

Biofuels from lignocellulose

Abstract

The conversion of biomasses into biofuel has been a hot topic around the world for the past couple of decades. Lignocellulosic biomass has in recent years been at the center of much debate as a new source for biofuel. Its potential has been noted throughout a vast array of chemistry journals because of its ability to efficiently make the most out of food and biofuel as possible. Cornfields can be harvested both for food and for fuel, as the corncobs are typically thrown away as they have no use as food even though they contain a great amount of lignocellulose. This paper is focused on the conversions of lignocellulose and its derivatives through the use of green and recyclable methods and catalysts. The conversion of corncob biomass to furfural followed by its conversion into furan derivatives is one of the more promising paths to reaching new sources of energy. In particular, 2-methylfuran (MF) and 2,5-dimethylfuran (DMF) are extremely useful biofuels that have been successfully extracted in the methods.

Introduction

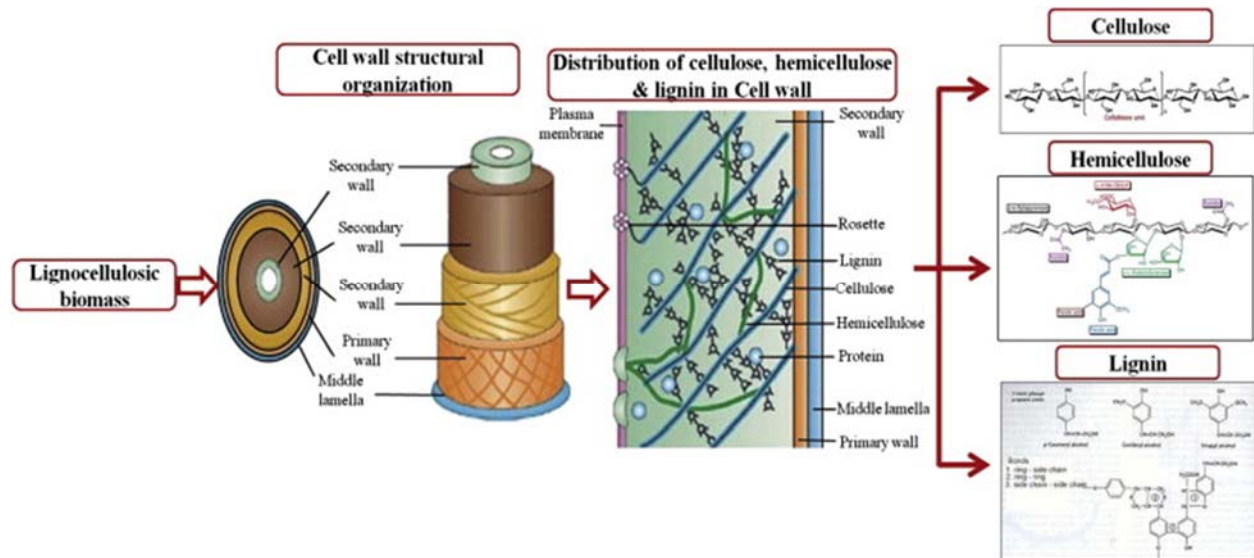


Figure 1, Illustration of the framework of lignocellulose².

Due to all of the harmful effects that traditional energy sources have had on the Earth's climate, such as negative climate changes due to greenhouse gases released from the combustion of materials (i.e. coal, gas, and oil), the study of biofuels has been heavily researched in the previous years. There is also a growing demand for alternate sources of fuel with the declining petroleum supplies the world is currently facing. While edible plant material has been refined into biofuels, the gain in biofuel results in a loss of food availability. The conversion of corn into biofuel is one such situation where food is being expended in order to produce ethanol fuel.

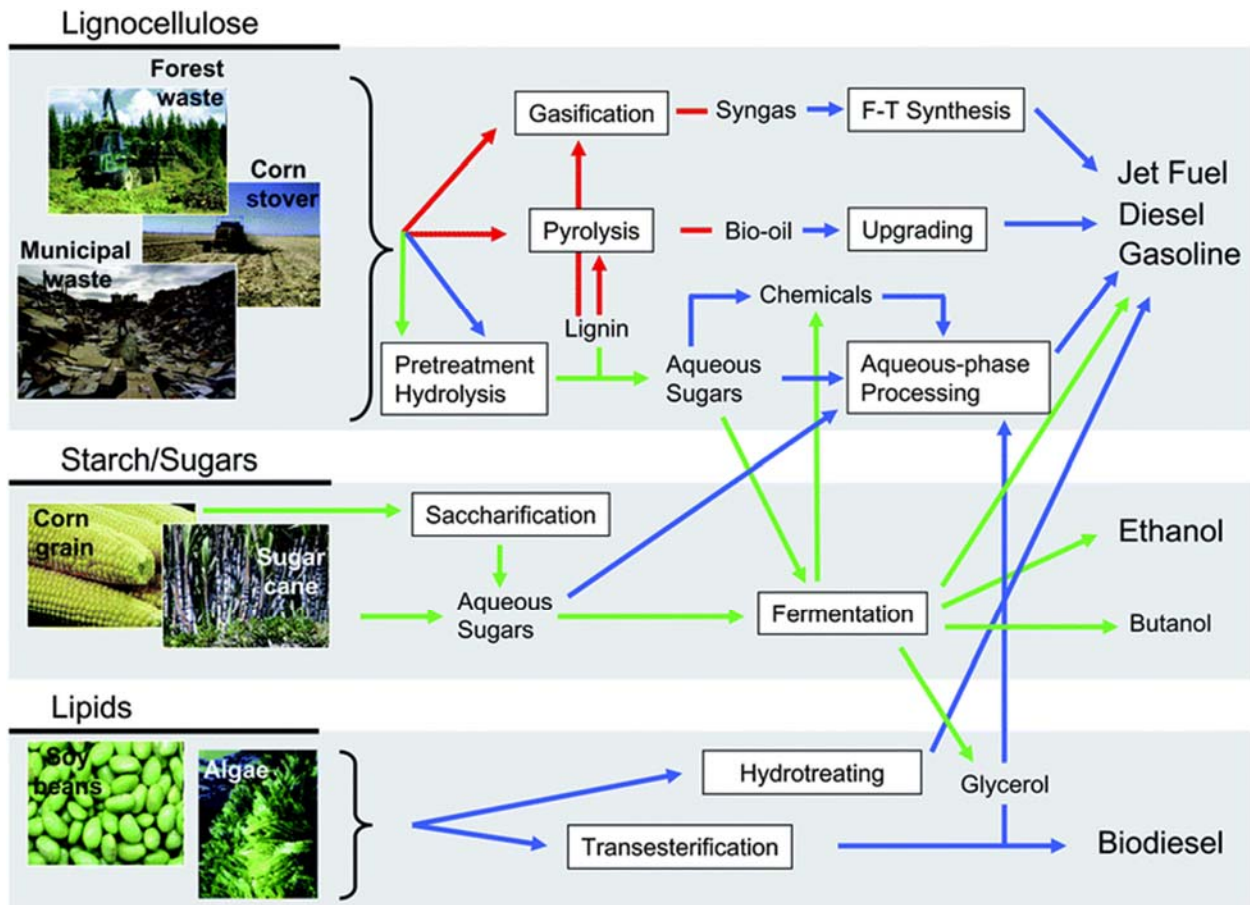


Figure 2, Routes for the conversion of biomass into various liquid fuels. Red arrows indicate thermal routes, green refer to biological routes, and blue refer to catalytic routes⁶.

Lignocellulose refers to the dry, non-edible plant material, and it is the most abundant resource for the production of biofuels. This biomass is found in the cell walls of plants. It is composed of mainly the carbohydrate polymers cellulose and hemicellulose, and the aromatic polymer lignin, the percent concentration of which vary among different plants. They can contain up to 60-70% of their weight in carbohydrates and are not used for food production. With the successful production of biofuel from lignocellulosic biomass, there would no longer be a choice between food or biofuel production. It is such a useful biomass that it can be converted into jet fuel diesel gasoline, ethanol, butanol, or biodiesel through different channels of reactions.

The issue is that the process of converting a lignocellulosic biomass into biofuel are very expensive currently. The process of converting the biofuels processed today involves hydrolysis of the starting material followed by fermentation and ending with distillation, which is where the biofuel product is formed. With lignocellulosic biomass, there is an additional step that must be undergone prior to these other steps, and that is where the bulk of the cost is. This is because lignocellulose is very stubborn as it does not easily undergo degradation due to the crosslinking of polysaccharides and lignin.

Feedstocks for lignocellulosic biofuels have been getting much deserved attention in this field. Particularly corncobs due to the fact that they are otherwise thrown away as waste and because they contain a large amount of furfural, a chemical compound that can be converted into biofuel. If hemicellulose is heated with sulfuric acid, it undergoes a hydrolysis to form xylose among other sugars. When xylose and five other sugars are reacted under more sulfuric acid and heat, it becomes furfural.

Furfural is a type of lignocellulosic biomass and refers to materials such as corncobs, oat, wheat bran, and sawdust. This particular species of lignocellulose is a focus in this report as it is directly related to feedstocks that are converted to biofuel. The chemical structure of furfural is a heterocyclic aldehyde with its formula being $C_5H_4O_2$; it has an odor resembling that of almonds and can be found in vanilla. As of 2013 statistics, 700,000 tons/year of furfural is produced worldwide. Two important derivatives of furfural are 2-methylfuran (MF) and 2,5-dimethylfuran (DMF), both of which have been studied for their usefulness as biofuels as they can be blended with gasoline at low concentrations for use in standard cars. While the production of furfural through sulfuric acid and heat has been used for quite some time, the results always

come up short of a good yield due to secondary reactions, wastewater and fume pollution from the sulfuric acid.

The United Nations Office has made it public that one of the greatest concerns for the advancement of mankind is to solve the water and sanitation emergencies. The objective of this paper is to find a successful way to convert a starting lignocellulosic biomass, particularly corncobs, into a final biofuel product through efficient and green processes. This is a two-step process. The first step is to reduce the lignocellulosic biomass into furfural, followed by the conversion of furfural into its derivatives which in turn can be used as biofuels.

Methods

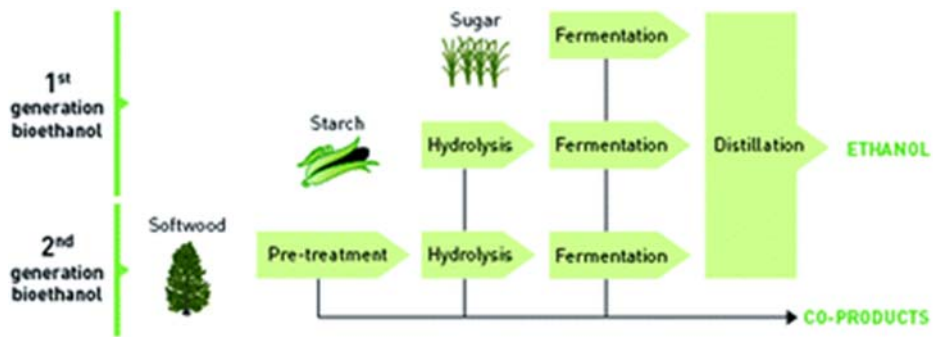


Figure 3, Conversion of first and second-generation feedstocks into ethanol via fermentation. Second generation feedstocks such as lignocellulose require the pre-treatment step⁵.

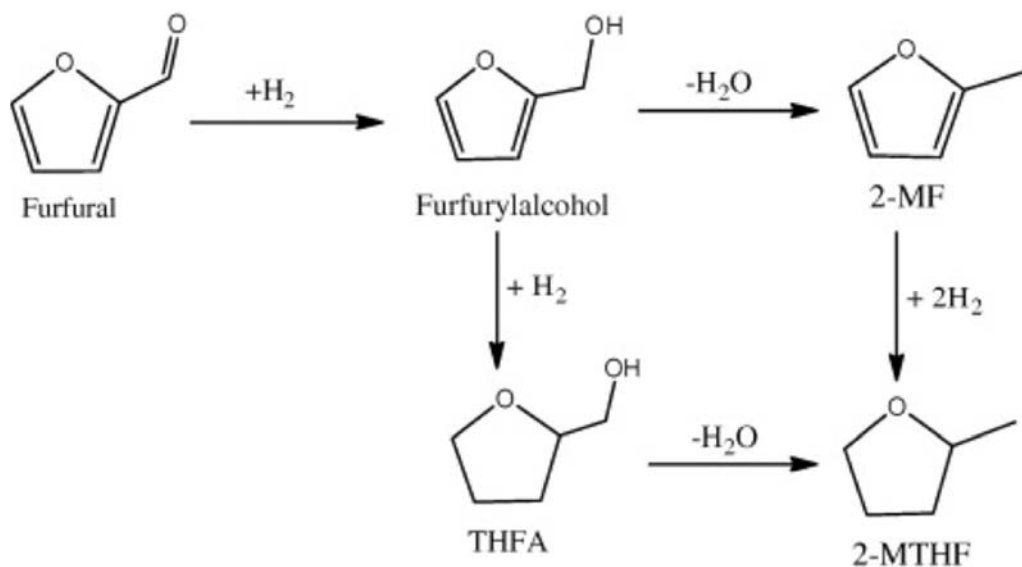
A big

issue facing

the conversion of lignocellulosic biomass into a biofuel is that the pretreatment of lignocellulosic biomass can be difficult and costly. One such method used a renewable resource, seawater, to act as a reaction medium in conjunction with 2 wt% acetic acid solution as a source of steam explosion as a pretreatment. Using feedstocks, particularly corncobs, they were able to produce great amounts of furfural from the raw material. In a semi-batch tubing bomb-reactor around 400 g of corncobs were reacted for 30 minutes with a thermocouple and pressure transducer located on the inside of the bomb-reactor to measure the temperature and pressure. FeCl₃ was then mixed

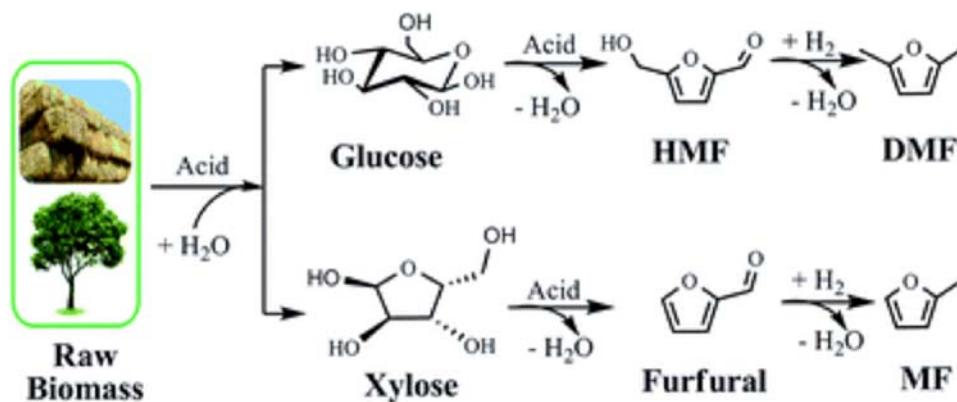
with either fresh water or seawater, depending on the experiment, and placed in the digester. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was chosen over several other acidic heterogeneous catalysts because of its superior capability of dehydrating xylose. It is also worth noting that FeCl_3 is an abundant and recyclable. Acetic acid (or in some cases furfural wastewater) was then placed inside an electric boiler and then heated to a predetermined pressure. Once at that pressure, it is continuously injected into the bomb-reactor to supply the catalyst and keep the system at a constant temperature. Through this steam distillation, acetic acid was able to extract the furfural out of the digester.

This furfural could then be used in another experiment to create MF. In order to do this, Furfural is added to an octane solvent in a micro-autoclave. Cu-Fe catalyst is then added to the micro-autoclave while the mixture is constantly being stirred. Air that is stuck inside the machine is flushed out with Argon gas before being pressurized with hydrogen gas. It was then cooled down to room temperature via water bath. Following the first filtration, which took place 30 minutes after the start of the reaction at a speed of 3000 rpm, a second filtration is performed using a polymer membrane and then dichloromethane to create a homogeneous phase.



Scheme 1, Hydrogenation of furfural to value-added chemicals¹.

Another method of extracting furan derivatives was also researched, and it has the ability of not only producing MF, but DMF as well. In this procedure, lignocellulosic biomass is placed in an autoclave similar to the previously mentioned one. This method also included the heating of the autoclave at a constant temperature while being stirred. Rather than flushing the system with argon, nitrogen gas was used. The resulting xylose and glucose were then placed back into the autoclave. After going through the same as the above mentioned process, the reaction medium was separated into an upper (organic) and lower (aqueous) phase. This was diluted with tetrahydrofuran (THF) and water. An HPLC was used to analyze the contents of the upper and lower phases.



Scheme 2, Conversion of lignocellulosic biomass to furfural and HMF and direct upgrading of them into liquid biofuels⁴.

Furfural and HMF were found to be in the upper (organic) phase. HMF could then be converted into DMF through several hydrogenation reactions using Ru/Co₃O₄ as a catalyst and THF solvent at 130°C and 0.7MPa in the autoclave. Furfural on the other hand simply needs to undergo one step of adsorption by Ru/Co₃O₄ in order to become MF.

Results and Discussion

Steam hydrolysis of lignocellulosic biofuels has traditionally been tested with fresh water, but one group of researchers decided to try using seawater as an alternative. To set base values for comparison of furfural yield among other things, corncob hydrolysis was first performed with 2 wt% acetic acid solution and fresh water at 180 °C. The resulting yield would only give around 33% of total potential furfural with 40% hemicellulose retained in the product.

The supplementation of fresh water for seawater did not improve the yields by any significant amounts, however, when concentrated (10X) seawater was used in the reaction, there was a noticeable increase in furfural yield. The yield was just below 40% for non-pre-treatment, and at around 39% when the reaction was pre-treated with steam explosion. When pre-treated with steam explosion the remaining hemicellulose diminished to only 36.32% and the remaining percentage lignin fell down to 70.39%, as compared to 85.87% remaining lignin when using

fresh water. Although these numbers indicated a direct correlation between furfural yield and concentration of seawater, the results were not as quantitative as was expected. This led to the mission of finding a suitable catalyst for this reaction.

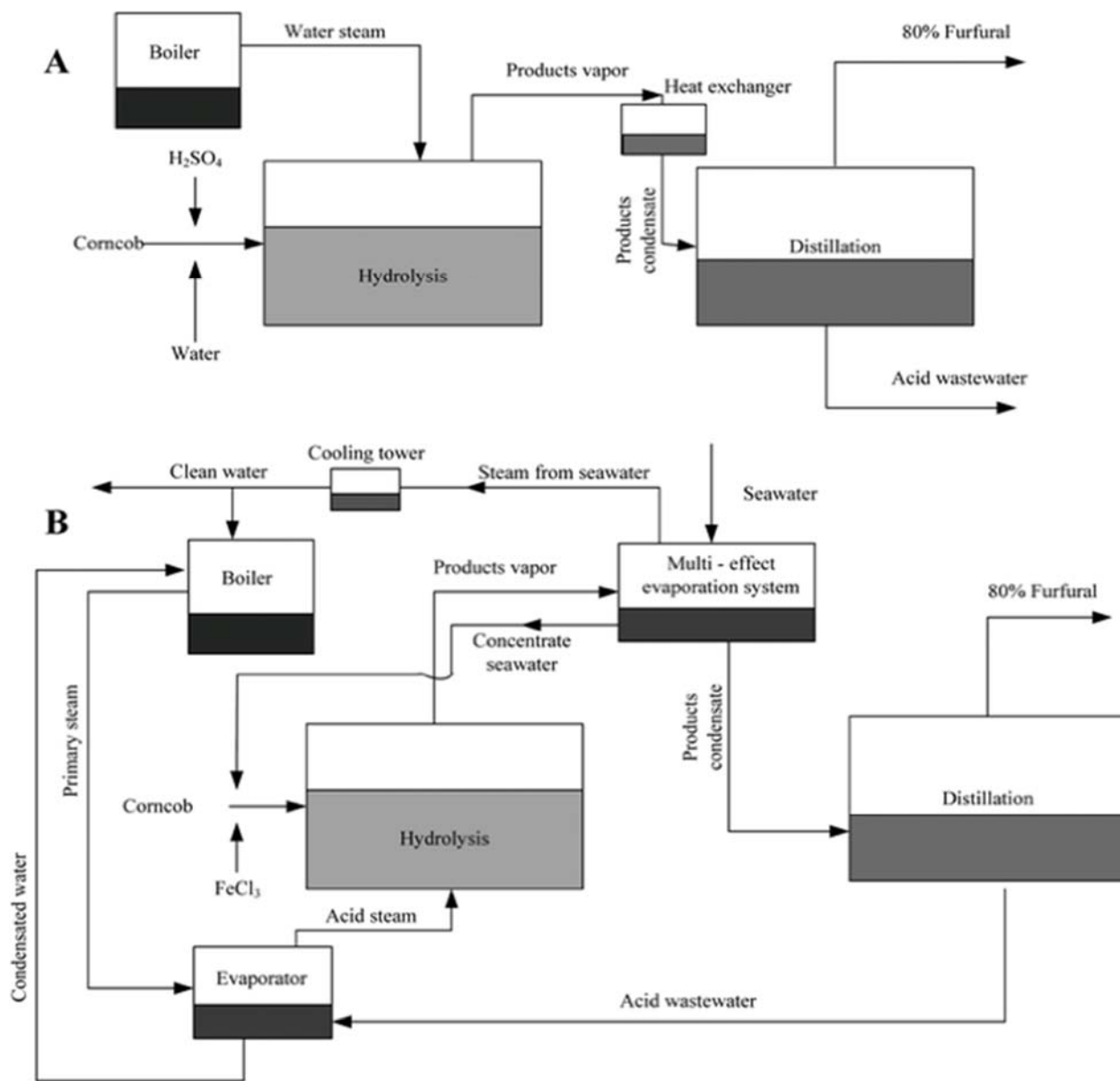


Figure 4, Conventional (A) process schematic of furfural production and conceptual (B) process with an integrated application of furfural water, waste energy, and seawater³.

With the addition of $FeCl_3$ catalyst, there was an amazing increase in furfural yield. As the temperature of the reaction was increased, there was a clear increase in furfural yield and

decrease in things such as hemicellulose, cellulose, and lignin. The exception was that at 200°C the furfural went back down in percent yield. Regular, non-concentrated seawater was used at every temperature, with its highest yield at 68.58% potential furfural recovered with no pre-treatment and 67.45% when pre-treated with steam blasting. The only greater value was found when the researchers had experimented with concentrated seawater (10X) at 190°C, where they were able to obtain around 73% furfural yield when either left without any pre-treatment or when steam blasted. In addition, the furfural wastewater collected contained around 1.98 wt% acetic acid and 0.69 wt% formic acid, and when used in replacement of the 2 wt% acetic acid gave impressive results as well. This is one of the benefits of having a renewable resource, if acetic acid is not readily available, the furfural wastewater collected can be used in place of it with only a slight difference in yield.

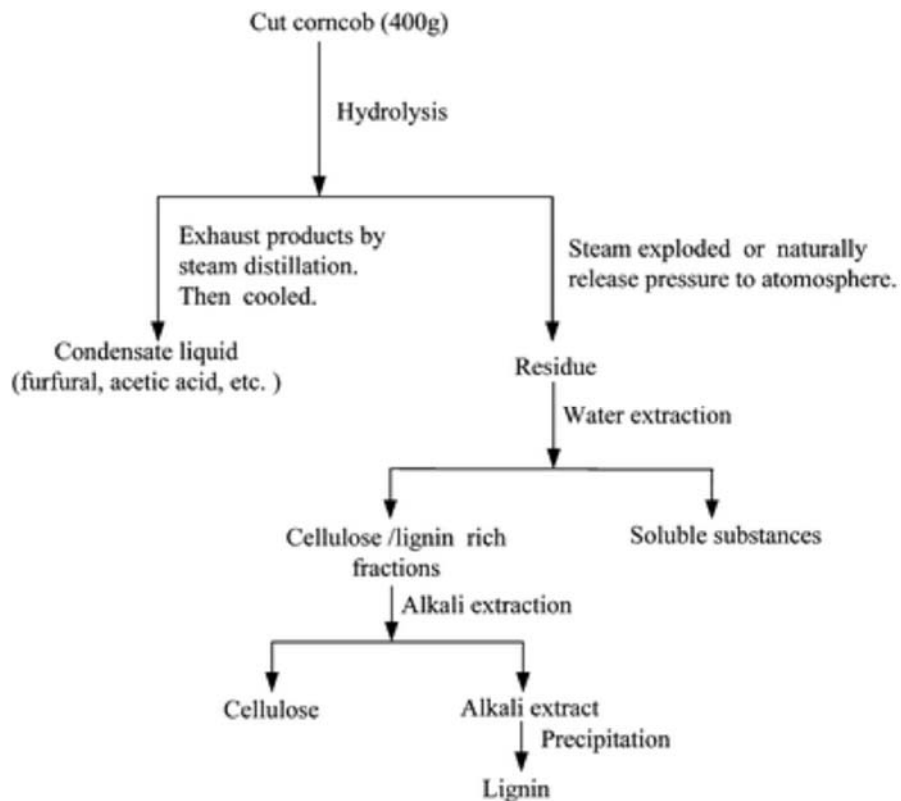


Figure 5, Flow diagram of furfural production and fractionation of the main components of steam-exploded corncob³.

The best conditions shown here for the extraction of furfural were at 180°C with regular seawater. The furfural yields were impressive and the decrease in cellulose, hemicellulose, and lignin were all significant, resulting in a furfural selectivity of over 70 in both cases [non-pre-treatment and steam explosion]. The only time that furfural selectivity was greater than it had been at the previously stated conditions was when the corncob hydrolysis was heated to 190°C but with concentrated seawater (10X) used rather than regular seawater. Due to the ease and ready availability of regular seawater, however, the former results seem to harbor some significance over the latter; that is not to say that concentrated seawater is not easy to produce, but normal seawater is always going to be available.

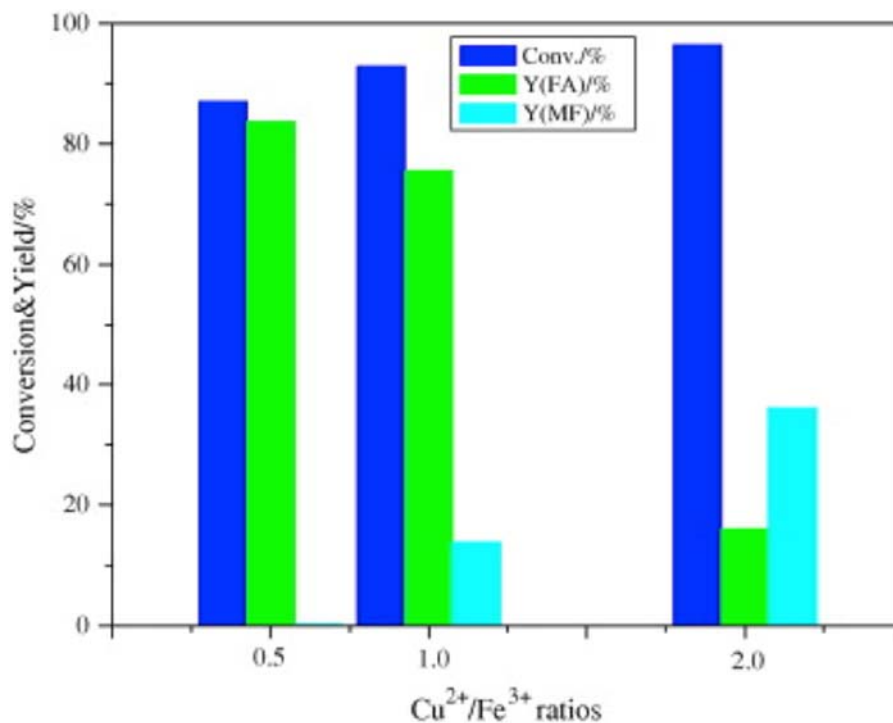


Figure 6, Catalytic performance of Cu-Fe catalysts in the hydrogenation of furfural. Conditions were held at a constant volume of 2.1 mL furfural and 5 mL, constant temperature of 200 °C, 0.2 g mass of catalyst, $p(H_2)$ of 60 bar, and a stirring speed of 1000 rpm. Note: Conv. is the conversion of furfural, Y(FA) is the yield of FA, and Y(MF) is the yield of MF¹.

Hydrogenation of furfural results in furfuryl alcohol (FA) and 2-methylfuran (MF), the product of further hydrogenation of FA. Using the eco-friendly Cu-Fe catalyst in conjunction with octane solvent and furfural. As the ratio of $\text{Cu}^{2+}/\text{Fe}^{3+}$ was altered, there was a change in FA and MF production. At a 0.5 ratio of $\text{Cu}^{2+}/\text{Fe}^{3+}$, produced 83.6% yield of FA from an 87% conversion of furfural, no significant amount of MF was produced. At a ratio of 2 $\text{Cu}^{2+}/\text{Fe}^{3+}$, the FA yield decreased to 15.9% and MF increased to 36%. When the ratio of $\text{Cu}^{2+}/\text{Fe}^{3+}$ was equal to one, 75.5% of FA yield and 13.7% of MF yield were observed with a 92.8% conversion of furfural. These changes in yields based on different ratios suggested that hydrogenation of furfural preferred to occur on the C=O group on furfural.

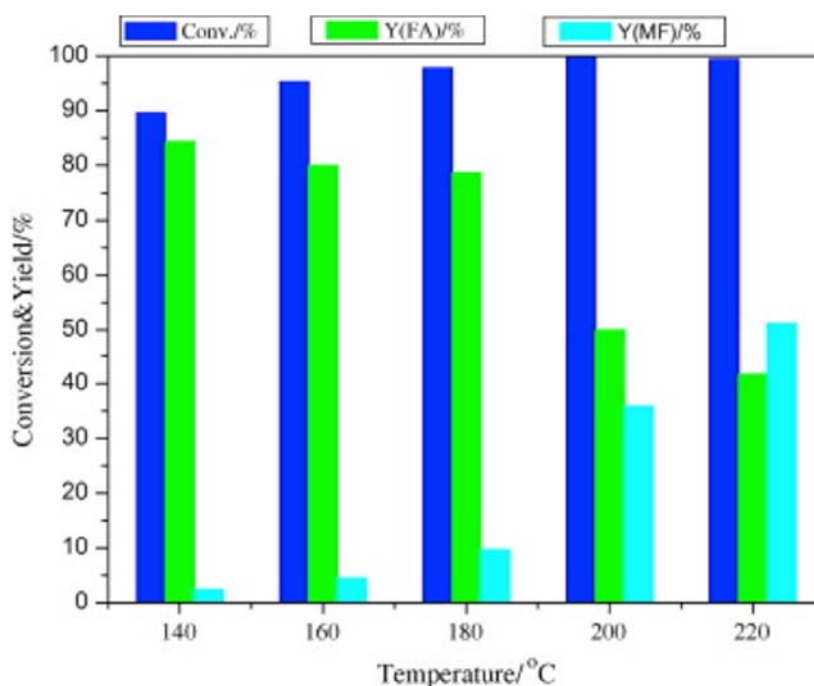


Figure 7, Reaction temperature influence on the catalytic activity under Cu/Fe ratio of 2. Many conditions remained the same as in Figure 6. The only changes were that there was now constant temperature and concentration of the catalyst, $p(\text{H}_2)$ is now 90 bars, and the reaction took 14 hours⁻¹.

As the temperature was increased towards 220 °C, the total percentage of FA and MF would get closer to total conversion of furfural as the temperature increased. At low temperature (under 180 °C), there was around a 75% yield in FA and under 10% yield in MF. When tested at 180 °C,

there was a FA yield of 78.6% and 9.7% in MF yield and a furfural conversion of 97.8%. The highest recorded temperature where furfural could still be retained rather than transformed into coke was at 220°C, and here there was a 51.1% yield in MF and 41.7% yield in FA. This is almost a complete conversion of furfural.

The conversion of furfural and HMF into furfural derivatives resulted in very efficient figures for MF and DMF, respectively. When HMF was put through the THF phase at 130 °C and 0.7 MPa H₂, there was a 93.5% recovery of DMF, the highest conversion for HMF to DMF. Other than that, there were constant high conversion rates throughout the rest of the trials that were run at 170 °C and 1.0 MPa from ~89% and above yield for both MF and DMF. The autoclave in this method was purged with nitrogen gas while the other method purged their autoclave with argon gas. This is most likely a matter of availability or preference as either gas would work to purge the system of H₂.

Conclusion

The process of converting lignocellulosic biomass is a very feasible opportunity. The integration of some of the methods that were analyzed in this paper would result in quantifiable results for the production of furfural and its derivatives. Between the integration of the first and second method versus the full process of the third method both are very efficient paths to choose from. The combination of the first two would convert corncobs into furfural followed by the conversion of furfural into MF through the use of a Cu-Fe catalyst is a great way to create biofuel. The third method involved the conversion of lignocellulosic mass into xylose and glucose, which are then converted into furfural and HMF, and these two products are finally converted into MF and DMF, respectively. The third method itself is most likely the most efficient way to go about this since it requires the same equipment and materials (for the most

part) throughout the entire process. In either case, both techniques are green, efficient, and cheap and have the potential to shift the move for biofuels into the mainstream.

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