares in the fundamental objective of optimizing the yields of desired products. The first discusses the relationship between the chemical composition of various biomass feedstocks to the product yields. The next purpose is to determine the effect of the addition of an oxidizing agent, along with the acid catalyst, in order to promote an increase in yields. The third section aim to gain a more fundamental understanding of the reactions involving the degradation (or deconstruction) of cellulose and hemicellulose. The fourth and final objective is to promote desired product formation by decreasing the amount of undesired side products.

## *3.1. Investigation of Chemical Composition and Product Yields*

In order to gain a better understanding of the production of ethyl acetate, ethyl formate, and ethyl levulinate from biomass, a critical investigation of the reactions that give rise to their formation must be performed. That is, this subsection elaborates upon the relationship between the chemical composition of the biomass feedstock and the product yields obtained using the AC3B process. Using the sequential procedure, figure 3-1 provides a first indication of this relation with wood chips, paper pulp, and switch grass as the feedstock used. Recall that the varying amounts of constituents contained within each feedstock are shown in table 1. The sequential procedure is used with the same reaction conditions aforementioned (see section 2.3). The results obtained demonstrates a clear relationship between the cellulose content of the biomass and ethyl levulinate yield. Paper pulp contains the highest portion of cellulose possessing approximately 78% whereas the other feedstocks have almost half that amount, 42% and 35% for wood chips and switch grass, respectively. The yield of ethyl levulinate originating from paper pulp resulted in 25.9 wt%, while wood chips and switch grass showed respective yields of 16.6 wt% and 13.8 wt%. Therefore, the relationship between cellulose content and ethyl levulinate yield is consistent between all three feedstocks; the greater the cellulose content, the larger the amounts of ethyl levulinate produced. This finding is in line with the literature [47] and accords with the reaction scheme presented in figure 1.17. In other words, upon the acid degradation of biomass only the cellulose constituent produces levulinic acid which subsequently undergoes esterification to form ethyl levulinate. However, upon closer inspection, there is a seeming inconsistency in that the yield of ethyl levulinate is not proportional to the cellulose content of the original feedstock. More specifically, we would have expected a much higher yield from the paper pulp as its cellulose content is much higher. What needs to be considered is that paper pulp is a processed material and, as such, its cellulose has a highly crystalline structure. Therefore, relatively harsher conditions would be required in order to facilitate the disruption of the rigid structure. Harsher conditions would imply utilizing higher temperature, or higher concentrations of acid.

While the yield of ethyl levulinate is an increasing function of cellulose content, such a direct trend does not carry over to the formation of ethyl formate as this product originates from both cellulose and hemicellulose. Even though the yields are not as divergent, 2-furaldehyde (an intermediate of ethyl formate) and ethyl formate yields remain higher with paper pulp compared to the other feedstocks. According to figure 1-18, ethyl acetate is derived exclusively from hemicellulose, through esterification of acetic acid, however, it is difficult to determine a clear relation since acetylation of hemicellulose occurs in a random manner [17]. Another observation is the significance of having small amounts of levulinic acid and 2-furaldehyde present in the reaction medium which signifies that the reaction conditions are sub-optimal. This is because both of these compounds are intermediates in the biomass degradation pathways thus full conversion did not completely occur. Considering the fact that the results for the formation of tars remain quite large, ranging between 58% to 73%, we now turn attention to the formation of tars. Due to the mutual exclusivity of the reactions, and as confirmed in the results obtained, higher yields of desired products result in decreased production of tar. In general, the feedstock material can undergo undesired incorporation into polymeric material through polymerization reactions. However, the confounding influences of the structural rigidity of cellulose as well as the influence of lignin contained within the cell wall matrix make it difficult to understand the extent to which each type of undesired reaction occurs. Two main explanations surrounding the fact that yields from lignocellulosic biomass are shown to be markedly lower than their pulp and paper counterpart. Recall that the level of holocellulose is lower than that found in pulp and paper, thus lower yields would be expected. Second, due to the fact that lignin is only partially disrupted and remains part of the structure of the cell wall (see section 1.3.2), causes it to prevent the acid catalyst from acting upon the cellulose fibrils embedded within the cell wall matrix.

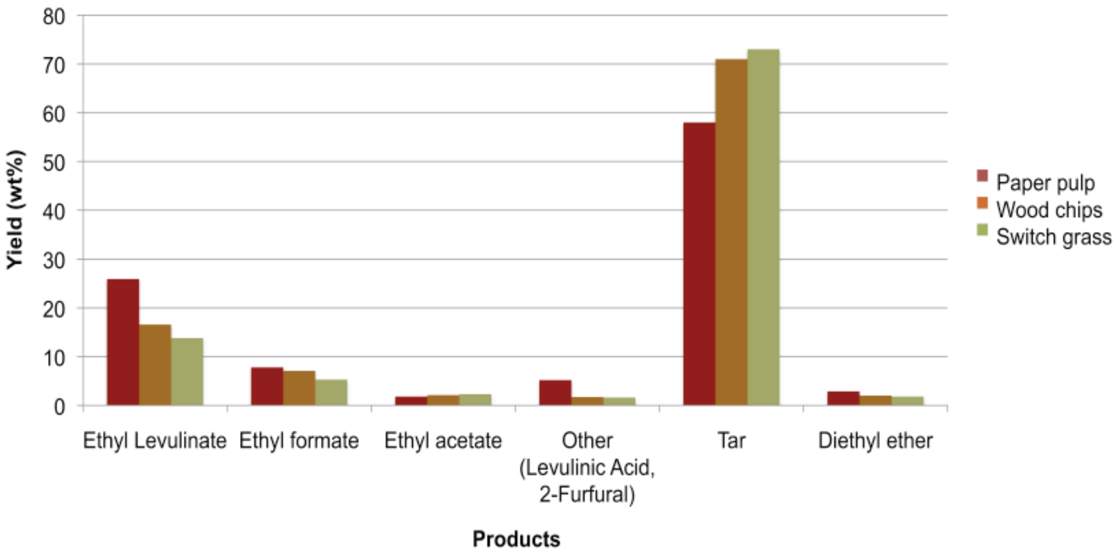


**Figure 3-1. Investigation of product yields using various feedstocks**

A final brief comment on the production of diethyl ether is addressed. This compound is not a product of biomass degradation, but rather forms solely from the bimolecular dehydration of ethanol, therefore is not considered a desired reaction product. Overall, the AC3B process has been shown to produce valuable products from different feedstock sources. While important trends have been observed, the production of large amounts of tars remains an issue to be addressed.

## *3.2. Comparison of Direct and Sequential Procedures*

Provided that the sequential method has demonstrated the essential reactions that occur in the AC3B technology, this section builds upon the previous by contrasting the two processes in terms of their product yields and energy requirements. As will be seen, the direct procedure measures up favourably against its sequential counterpart. The comparison of these procedures was performed using wood chips and paper pulp feedstocks. Figure 3-2 illustrates the product yields arising from these parallel processes with parts (a) and (b) representing yields from paper pulp and woodchips respectively. As can be seen, the yields of desired products obtained are similar thus suggesting a certain level of correspondence between the two versions of the AC3B technology. In terms of yields, the only main difference between the procedures is the production of diethyl ether. This is not surprising as the direct procedure is carried out in ethanol medium.

For our purpose, this result is favourable in that the direct procedure can be readily adopted without compromising the yield levels. More specifically, the desirability of the direct method arises from having greater energy and time efficiency without reducing the formation of desired products. Recall that the direct procedure involves one reaction step, ethanolysis, whereas the sequential involves two steps; hydrolysis with subsequent esterification. In terms of energy consumption, having one reaction at 157°C (direct procedure) is more advantageous compared to two reactions in the sequential process at 192°C and 145°C. As previously mentioned, the removal of water is a necessary step in the sequential procedure prior to esterification. This extraction step adds an additional premium in terms of both energy and time requirements and is not needed in the direct method as water is not used as a solvent. Regarding time consumption, the residence time for the sequential procedure is a total of 4 hours whereas that of the direct procedure is 3 hours. Thus, based on the criteria of energy and time, the direct method incorporates many valuable improvements over the sequential process. As such, this procedure is adopted for further optimization of product yields.

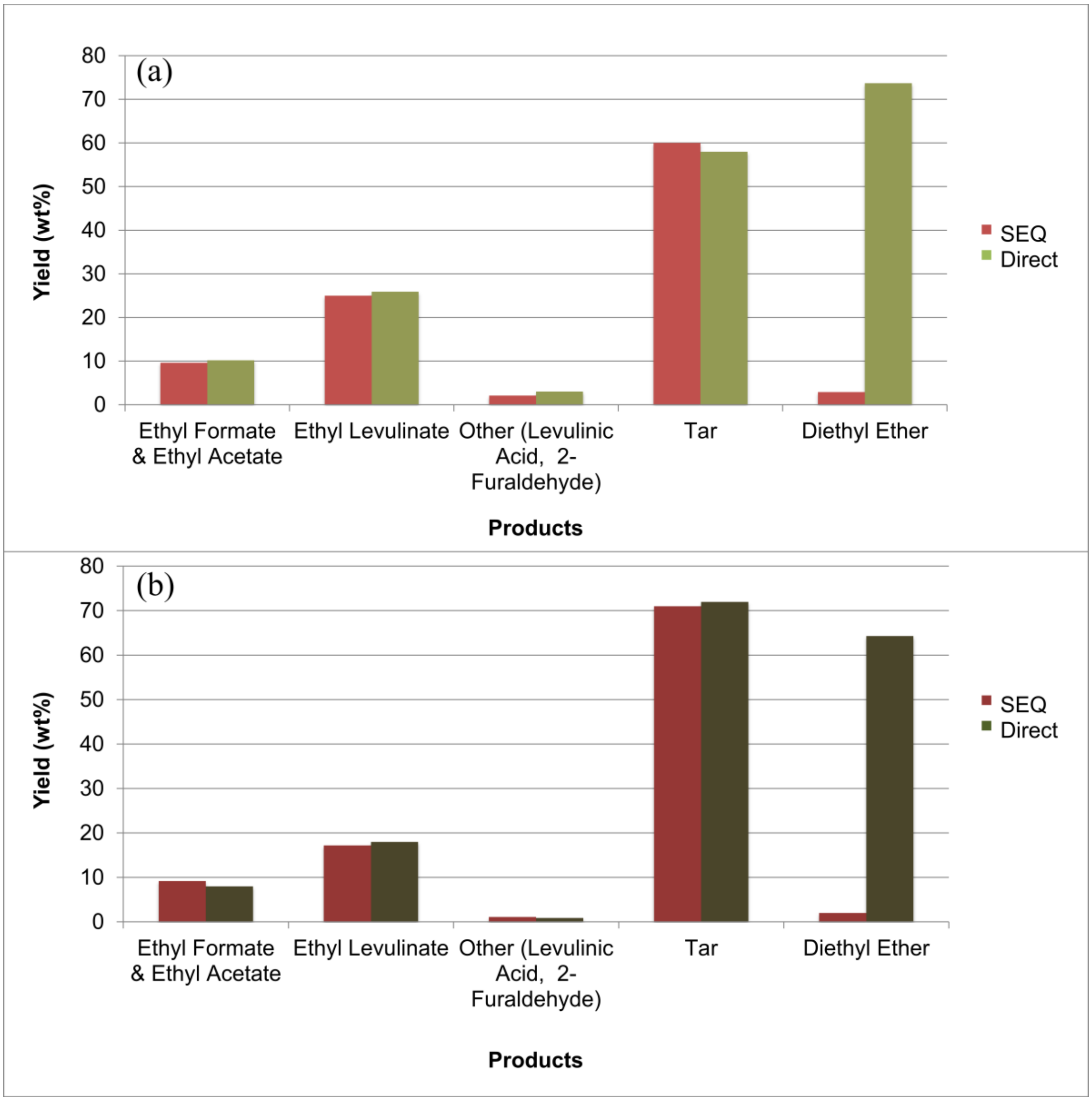


**Figure 3-2. Comparison of sequential and direct procedures using (a) paper pulp and (b) wood chips**

Despite its many advantages, the direct procedure suffers from the same shortcoming as the sequential, namely a relatively high proportion of the constituents are converted into tar as opposed to desired products. This is particularly true using lignocellulosic biomass where the lignin component is not typically used to produce desired products as it remains as tar. Comparison with feedstock with higher polysaccharide content (e.g. first generation feedstocks) the later typically provide higher product yields. This translates to having to utilize much more starting material of lignocellulose to produce a significant or comparable amount of biofuels and biochemicals. Another issue is that the present value of the desired products obtained in the AC3B process is not high. Therefore creating this one-pot process and reducing the number of steps reduces the energy and time needed which makes the technology more economically feasible.

## 3.3. Coupling of Oxidizing Agent and Acid Catalyst

The use of an oxidizing agent in conjunction with an acid catalyst provides a distinctive advantage in terms of the yields of desired products. It allows the AC3B process the opportunity to utilize the three constituents of lignocellulosic biomass (cellulose, hemicellulose, and lignin) instead of only taking advantage of the holocellulose. Since the lignin typically remains as tar, it is considered a major byproduct in the production of biofuels. Thus, deriving desired products from lignin would increase the value of the AC3B process. Presently, tars are used as a direct fuel source to supply energy for the process, however, its commercial value is fairly low [56]. In dilute acid medium, the lignin remains unaltered [17], and if there is a small amount of lignin that solubilizes, it will quickly precipitate [57]. However, when an oxidizing agent is added, the lignin constituent is shown to produce desired products. Furthermore, the addition of an oxidizing agent promotes depolymerization of cellulose and hemicellulose increasing the yield from these constituents as well. Thus, as will be explained further in the following subsections, the process is significantly improved through the use of an oxidizing agent.

### 3.3.1. Catalytic Oxidation of Lignocellulosic Biomass

Oxidation of biomass in alkaline medium has been known for quite some time. It has mostly been used in the pulp and paper industry for bleaching purposes or to remove lignin [28]. Comparatively, less is known for the oxidation of biomass in acidic medium. However, as illustrated in figure 3-3, Xiang et al. [58] have discovered that treating lignin with hydrogen peroxide in acidic conditions, results in partial disruption of its chemical structure.

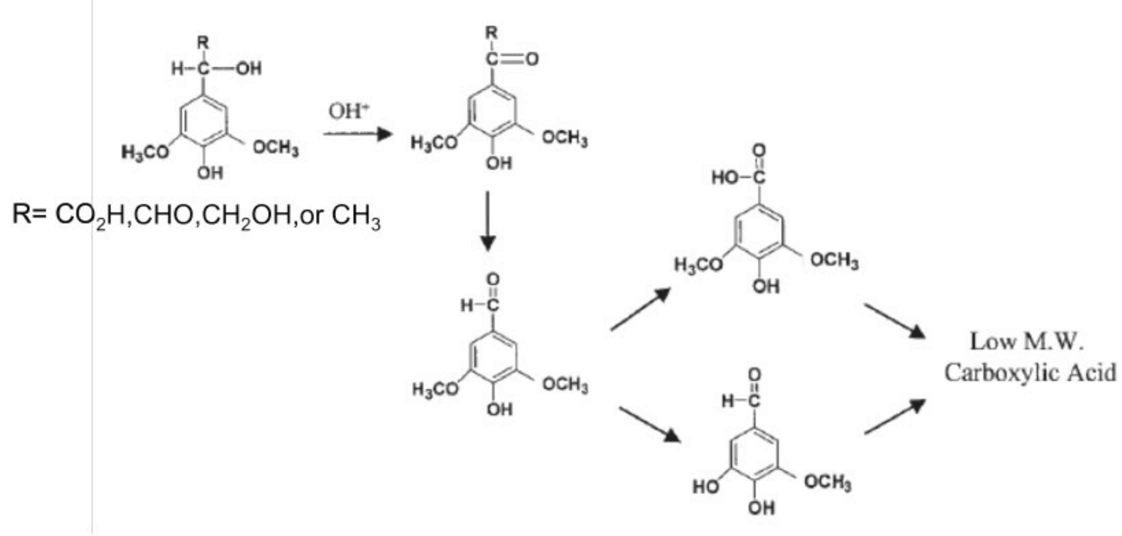


**Figure 3-3. Oxidative degradation of phenyl propane groups within lignin in acidic medium [58]**

The research group proposes a mechanism where the hydrogen peroxide becomes protonated and has been shown to produce an electrophilic species ($OH^+$) responsible for the acid degradation of lignin.

$$H_2O_2 + H^+ \rightleftharpoons H_2{}^+OOH \rightleftharpoons H_2O + OH^+$$

**Figure 3-4. Equilibrium of hydrogen peroxide in acidic medium [58]**

The protonated hydrogen peroxide promotes the degradation of the aliphatic side chains which results in the production of low molecular weight carboxylic acids, i.e. acetic acid and formic acid as well as methanol [59]. Under harsher conditions of higher acidity and temperature, the literature shows that succinic acid can also be produced [58, 59]. More severe conditions are required for succinic acid formation since this involves disrupting the aromatic rings of the lignin structure, as shown in figure 3-5.

It is important to note that Xiang's work was carried out on lignin alone. In so far as lignocellulosic biomass contains a greater number of constituents, we must consider that the addition of hydrogen peroxide will give rise to alternate and parallel reactions causing it to react differently compared to lignin on its own. The reactivity of lignocellulosic biomass, as a whole, is more complex than the reactivity of its isolated constituents. The results shown in table 3 below compare the yields obtained from experiments undergone using the same reaction parameters with the exception of 3.57 wt% of hydrogen peroxide (right column). The starting material used for the experiments is wood chips.

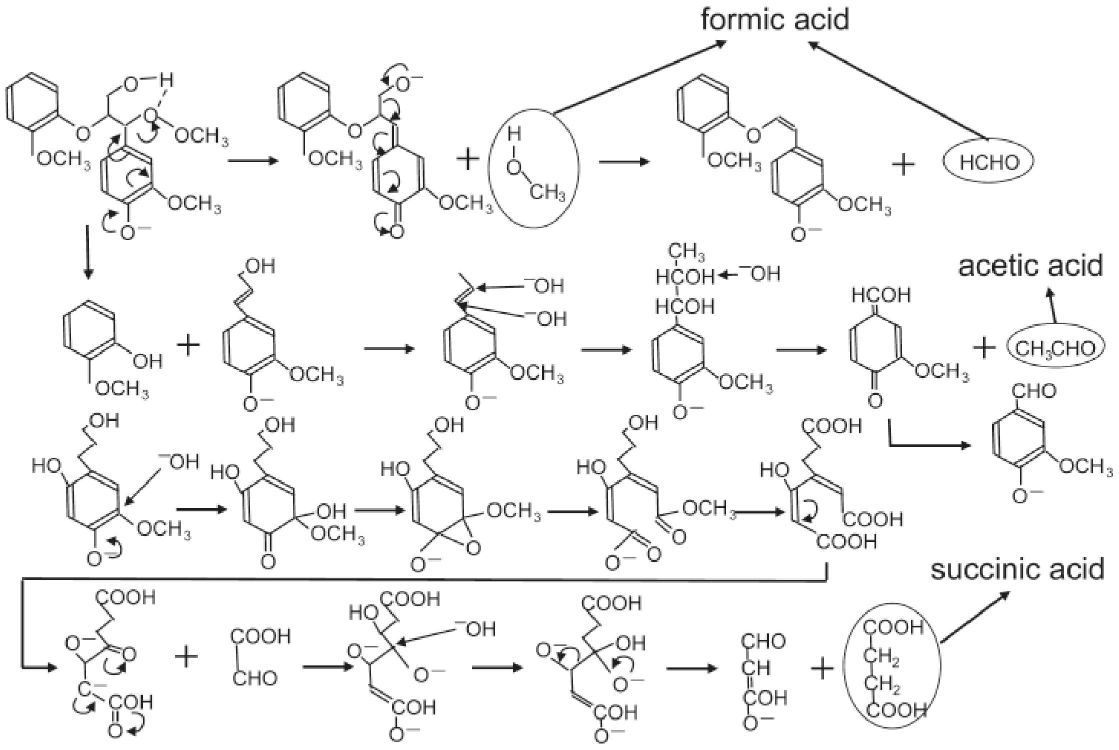
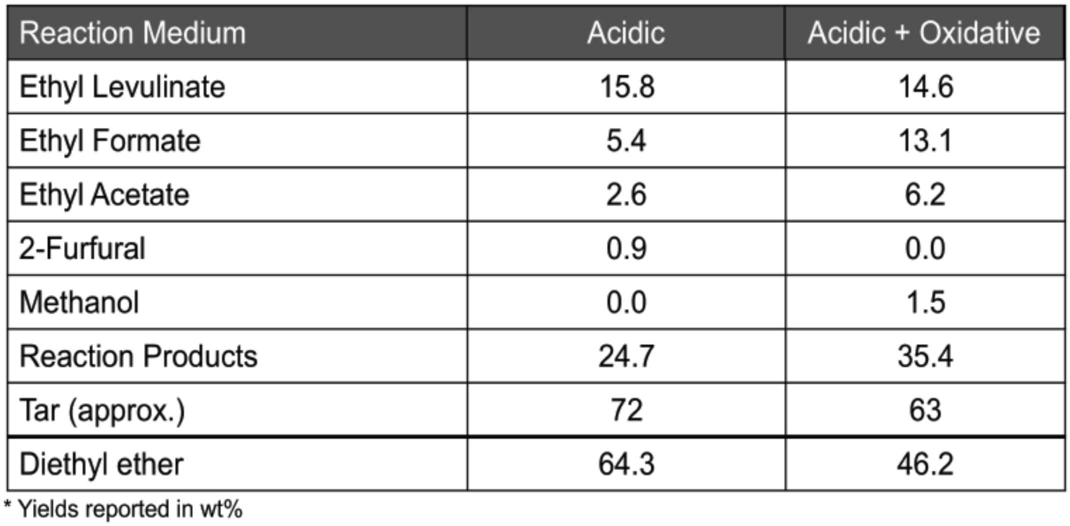


**Figure 3-5. Formation of carboxylic acids through degradation with hydrogen peroxide [59]**

The presence of the oxidizing agent increases the yields of light products. There is a clear increase in yield, almost double of ethyl formate and ethyl acetate. Ethyl formate increased from 5.4 to 13.1 wt% and ethyl acetate increased from 2.6 to 6.2 wt%. This increase in yield of desired products is accompanied by a decrease in tar formation. This is in agreement with the literature previously cited, where the presence of hydrogen peroxide increases carboxylic acid formation thus reducing the degree to which polymerization reactions occur. The carboxylic acid compounds being acetic acid and formic acid, which in turn is converted to ethyl acetate and ethyl formate. What was not observed in our previous experiments without the oxidizing agent, however, is the formation of methanol which also implies that the lignin structure is being partially disrupted. This reflects the results obtained by Hasegawa et al [59], where methanol can also be obtained through the oxidative degradation of lignin. The temperature used for the reaction as previously stated is 157°C, at this temperature hydrogen peroxide readily decomposes to produce dioxygen and water thus the reactive peroxide electrophile has predominantly affected the amorphous hemicellulose fraction [56]. The amorphous regions being more easily susceptible to attack compared to the crystalline structure of cellulose. The ethyl levulinate yield did not increase, having yields of 15.8 wt% without hydrogen peroxide and 14.6 wt% in the presence of hydrogen peroxide. This suggests that hydrogen peroxide did not have access to the cellulose as it is much more difficult to disrupt owing to the recalcitrance of the structure towards chemical attack. This leads to the conclusion that hydrogen peroxide does not have enough time to interact with cellulose. It is also worth noting that 2-furfural, an intermediate for ethyl formate formation, shows a loss in production when hydrogen peroxide is added to the medium. Another possible implication that adding the oxidizing agent promoted the desired reaction pathway.

**Table 3. Effect of the addition of hydrogen peroxide on product yields**



| Reaction Medium | Acidic | Acidic + Oxidative |
|---|---|---|
| Ethyl Levulinate | 15.8 | 14.6 |
| Ethyl Formate | 5.4 | 13.1 |
| Ethyl Acetate | 2.6 | 6.2 |
| 2-Furfural | 0.9 | 0.0 |
| Methanol | 0.0 | 1.5 |
| Reaction Products | 24.7 | 35.4 |
| Tar (approx.) | 72 | 63 |
| Diethyl ether | 64.3 | 46.2 |

* Yields reported in wt%

If the above interpretation is correct and hydrogen peroxide does not have sufficient time to react with cellulose then, logically, the next step would be to increase the contact time between hydrogen peroxide and the biomass. In order to promote the decomposition of cellulose, and thus increase yield of ethyl levulinate, a delignification step was introduced. This additional step was carried out by initially keeping the stir tank at 140˚C, below the boiling point of hydrogen peroxide for various time durations, from 0 to 120 minutes, and then proceeding with the reaction as usual. The feedstock used is woodchips, and the results are shown in figure 3-6. Recall that the reactivity of biomass is more complex than that of a single constituent alone. In this light, delignification increases the accessible surface area of the polysaccharides, particularly cellulose, making them more susceptible to chemical attack. Therefore the objective of delignification is to disrupt the lignin portion of the biomass. More specifically, the hydrogen peroxide is believed to partially decompose the lignin via the process previously described by Xiang et al. Aside from making cellulose more physically accessible, hydrogen peroxide serves a second function by also chemically altering the structure.

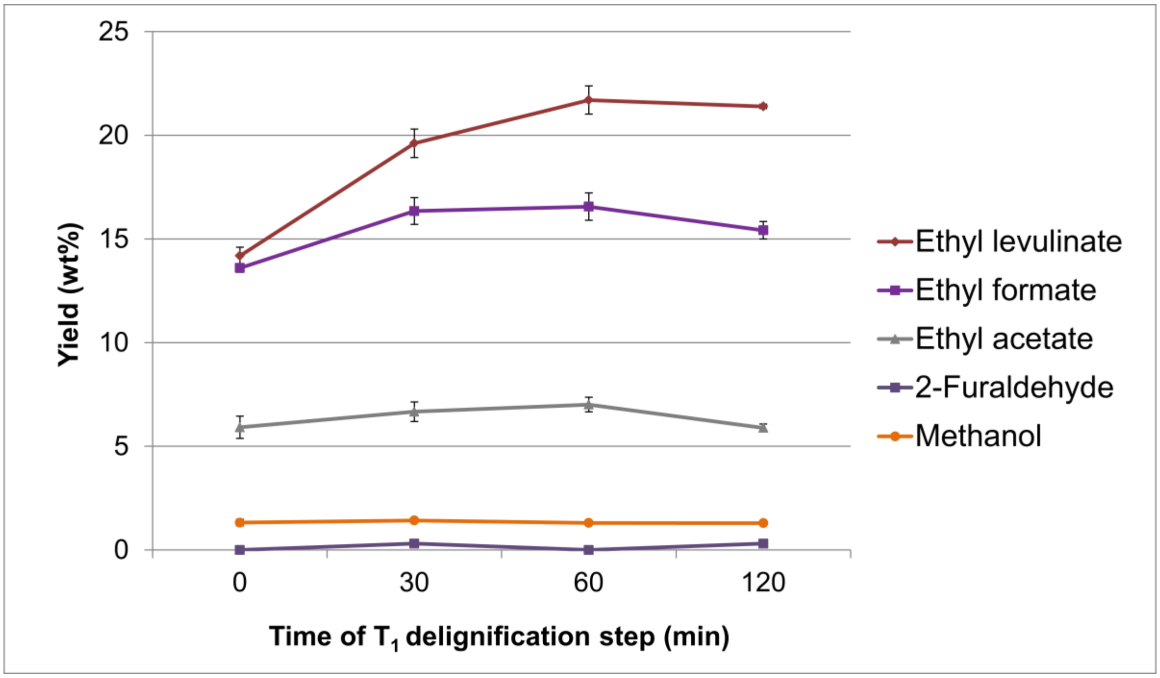


**Figure 3-6. Effect of delignification step on product yields (n=3)**

When coupled with an acid catalyst, this oxidizing agent increases the number of functional groups in addition to the hydroxyl groups of the cellulose, i.e. carbonyl and carboxyl groups, as shown in the figure 3-7 [60]. Literature suggests that the hydroxyl groups of cellulose are oxidized at the C6 positions as well as the vicinal diols on the C2 and C3 positions. This results in the cleavage of the C2-C3 bond yielding the carbonyl and carboxyl functional groups [61, 62], adding further functionalization of the oxidized constituents. Not only does this render the cellulose more susceptible to chemical attack but it also helps disrupt the extensive hydrogen bonding that is primarily responsible for its rigid structure. Thus this coupling effect weakens the cellulose fibrils, facilitating depolymerization, and thus increasing product yields.

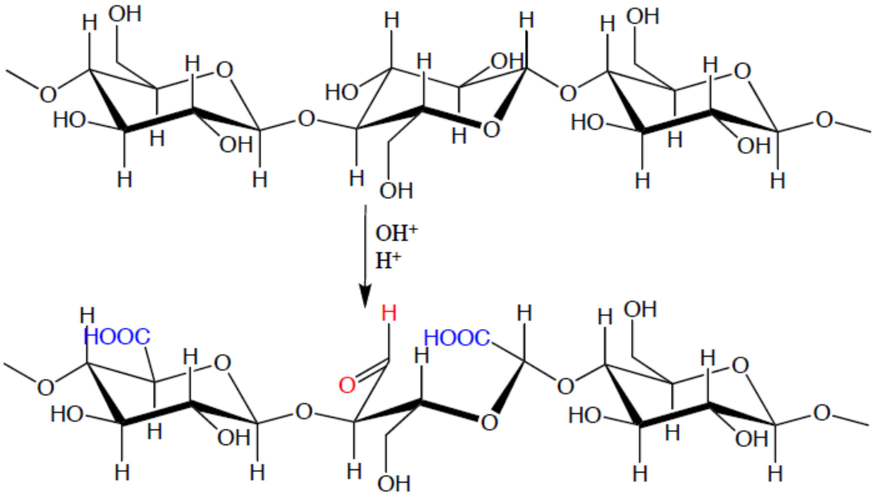


**Figure 3-7. Effect of hydrogen peroxide on the polysaccharides [modified from 60]**

Experiments were carried out in order to determine the optimal setting which take advantage of the influence of hydrogen peroxide. As shown above in figure 3-6, the addition of a delignification step at 140°C resulted in an increase of all desired products but most significantly after 60 minutes of reaction time. The boiling point of hydrogen peroxide is about 155°C, therefore by allowing the hydrogen peroxide to remain in liquid form at 140°C, allows for more time to access the polysaccharides. After 30 minutes, an increase in product yields is already shown and especially after 60 minutes of delignification. Particularly ethyl levulinate increased from 14.6 wt% with no delignification step to 21.7 wt%. The maximum theoretical yield of ethyl levulinate from the cellulose is 69.2%, due to the coproduction of ethyl formate. Wood chips possess

42% of cellulose (shown in section 2.1) therefore the percent yield obtained is 74.7% of the theoretical maximum. After 120 minutes of delignification, it seems that the yields are slightly decreasing, this can be interpreted as favouring repolymerization and condensation reactions. Though covered at greater length in section 3.5.2, the concentration of 2-furaldehyde remains at a very low maximum therefore indicating that it can possibly be an intermediate for the production of ethyl formate. Also, the remaining furaldehyde intermediates (HMF, EMF, and 5-ethyl-2-furaldehyde) have never been observed in the final reaction mixtures. As shown in figure 3-8, this suggests that the dehydration from these intermediates into ethyl formate and ethyl levulinate is much faster than the conversion from the polysaccharides into their respective intermediates [46].

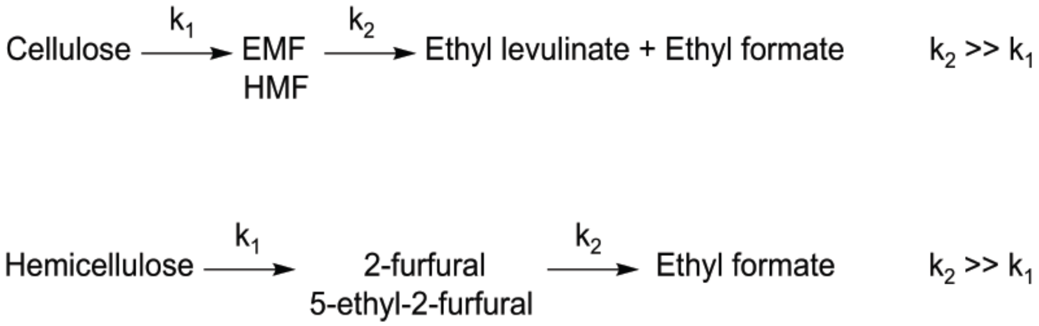


**Figure 3-8. Kinetics of cellulose and hemicellulose degradation**

The results in figure 3-6 are obtained using the delignification step illustrate a marked increase of ethyl levulinate yield. This demonstrates that the hydrogen peroxide may also favour the oxidation of the carbohydrates as well as the lignin. In summary this subsection has reviewed two fundamentally important phenomena that result from the use of hydrogen peroxide. First, partial disruption of the lignin gives rise to the formation of desired products from lignin itself, i.e. ethyl acetate and ethyl formate as well as methanol. In turn, this also renders the structure of the polysaccharide constituents more accessible to chemical attack. Second, considering the additional availability of cellulose, hydrogen peroxide can further oxidize the carbohydrates, disrupting the rigid crystalline structure of the cellulose. This further yields functional groups other than the alcohol groups, but also, carbonyl and carboxylic acids of the polysaccharides [60]. In light of this, the acid catalyst is able to depolymerize the polysaccharides and increase overall yields by about 12 wt%. The results demonstrate that the oxidizing agent has a positive effect in terms of altering the physical and chemical features of the biomass. Catalytic oxidation facilitates the disruption of the rigid cellulose structure, this being directly linked to the intermolecular and intramolecular hydrogen bonding.

### 3.3.2. Catalytic Oxidation of Cellulosic Biomass

The catalytic oxidation of cellulosic biomass allows for the verification of the role of delignification as well as a better understanding of the reactions at hand. Due to the fact that cellulosic biomass does not contain lignin, it is possible to verify whether or not lignin plays the role proposed in section 3.3.1. Paper pulp is subjected to ethanolysis while varying the reaction parameters; acidity, oxidizing agent and reaction temperature. The results from figure 3-9 provide insight into the function of hydrogen peroxide and holocellulose. Comparing reactions 1 and 2, it can be seen that the presence of hydrogen peroxide with the delignification step significantly increases the yields of light products; ethyl formate and ethyl acetate. Also, as the reaction conditions become more favourable for desired product formation (reaction 2), 2-furaldehyde disappears where we can observe ethyl formate production increasing. Ethyl levulinate, however, remains fairly constant at about 25 wt % yield. Our hypothesis for this invariability arises from the fact that the cellulose in paper pulp is increasingly rigid. The reason is that paper pulp is not a raw material as switch grass and wood chips but a processed material having undergone various treatments. It is well known that the higher degree of crystallinity of cellulose, the less susceptible it is to chemical attack [17]. Therefore, this lead to performing reaction 3, where the reaction condition become slightly more severe. The parameters changed in this case compared to reaction 2 is the reaction temperature and acidity was slightly increased. Evidently, this change in conditions resulted in an increase in ethyl levulinate yield confirming the fact that harsher conditions are required to disrupt the cellulose structure. Hydrogen peroxide remained present in the reaction medium however, the delignification step was removed in reaction 4. For this reaction, we observe no net change in the yields of all the desired products indicating that the delignification step is not required when lignin is not present. Without the lignin present, the hydrogen peroxide can have direct access to the polysaccharides.

| Reaction Conditions | Reaction 1 | Reaction 2 | Reaction 3 | Reaction 4 |
|---|---|---|---|---|
| Acid (wt%) | 2.60 | 2.60 | 2.75 | 2.75 |
| $H_2O_2$ (wt%) | No | 3.57 | 3.53 | 3.53 |
| Temp 1 (°C) (min) | No | 140 (60) | 143 (60) | No |
| Temp 2 (°C) (min) | 157 (180) | 157 (180) | 160 (180) | 163 (180) |

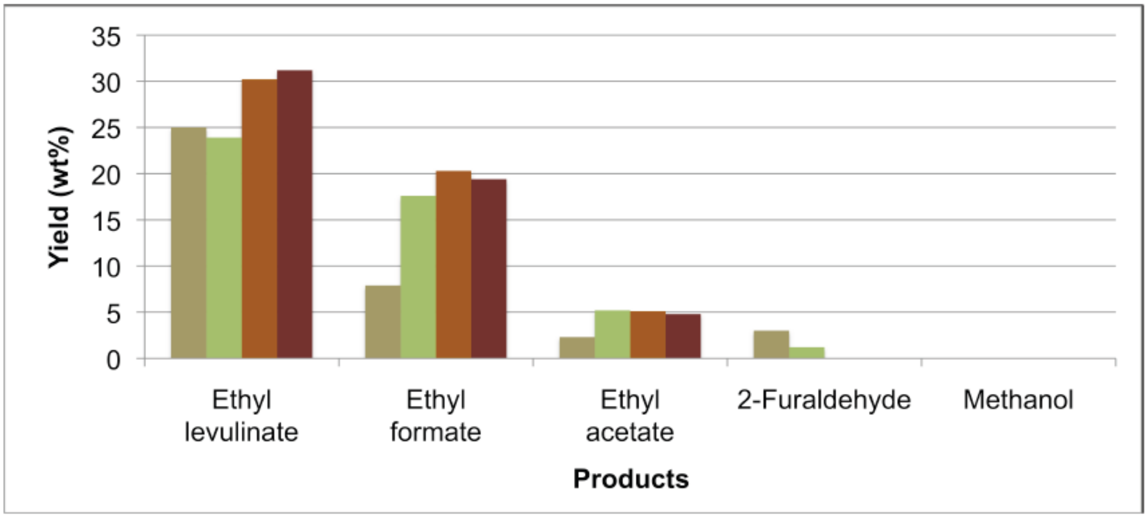


**Figure 3-9. Analysis of delignification on paper pulp**

Interestingly, as shown in the figure 3-9, methanol is not formed in any of the reactions 1 through 4 performed with paper pulp. This confirms that methanol is indeed a product that originates from lignin degradation. In sum, the delignification step is not required when using cellulosic material however the action of using an oxidative agent along with the acid catalyst demonstrated an increase in desired products. This illustrates the importance of disrupting the crystalline structure of cellulose in order to facilitate the production of desired products, as demonstrated also by the results obtained with the wood chips.

## 3.4. Effect of using Fenton Reagent on Product Yields

While experimentation corroborated the hypothesis that an oxidizing agent increased product yields, further verification and optimization of the AC3B process can be accomplished by using a stronger oxidizing agent than hydrogen peroxide. Such an oxidizing agent would be the Fenton reagent, which makes use of Iron(II) ions and hydrogen peroxide [56]. Generally, the iron acts as a co-catalyst in an oxidation-reduction cycle (figure 3-10, [63]) with hydrogen peroxide where the hydroxyl radical produced possesses strong oxidizing ability.

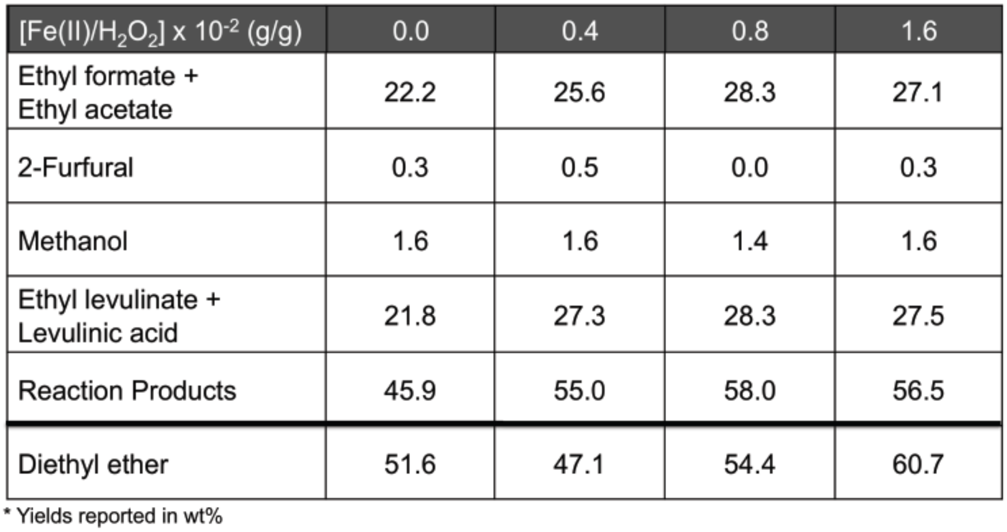
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+}$$

**Figure 3-10. Fenton reagent oxidation-reduction cycle [63]**

Experiments were performed using the direct procedure and wood chips as the starting material. The results in table 4 below demonstrate a significant increase in reaction products compared to the analogous results of hydrogen peroxide alone (in the first column). With the use of a stronger oxidizing species, the overall yield increased by roughly 12%. With 1.2 g of ferrous sulfate in 250 ml of reaction medium, the yield of ethyl levulinate is 28.3 wt% which is an increase to 97.4% of the theoretical maximum. Close to complete conversion of cellulose is attained using Fenton’s reagent.

**Table 4. Fenton reagent effect on product yields**



| $[Fe(II)/H_2O_2] \times 10^{-2}$ (g/g) | 0.0 | 0.4 | 0.8 | 1.6 |
|---|---|---|---|---|
| Ethyl formate + Ethyl acetate | 22.2 | 25.6 | 28.3 | 27.1 |
| 2-Furfural | 0.3 | 0.5 | 0.0 | 0.3 |
| Methanol | 1.6 | 1.6 | 1.4 | 1.6 |
| Ethyl levulinate + Levulinic acid | 21.8 | 27.3 | 28.3 | 27.5 |
| Reaction Products | 45.9 | 55.0 | 58.0 | 56.5 |
| Diethyl ether | 51.6 | 47.1 | 54.4 | 60.7 |

* Yields reported in wt%

Overall, the results obtained demonstrate how product yields can be substantially increased even when using minimal amount of oxidizing agent. Also, the absence or reduced amount of any environmentally harmful reagents conserves the AC3B process as a ‘green’ process.

## 3.5. Analysis of the Acid Degradation Pathways

The experiments carried out have verified that the AC3B process gives rise to the desired products and have attempted to optimize these yields. As essential as this may be, one should not neglect the importance of gaining a more profound understanding of the biomass acid degradation process. Grasping the precise nature and extend to which reactions occur underpins a confidence in the AC3B process and may eventually provide new insight into further methods of optimization. Provided that multiple competing reactions take place within a one-pot system, it is important to further recognize that the alteration of even one reaction parameter may influence multiple reactions simultaneously, thus giving rise to overlapped effects. Therefore, it is advantageous to conduct a fundamental investigation by submitting a single constituent to the AC3B process. It is important to note that the relationship observed between a single constituent, e.g. cellulose, and the products derived there from should not be directly extrapolated to biomass in general. That is, these overlapping effects may also be altered depending on the starting reactants.

### 3.5.1. Investigation of the Cellulose Degradation Pathway

In this section, investigation is done using cellulose as the starting material alone. To explore the scope of the reaction, cellulose was subjected to the direct procedure at 163°C for 3 hours as previously done with paper pulp. As aforementioned, the cellulose component of the biomass is highly crystalline which makes the conversion process quite difficult. The results shown below in figure 3-11 demonstrate that ethyl formate and ethyl levulinate are products that originate from cellulose. Also the yields shown for both ethyl formate and ethyl levulinate translate to a 1:1 molar ratio, this being in agreement with the reaction stoichiometry presented in the reaction scheme in figure 1-19. This result indicates that these products are stable in the conditions used and do not decompose into other products [46]. Another independent reaction was performed where levulinic acid was used as the starting material. The levulinic acid reached complete conversion into ethyl levulinate where no tars were formed. These results demonstrate that the products are not sources of tar formation. Interestingly, ethyl acetate is also a conversion product, to the author's knowledge, there is no mention in the literature concerning this finding. It is possible that the cellulose used was contaminated with pentose sugars [64]. However, ethyl acetate may very well be a possible product not only from the hemicellulose constituent but also cellulose. These experiments performed with cellulose confirm that ethyl formate, ethyl levulinate and possibly ethyl acetate are products that arise from cellulose.

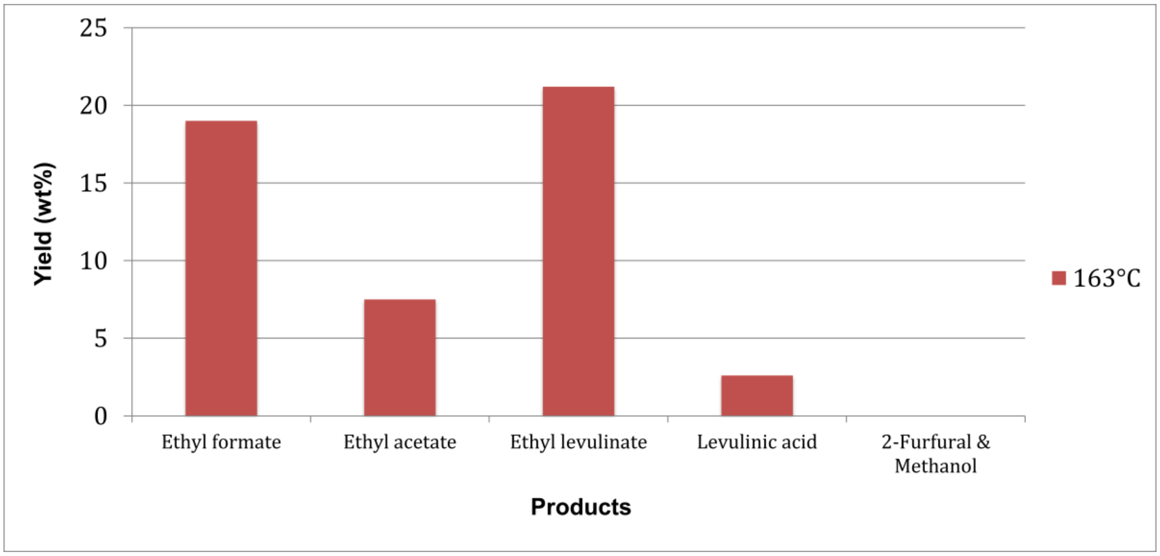


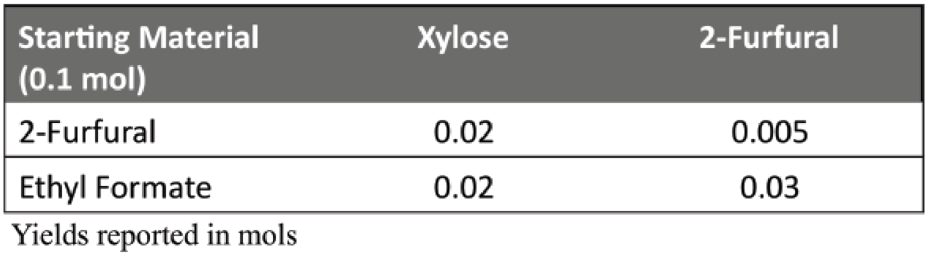
**Figure 3-11. Product yields derived from cellulose degradation**

The remaining major product not shown in figure 3-11 are large amount of tars (almost 50%). Since cellulose possesses a very rigid structure, it is reasonable to assume that a portion of the tars are formed from unconverted cellulose, or cellulose that has been partially degraded (e.g. cellobiose, cellotriose, etc.) but ultimately became incorporated into tar. That is, cellulose has not fully converted to the monomer glucoside, but remained as several smaller chains of cellulose. Another source for tar formation can be through various reversion products where intramolecular and intermolecular condensation reaction of the intermediates can occur [47]. In a later section 3.6.1, the formation of these undesired products will be limited through the use of polymerization inhibitors.

### 3.5.2. Investigation of the Hemicellulose Degradation Pathway

There is much controversy in the literature as to whether 2-furaldehyde is an intermediate in the formation of formic acid or if it remains as a final product of the hemicellulose degradation pathway. Ahmad et al. [65] have proposed that both formic acid and 2-furaldehyde are final products from xylose. The conditions used by the research group utilized low acidic deuterium oxide at 96°C. Through $^1$HNMR, they have determined that both products are derived solely from pentose carbons, and that formic acid formation did not occur via 2-furaldehyde. The Biofine process [15], previously described, reported having obtained 50 wt% of 2-furfural and not formic acid starting from pentose, the remaining product formed are tars. Antal et al. [66] also obtained 2-furfural as the final product with and also without the use of a sulfuric acid catalyst at 250°C. In all these publications, under varying conditions of temperature and acidity, 2-furfuraldehyde is reported as the final product. Interestingly, Qi et al [67] also investigated the degradation of xylose using water with the temperature ranging from 180°C to 220°C. Under such conditions and using varying reaction times, they have shown that xylose decomposes to 2-furfural which can then further degrade to form formic acid. Another recent study by Girisuta et al. [47] conducted experiments ranging from 140-200°C with 0.05 to 1 M sulfuric acid and determined 2-furfural to be an intermediate to the production of formic acid. In our laboratory this topic was addressed through the use of the direct procedure with xylose as the starting material. The results are shown in the first column of table 5. Formic acid production was measured indirectly through the quantification of its ester homologue; ethyl formate.

**Table 5. Products obtained for the hemicellulose degradation pathway**



| Starting Material (0.1 mol) | Xylose | 2-Furfural |
|---|---|---|
| 2-Furfural | 0.02 | 0.005 |
| Ethyl Formate | 0.02 | 0.03 |

Yields reported in mols

When xylose was used as the starting material, both 2-furfural and ethyl formate were recovered. This can be an indication that 2-furaldehyde is a possible intermediate, however not all of the xylose was converted to ethyl formate. There is equal mols of 2-furaldehyde as there is ethyl formate, although not shown the remaining material was converted into tars. A possible explanation of this incomplete conversion is that suboptimal reaction conditions prevented complete conversion into ethyl formate. In order to validate the results, another reaction was performed by using 2-furaldehyde as the starting material. As shown, only a small amount of 2-furaldehyde remained unconverted, and about 30% was converted into ethyl formate. This reaction does in fact suggest that 2-furaldehyde is an intermediate in the hemicellulose degradation pathway. The remaining material resulted in formation of polymerization and condensation products known as tars. It is interesting to observe that most of the product obtained from the xylose and particularly the 2-furaldehyde are tars. This indicates that a principal source of tar formation originates from the furaldehyde intermediates. This phenomena is explained further in the next section.

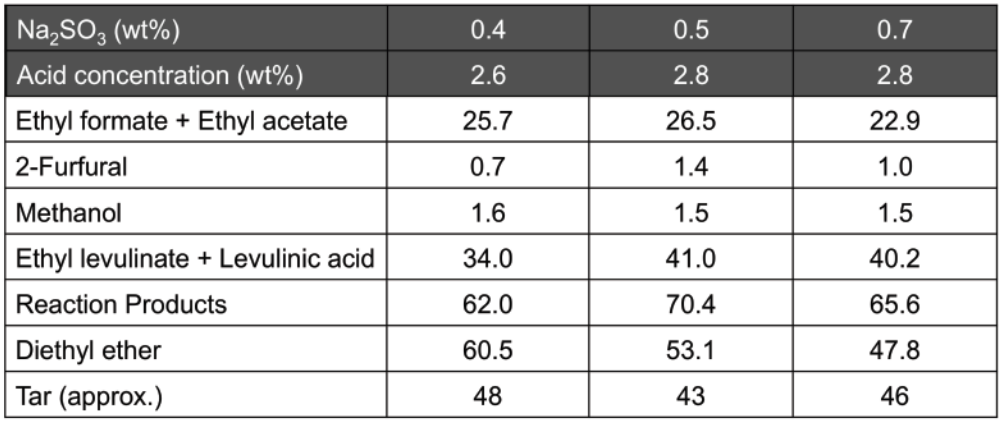
## *3.6. Reduction of Undesired Reactions in the AC3B Process*

The AC3B process is a technology used to produce biochemicals and biofuels, however, undesired products are also formed throughout the process. The goal of this section discusses the manners in which undesired reactions can be discouraged or possibly changed into a more favourable product.

### 3.6.1. Reducing Polymerization Reactions – Promoting the Formation of Desired Products

As aforementioned, much of the tar formation is a result of polymerization and condensation reactions of the furaldehyde intermediates. It is quite difficult to eliminate these undesired reactions since desired product and tar formation are competitive reactions which favour overlapped effects of the reaction parameters. The AC3B process is a one-pot process where the reactions do not occur linearly or as directly, there exists a network of cross-reactions. Furaldehydes especially can rapidly polymerize to form condensation and polymerization products [34]. This is possibly due to the furan ring undergoing electrophilic substitution [68], mainly because of the electron donating effects of the oxygen atom. Also, thermal or oxidative cleavage of the chemical bonds in the biomass leads to production of free radicals in the system [69]. Thus, at elevated temperatures the formation of polymerization reactions from furaldehydes can be easily favoured. In this vein, Samuels is a holder of a patent [70] where thiocyanates are used as a polymerization inhibitor of furaldehydes. However, the addition of thiocyanates into the AC3B process would make it substantially less environmentally friendly. Such an addition would also raise important health concerns associated with industrial application of the process. Instead, the effects of adding an alternate polymerization inhibitor, sodium sulphite [71], to wood chips are investigated. The results are shown below in table 6. The environmental and health effects of sodium sulphite are significantly moderated while also allowing for decreased polymerization.

**Table 6. Sodium sulphite effect on product yields versus tar formation**



| $Na_2SO_3$ (wt%) | 0.4 | 0.5 | 0.7 |
|---|---|---|---|
| Acid concentration (wt%) | 2.6 | 2.8 | 2.8 |
| Ethyl formate + Ethyl acetate | 25.7 | 26.5 | 22.9 |
| 2-Furfural | 0.7 | 1.4 | 1.0 |
| Methanol | 1.6 | 1.5 | 1.5 |
| Ethyl levulinate + Levulinic acid | 34.0 | 41.0 | 40.2 |
| Reaction Products | 62.0 | 70.4 | 65.6 |
| Diethyl ether | 60.5 | 53.1 | 47.8 |
| Tar (approx.) | 48 | 43 | 46 |

Yields reported in wt%

The data obtained here demonstrate a decrease of tar formation with varying amounts of sodium sulphite added. The yields reached a maximum of 70.4 wt% when adding 0.5 wt% of sodium sulphite with a corresponding minimum of tar formation with

43%. Comparing the results obtained with the addition of Fenton reagent alone (table 4), a large increase in yield of ethyl levulinate is observed, 13 wt% increase from 28.3 wt% to 41.0 wt%. This confirms the notion that polymerization reaction can be decreased thus leading to an increase in the formation of desired products. The 41.0 wt% yield of ethyl levulinate translates to a 141.1% of the theoretical maximum from the cellulose. Such a yield is due to the fact that ethyl levulinate does not necessarily originate solely from cellulose but there are also hexose monosaccharides present in the hemicellulose as well (recall section 1.3.2.2.). Characterization of the biomass should be done in order to determine the exact composition of the constituents. It is unknown at the moment the manner in which sodium sulphite can inhibit polymerization reactions [56]. It is possible that the sulphite becomes oxidized to sulfate or sodium dioxide may also be the species responsible for inhibiting polymerization. These species may react with the radicals spontaneously generated within the system. By doing so, there are less radicals available to react with the furaldehyde intermediates allowing them to proceed towards the formation of desired ester products. Therefore the decoupling of the undesired reactions is carried out with polymerization inhibitors and thus decreasing the efficacy of these reactions.

### 3.6.2. Suppressing Diethyl Ether Formation

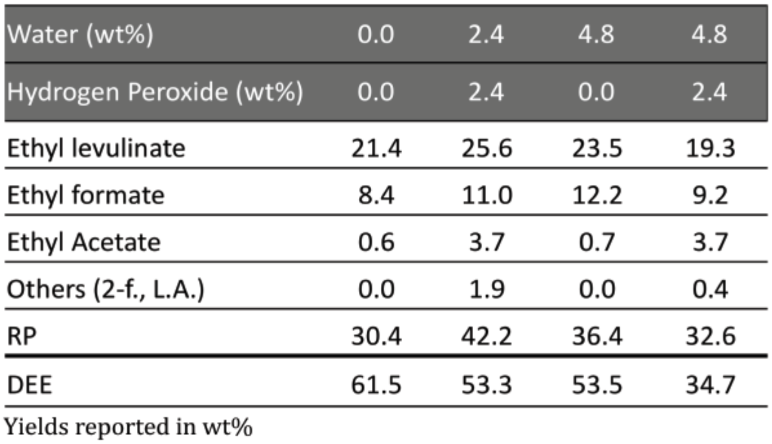
The AC3B process sees the formation of large amounts of diethyl ether through the bimolecular dehydration of ethanol. In this section focus is given to the suppression of diethyl ether formation. A first attempt was to incorporate water into the reaction medium before the reaction occurs, this may potentially suppress the equilibrium shown in figure 3-12 towards diethyl ether formation [41].

$$2CH_3CH_2OH \rightleftharpoons CH_3CH_2OCH_2CH_3 + H_2O$$

**Figure 3-12 Favouring the equilibrium toward ethanol with the addition of water**

This hypothesis was investigated using paper pulp with the direct procedure, with varying amounts of water. The results are shown in the table 7 below. By using relatively small amounts of water the production of diethyl ether was substantially reduced. More specifically, with the addition of 4.8% water, the production on diethyl ether was decreased to roughly half the amount with no significant change to the desired product yields. Regardless of this finding, large amounts of diethyl ether, 34.7wt%, remains undesirable therefore other avenues of investigation were perused.

**Table 7. Effect of the addition of water on ethanol dehydration**



| Water (wt%) | 0.0 | 2.4 | 4.8 | 4.8 |
|---|---|---|---|---|
| Hydrogen Peroxide (wt%) | 0.0 | 2.4 | 0.0 | 2.4 |
| Ethyl levulinate | 21.4 | 25.6 | 23.5 | 19.3 |
| Ethyl formate | 8.4 | 11.0 | 12.2 | 9.2 |
| Ethyl Acetate | 0.6 | 3.7 | 0.7 | 3.7 |
| Others (2-f., L.A.) | 0.0 | 1.9 | 0.0 | 0.4 |
| RP | 30.4 | 42.2 | 36.4 | 32.6 |
| DEE | 61.5 | 53.3 | 53.5 | 34.7 |

Yields reported in wt%

The suppression of diethyl ether was also studied using wood chips as the starting material along with acidic ultrastable Y (H-USY) zeolites. Briefly, H-USY zeolites are microporous aluminosilicate minerals with tetrahedral Al(III) and Si(IV) atoms connected by O atoms. A charge imbalance is created which can be neutralized by a proton, thus behaving as a Bronsted acid [72]. Since H-USY zeolites possesses acidic properties, it can have a positive effect in terms of potentially decreasing the production diethyl ether. The results, shown in table 8, illustrate the effect of adding increasing amounts of zeolites (0.0 to 10.0 g) to the reaction medium.

**Table 8. Effect on diethyl ether production using H-USY zeolites**

| amount of H-USY (g) | 0.0 | 5.0 | 7.5 | 10.0 |
|---|---|---|---|---|
| Ethyl levulinate | 15.6 | 15.6 | 14.9 | 13.2 |
| Ethyl formate | 5.4 | 5.7 | 3.8 | 4.8 |
| Ethyl Acetate | 2.6 | 3.5 | 3.8 | 4.4 |
| Others (2-f.,L.A.) | 3.3 | 5.5 | 3.2 | 2.9 |
| RP | 26.9 | 28.1 | 27.3 | 25.3 |
| DEE | 64.3 | 44.2 | 35.0 | 29.3 |

Yields reported in wt%

The presence of 10.0g of H-USY is demonstrated to have decreased the production of diethyl ether by more than half, a drop from 64.3% to 29.3%. While the production of desired products remains relatively constant as shown in the total reaction products. There are two plausible hypotheses as to how this reduction was achieved. First, the diethyl ether may be adsorbed on the acidic surface of the zeolite and rehydrated to ethanol. Second, it is also possible that the sulfuric acid in ethanol is adsorbed and reduces the rate by which ethanol dehydration occurs [23].

In both cases, that is, with the addition of water or with zeolites, the suppression of diethyl ether remains insufficient. Our research team has further investigated the problem with diethyl ether production and have successfully converted the diethyl ether into commercially valuable hydrocarbons [56].

# Chapter 4. Conclusions and Future Work

Using the AC3B process, two procedures have been developed for the production of biofuels and biochemicals; sequential and direct procedures. Yield data obtained were consistent with those reported in the literature. The sequential procedure involves two steps, first, hydrolysis using dilute acid in aqueous medium followed by esterification with the addition of ethanol. The direct procedure is carried out in a one reaction with dilute acid in ethanol medium thus favouring esterification. In terms of the energy and time requirements, the direct procedure has been demonstrated to be more advantageous. A strong correlation was observed between the yield of desired products and the amount of each structural component found within each biomass feedstock. That is, the yields arising from each structural constituent increased and decreased as a function of the structural component from which it arises; cellulose, hemicellulose and lignin.

The direct procedure has undergone a number of important optimization steps which have served to significantly increase the yield of desired products. Relative to its original counterpart, three main adjustments have been responsible for this increase. Taken together, figure 4-1 below generalizes the overall dynamic influences arising from the concatenation of these three interrelated modifications.

First, represented by effect 1 in the figure above, the addition of an oxidizing agent, in this case Fenton reagent, has been shown to increase the depolymerisation of lignin. Until recently, lignin has remained a major byproduct of technologies that convert lignocellulosic biomass into biofuels, with the author not knowing of any exceptions in the literature. In our laboratory, however, the results obtained using lignocellulosic biomass have shown that the addition of an oxidizing agent, along with the use of an acid catalyst, not only partially degrades lignin but also gives rise to valuable products, effect 2 above. In other words, the augmented levels of ethyl formate and ethyl acetate enhance the value of lignin which can significantly affect the economics of our overall process. Effect 3 is perhaps best illustrated through the delignification step that has been introduced. This step further enhances the decomposition of lignin and allows the oxidizing agent to penetrate deeper into the structure of the cell wall so as to gain increasing access to the cellulose fibrils. A significant advantage of the coupling effect has also facilitated a problematic task well known in the literature, of depolymerizing the crystalline structure of cellulose. The oxidizing agent promoted further functionalization of cellulose which made the depolymerization step possible. Thus aiding in their depolymerisation, a prerequisite for the formation of ethyl levulinate production. While effect 4 is similar to effect 3 it remains conceptually distinct in that the oxidizing agent then further serves in facilitating depolymerization of the polymer sugars. Finally, effect 5 arises from two different phenomena. First, the overall increase of yield resulting from the previous four effects serves to reduce tar formation. Second, and more notably, the addition of a polymerization inhibitor reduced tars formation. This was shown by adding varying amounts of sodium sulphite to the reaction medium. By doing so, polymerization, particularly of furaldehyde intermediates is reduced, since the radicals in the system react preferentially with sodium sulphite. Therefore these two influences decrease condensation and polymerization reactions which in turn promotes the desired reaction pathways. By doing so, the AC3B process is the first that we know of that derives products from all three constituents. The research strategy as devised by Dr. R.

Le Van Mao [56] focuses on coupling of desired reactions (oxidative cracking) and at the same time decouple undesired reactions (polymerization inhibitor) that hinder in the formation of desired products.

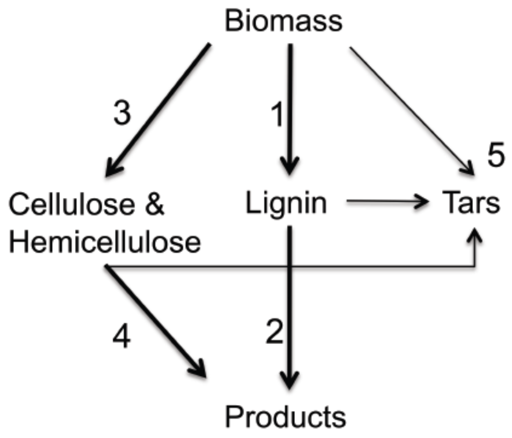


Figure 4-1. Representation of acid degradation of biomass

Throughout the development and optimization process careful attention was given to creating a 'green' conversion technology. While hydrogen peroxide and sulphuric acid are used in small amounts, the technology does not make use of any environmentally detrimental chemicals. It is also important to note that the amount of chemical energy contained in a particular feedstock is (roughly) constant and, thus, the conversion of this material into biofuels and biochemicals has an upper limit. However, the amount of energy recovered from the biomass is dependent on the conversion technology. In this light, the fact that the AC3B technology derives desired products from all three constituents is a notable accomplishment. In fact, overall yield of reaction products increased from 24.7 wt% to 70.4 wt% (this is using Fenton reagent, sodium sulphite and a delignification step).

Despite these advances important gaps remain in our understanding of the system of reactions that occur in this one-pot process. This is due to the complexity of the, as of yet incompletely understood, schema of reactions that occur. In this light, venturing to claim that all interventions introduced here worked maximally or exclusively in concert would only illustrate the naivety of the researcher. There exists a busy network of chemical reactions favouring overlapped effects of the operating parameters. More in depth investigations should be performed by manipulating the various parameters such as reaction temperature, time, catalyst acidity, solvents used, starting materials, etc. Furthermore, it may be helpful to investigate each constituent independently in order to understand the nature of their reactivity under varying reaction parameters. This would help understand the difference in reactivity when the constituents are separated compared to the biomass as a whole. Essentially, this would lead to a more fundamental understanding of the chemical and physical mechanisms that occur during the conversion of biomass. This information would provide invaluable insight into the reaction dynamics which could then be used as the basis for a more systematic optimization.

Another important avenue of future investigation includes gaining more insight into the conversion process through the development of a kinetic model [73-75]. More quantitative information that relate how the reaction conditions affect the degradation pathways would allow for better targeting of windows of maximal yield. Investigating the kinetics of the acid degradation of lignocellulosic biomass can be performed while varying the reaction parameters of the system, that is of catalyst acidity, temperature, residence time and so forth. A systematic approach by having collaboration between kinetic parameters and experimental data would excel the AC3B process optimization.

In the literature, controversy surrounds the question of whether 2-furaldehyde is an intermediate in producing formic acid or final product of hemicellulose degradation. The results obtained in our laboratory support the notion that 2-furaldehyde is an intermediate. A possible experiment that may be performed in order to confirm that 2-furaldehyde is in fact an intermediate in the acid degradation of xylose, is to terminating the reaction at different time intervals. If it is an intermediate, one would expect 2-furaldehyde to disappear as the reaction proceeds. This would also be accompanied with a corresponding increase in the formation of ethyl formate.

Another valuable consideration would be the undertaking of a life cycle assessment and sustainability for the feedstocks used [11, 17]. In order to be certain that the AC3B process, particularly the direct procedure is environmentally sound, an evaluation of the feedstocks used and the process should be performed. Performing a life cycle assessment is important in order to determine the environmental impacts related to the growing and processing of feedstock and the benefits (costs) arising from the use of the AC3B process overall. That is, in terms of overall carbon emissions, time frame needed for feedstock growth and other important factors, what advantages or disadvantages does the AC3B process have over alternate energy sources? While these important questions remain unanswered, considering the milestone reached thus far and outlined above, the author remains optimistic that this process will measure up favourably against many alternatives.

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