



The Third Generation Technology of Biorefining: Dawn

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Abstract

The second-generation technologies of biorefining cannot overcome the profit obstacle. Compared with coal chemical processes or fermentation processes, these technologies have many drawbacks such as very low product yield, high energy consumption, and too much waste. The third-generation technology of biorefining can produce both liquid transportation fuels and chemicals in a way similar to that of petrochemical process. Quantitative conversion and high product selectivity are the key characteristics of the third-generation technology of biorefining, and these novel processes are unfolding in front of us.

Keywords: biorefining, lignocellulose, petro-chemical, quantitative conversion.

1. Introduction

This paper is not intended to perform a comprehensive review of all biorefining methods; there are already many such reviews in the literature. This paper will summarize the drawbacks and knots of the second-generation technologies of biorefining, then leading into an introduction of the third-generation technologies of biorefining that are unfolding in front of us.

To support the existence and living of human beings, we need food, energy and materials. In a contemporary society, human

beings produce food from the grains of plants; they derive energy from fossil carbons, and manufacture other necessary materials from petroleum oil. Unfortunately, with exponential population increases, the first-generation technologies of biorefining that manufacture chemicals and liquid fuels from food have become impractical. In addition, the huge consumption of fossil carbon has caused severe environmental pollution and global warming. On Earth Day 2012, human beings began believing that we are approaching the “Turning Point in the Fight against Global Warming.” In July, 2012, scientists confirmed that extreme weather events

are caused by man-made climate change (1). Explosive population growth shrinks the ability to sustain life on earth. The survival of human beings depends on how soon we can replace petroleum oil with regenerable resources, such as non-edible biomass. Fossil oil is considered the blood of contemporary human society, because it is the raw material of two necessities:

1. Transportation liquid fuels (energy);
2. Fundamental organic chemicals (key materials).

In light of increased demands for energy, coupled with a rapid depletion of fossil oil resources, extensive research has been carried out to identify fossil fuel alternatives, especially for renewable resources that possess the following criteria: availability, economics, acceptability, environmental and emissions, national security, technology, and versatility.

2. The first and second-generation technologies of biorefining

Unfortunately, there is no technology available for replacing petroleum oil with renewable resources. The first generation technologies of biorefining use edible resources, such as sugar, starch and fat acids. The second-generation technologies, such as thermo-chemical methods (gasification followed by SynGas transformation, pyrolysis followed by hydrogenation upgrading, and liquefaction followed by hydro-deoxygenation upgrading), and bio-chemical methods (called sugar

intermediate methods, such as cellulosic ethanol process, or butanol from pentose) cannot overcome the profit obstacle (2). Because these thermo-chemical methods were developed based on coal-refining technologies, so they have no product selectivity; and, compared with coal, biomass has much lower percentage of carbon content and a very low density. Bio-chemical methods are developed based on grain-fermentation methods, but the cost of monosaccharides made from lignocellulose is high because the total sugar content (cellulose and hemicellulose) of lignocelluloses is lower than the sugar content of grains, and breakdown of the crystal structure of cellulose is energy intensive (3, 4, 5). As the liquid products from liquefaction have high water and oxygen content, high viscosity, low pH values, and low heating values, these liquid products are corrosive, reactive, and contain too many poisons for a hydrogenation catalyst (6). Liquefaction is not considered a viable method for transportation liquid fuels. An economic analysis of all other second-generation technologies of biorefining was completed and published in 2010 (7). Technologies that produce fat through algae and microbial cultivation all need monosaccharides as the intermediary. The cost of goods is much higher than cellulosic ethanol, so these processes are represented by the methods of acid hydrolysis/EtOH and enzymatic hydrolysis/EtOH. The results confirmed my logical prediction about their profit obstacle (**Table 1**).

Table 1. Product cost and value of 2nd generation biorefining technologies

Technology	Cost of product (\$/gallon)	Selling price (% gasoline)	Potential other products
Pyrolysis	3	~50	
Gasification/EtOH	5-8	70	
Gasification/Diesel	7-10	~150	
Acid hydrolysis/EtOH	7.5-10.5	70	Acid, furfural, lignin
Enzymatic hydrolysis/EtOH	5.4-9.5	70	Lignin

The data is extracted from reference 7.

Unlike petro-chemical methods, the second generation technologies of biorefining give only

one product, either chemicals, such as lactic acid, or liquid fuels, such as ethanol. But there are

some organic materials left from bio-chemical technologies, such as lignin, organic acids, and furfural; the valorization of these organic materials, especially lignin, was proposed for solving profitable problems.

3. Modifications of the second generation technology of biorefining

Based on many experimental results and economic analyses, it is generally acknowledged that technology should produce both chemical products and transportation liquid fuels (8), similar to petro-chemical methods. The reported one-pot catalytic hydrogenation of wood consumes double the amount of methanol to produce alkanes (9), and cannot produce chemicals due to a lack of product selectivity. There are two approaches have been proposed for overcoming the profit obstacles of the second-generation technologies of biorefining.

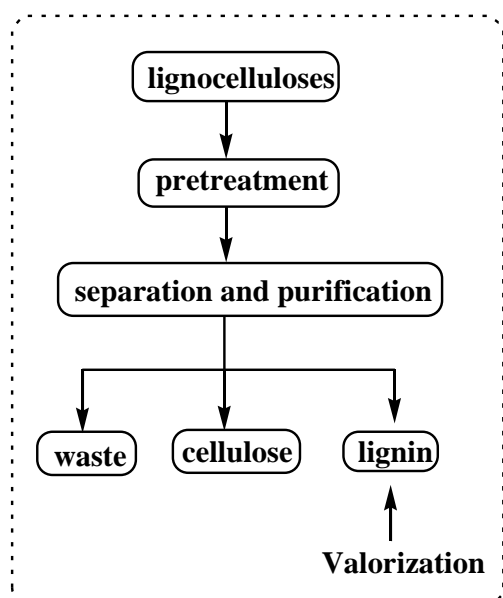


Figure 1. The first version for the modification of the bio-chemical technology

The first approach is the modification of bio-chemical methods, called an improvement of second-generation technology, or using integrated biorefineries to solve the economy through product diversity, such as proposed by USDOE (10) and Zhang (8). There are two versions of this

suggestion. One version is focused on the valorization of lignin as shown in **Figure 1**. The waste stream is not considered, because the isolation of pure chemicals from the waste stream is very difficult, and the cost of the good will be extremely high.

The catalytic valorization of lignin for the production of renewable chemicals and liquid transportation fuels, such as lignin dissolution, cracking and hydrolysis, lignin reduction and oxidation, is not profitable using the current technologies (11). A one-step conversion is needed convert lignin to small molecular aromatics or transportation liquid fuels, without significant loss of organic carbons. To make this modification profitable requires long-term R&D efforts. “Long-term” in this case means something beyond decades, requiring significant, new, fundamental knowledge and significant technological developments (12).

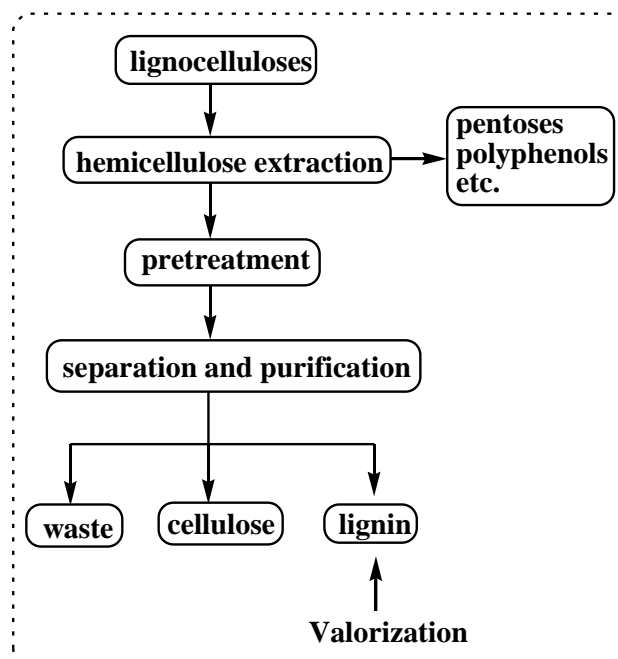


Figure 2. Hemicellulose was extracted out first for additional products

Another version of the first kind of modification is shown by **Figure 2**. In this modification, hemicellulose was extracted out first. Pentoses, such as xylose, were used for xylitol products or fermentation to produce butanol. The usage application of xylitol is narrow, including items such as chewing gum, so

the market capacity of xylitol is limited. Though the microorganism for xylose fermentation to produce butanol is not fully optimized, and it may take long time to do so, the cost of butanol is much higher than that of the petro-chemical method. The rest of the process scheme is similar to that of the first modification version. This modification cannot solve the profit challenge.

The loss of organic materials is higher than 10% for second-generation technologies. There exist more than ten percent of other organic chemicals in lignocelluloses besides lignin, cellulose, and hemicellulose. They are proteins, fats and oils; wax, acids, and alcohols; and polyphenols such as tannins, flavonoids, and quinines; starch, pectic materials, and acid soluble lignin (13, 14, 15). These organic materials went to the waste stream in biochemical refining technologies.

Extreme approaches have been carried out trying to solve the profit obstacle of the second-generation biorefining technology (Bio-Chemical method). One attempt was the genetic modification of lignin biosynthesis for improved biofuel production. This is known as an anti-evolution method. Lignin is considered as reinforcement components of the stem, similar to the steel in reinforced concrete. Plants with reduced lignin contents are fragile (lodging) and crop yields are also depressed (16).

Other approaches have to be investigated, approaches that are derived neither from coal-chemical methods nor from sugar fermentation methods.

4. The third-generation technologies of biorefining

The key step of biomass refining is the conversion of natural organic polymers into small molecular organic compounds. Small molecular organic compounds are the proper starting materials for producing transportation liquid fuels and chemicals. These chemicals are the starting materials for polymers, medicines, dyes, etc. There are several requirements about depolymerization steps for economic reasons.

1. Conservation of organic carbons should be as high as possible. The desired

scenario is that neither gasification nor black tar formation should be observed during the conversion.

2. Product selectivity is high enough for easy separation of pure compounds. Most of the current chemical manufacturing processes are developed using pure chemicals as starting materials. High purity means a high selling price, and thus high profits.
3. The cost of the conversion should be as low as possible.

To meet these requirements, we can conclude that the ideal technology will be a catalytic, one-pot, quantitative conversion of biomass into small organic molecules with good selectivity. There will be no loss of organic compounds, as all components of biomass are in one-pot; this includes proteins, fats and oils; wax, acids, alcohols; polyphenols, such as tannins, flavonoids, and quinines; starch, pectic materials, and soluble lignin. The reaction conditions have to be as mild as possible in order to avoid the gasification and black tar formation, so the cost of operation will be small. Compared with the second-generation technologies of biorefining, it will be ideal if the operation costs are similar to those of the current biomass pretreatment. Is it possible to develop such kind of technology? In theory, the proposed third generation technology is possible.

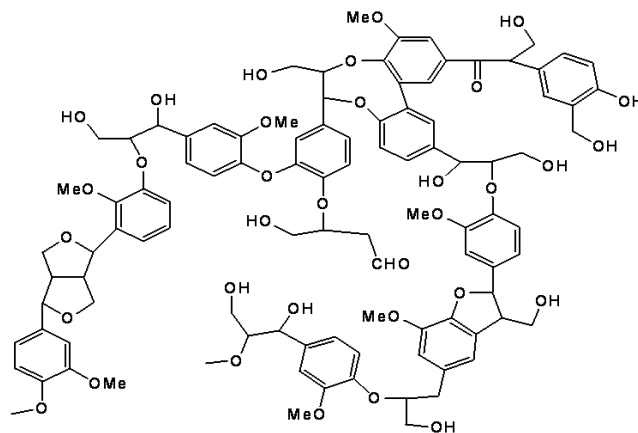
First, all organic materials of lignocelluloses can be divided into two categories: carbohydrates (such as cellulose, hemicellulose, starch, pectic materials, alcohols, acids, proteins, wax) and aromatics. Properly selected target products will be a key factor of research success.

The majority of aromatics are lignin. Lignin is one of the main constituents of lignocelluloses, an aromatic polymer of coniferyl alcohol, sinapyl alcohol, and coumaryl alcohol (**Scheme 1**). It is accounted for up to 30% by weight and 40% by energy. Considering the current product market, the expected products from lignin are small molecular aromatics, such as phenols or alkyl-substituted benzenes. Alkyl-substituted benzenes are a major octane number enhancer, and the starting materials for toluene and xylenes (**Scheme 2**). Phenol is also an important organic

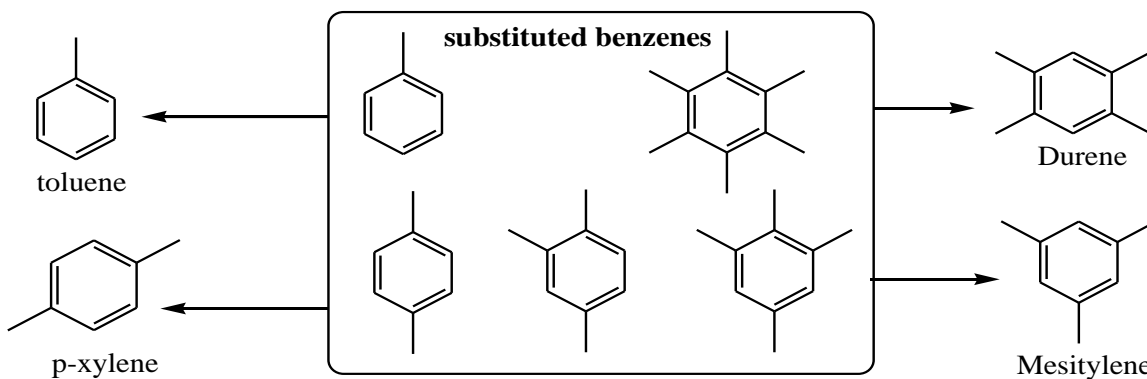
compound. The destiny of other aromatics, such as tannins, should be alkyl-substituted benzenes or phenols. These chemicals have a reduced oxygen content compared to lignin. So, removing oxygen from lignin would produce high value products.

Based on the current knowledge, organic acids are the most attractive products produced from biomass. Most organic acids are currently produced using petro-chemical processes or from sugar fermentation. Organic acids are important commodity products with broad applications in many areas. For example, organic acid esters are better solvents for paints and ink than alkane-based organic solvents, because esters are biodegradable and have excellent dissolving power (17). Esters are also better liquid fuels than ethanol; they have a higher or similar heat of combustion compared to ethanol, and they are an easier starting material with which to make anhydrous products compared to ethanol. Additionally, they are non-toxic and, unlike

ethanol, non-corrosive. Organic acids also can be converted into many useful chemicals. For example, **Scheme 3** shows the products that can be made from lactic acid using current known chemical reactions. Other minor components of lignocelluloses, such as alcohols, wax and oil, and pectic materials, can easily be converted to organic acids.



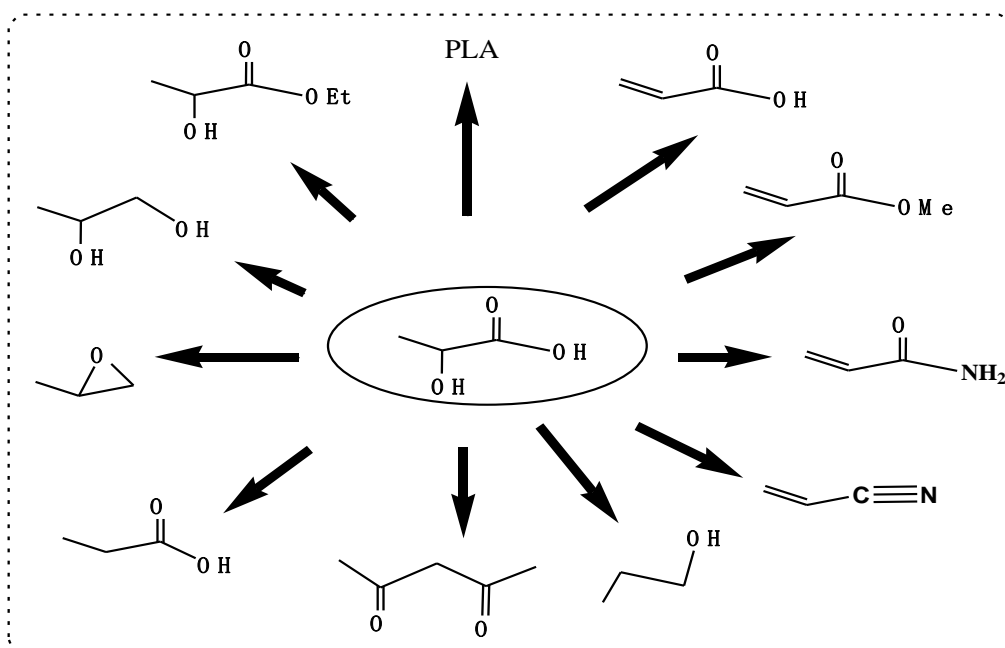
Scheme 1. Illustrated structure of lignin



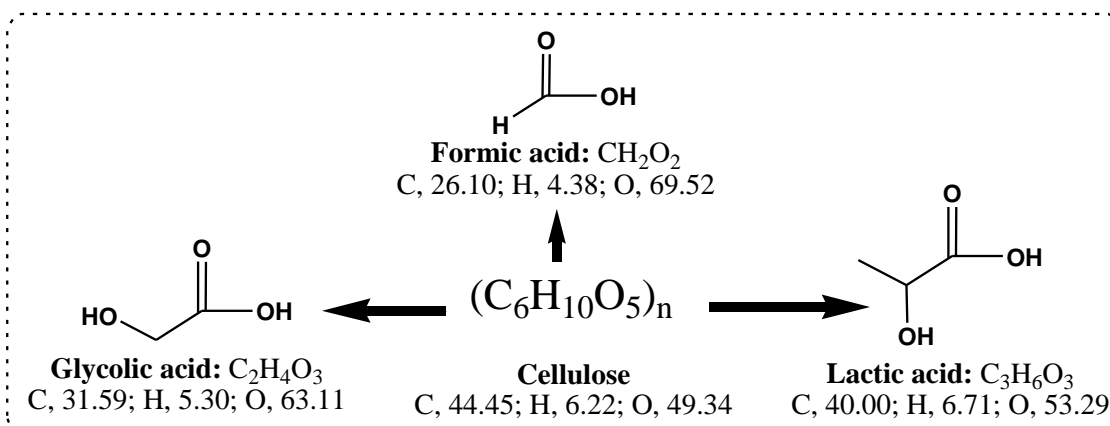
Scheme 2. Important aromatics made from substituted benzenes

From the reported literatures (18, 19, 20, 21), we have concluded that the major small organic acids derived from carbohydrates could be managed to create formic acid, acetic acid, glycolic acid, and lactic acid. These organic acids are useful organic chemicals. For example, formic acid is the precursor of hydrogen. Glycolic acid and lactic acid can be conveniently transformed into diols, and they are the

intermediates for many other organic compounds. Glycolic acid and lactic acid are also useful in specific cleaning applications, such as semiconductors, and can be converted together or separately into biodegradable polymers that have the potential to replace current plastics. Compared with cellulose, these organic acids have a higher oxygen content (**Scheme 4**).



Scheme 3. Products that can be made from lactic acid

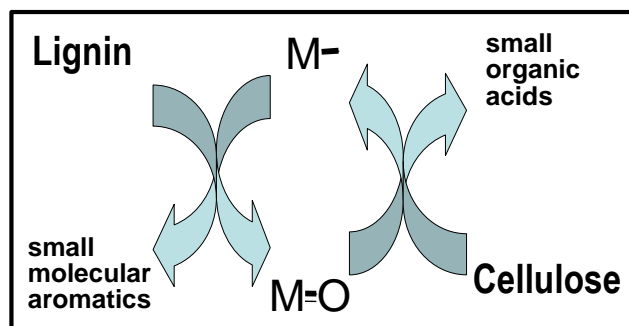


Scheme 4. Oxygen contents are increased in organic acids

Based on the oxygen content analysis, it is known that lignin has extra oxygen, and cellulose needs extra oxygen to form organic acids. If we can invent a catalytic system that could transfer oxygen from lignin to cellulose, the one-pot conversion method could be developed (**Scheme 5**). For almost all known catalytic atom transfer reactions, such as the hydrogen transfer, the reaction conditions are mild; therefore neither

gasification nor black tar formation was observed during these reactions.

If the proposed third generation technologies of biorefining are successfully developed, it is easy to separate small molecular aromatics from small organic acids. These two kinds of chemicals have great physical property differences.



Scheme 5. Possible oxygen transfer catalytic cycle

5. The Dawn

The third generation technologies of biorefining were implied by Kamm (22) and Holladay (12). The description of the third-generation of biorefining was proposed by me (23): Using lignocelluloses as starting materials, a one-pot quantitative conversion of biomass into small organic molecules with good selectivity could be used to produce high yield chemical products and transportation fuels. There is no loss of organic carbons during depolymerization. The total yield of biorefining is expected to be higher than 60%, similar to that of petro-chem methods.

This breakthrough was realized in my company (23). A possible oxygen transfer was observed for several catalytic systems that have both stable lower oxidation states and higher oxidation states, such as Fe (II) and Fe (III). The oxygen from lignin may bind with a lower oxidation state first to convert the lower oxidation state to a higher oxidation state, and then transfer oxygen from the higher oxidation state to cellulose, regenerating the lower oxidation state. One of the systems was published later, reporting that the black liquor from kraft pulp could convert biomass into simple small organic acids and small molecular aromatics with good selectivity (24). Unlike alkaline hydrothermal methods that yield a mixture of products containing more than a hundred different chemicals, this reported system provides specificity for simple organic acid products. The products formed consist exclusively of simple organic acids, such as formic acid, acetic acid, glycolic acid, lactic acid, and succinic acid, with lactic acid content up to 50%.

Comparing the manufacturing processes,

This reported process:

Lignocellulose → One-pot Hydrolysis → lactic acid (two steps)

Cellulosic ethanol process:

Lignocellulose → Pretreatment → Cellulose isolation & Purification → Hydrolysis → Fermentation → ethanol (six steps)

It was found out that the one-pot hydrolysis step is an exothermic reaction, and the cost of the One-Pot Hydrolysis step is similar to that of the Pretreatment step in the cellulosic ethanol process. So this novel method produces twice the yield of lactic acid with a lower cost of energy consumption; therefore, the conversion of cellulose into organic acids using the method reported in this study is much more economical than the cellulosic ethanol process, wherein 36.4g ethanol was the maximum yield from 125g cellulose (25). Black tar formation and gasification were only observed in the reactions without the black liquor. Asphalt-like, sticky black residue is the sign of black tar formation. A higher ending reaction-pressure than initial reaction-pressure, and the detection of gaseous small alkanes, such as methane and ethane, was used for the conclusion of gasification. In this study, three kinds of lignocellulosic biomasses were used: wheat straw as an agricultural residue example, pine wood chips (**Figure 3**) as an example of softwood, and Chinese date wood chip as an example of hardwood. The results show that all kinds of lignocelluloses that grow on land are suitable starting materials.

Lignin is a complex natural polymer that has a molecular weight from above 3000 to 30,000 (26, 27). They are too big for the active cavities of the catalysts, so they have to be depolymerized first, and then converted into useful molecules. Lignin depolymerization has always resulted in gasification or/and black tar formation causing significant loss of organic carbons (11).

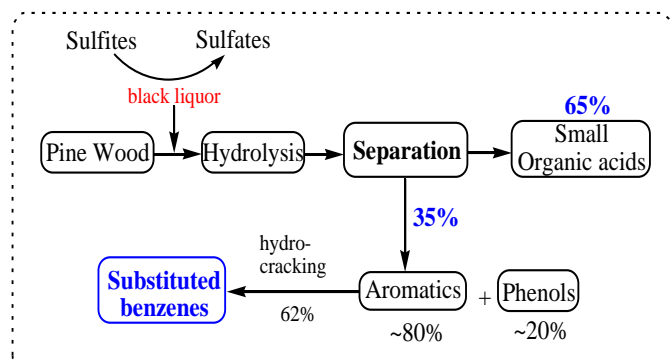


Figure 3. Mass balance from biomass hydrolysis mediated by black liquor

The result is a surprising one in our reported conversion of carbohydrates into lactic acid facilitated with black liquor. All lignin in lignocelluloses was transformed into small molecular aromatics. About 20% of them are phenolic compounds (about 36% is guaiacol for pinewood), while the rest of them are the oligomers of phenyl rings (OPR). For these oligomers of phenyl rings, more than 85% have a molecular weight less than 400Da. Compared with enzymatic mild acidolysis lignin (EMAL: C 58.2%, H 5.5%, O 36.3%) (26), lignin from black liquor (LBL: C 63.5%, H 5.5%, S 1.6%, O 29.2%), and the small molecular aromatics (OPR: C 71.8%, H 7.6%, O 20.6%) obtained from the biomass reaction facilitated with black liquor, the oxygen content of OPR dropped significantly.

Unlike all known biomass reactions, this one-pot hydrolysis reaction (facilitated by black liquor) proceeds in a very unique way. Neither gasification nor black tar formation was observed. No levulinic acid was observed, but a significant amount of formic acid was formed. The selectivity for small organic acids and small molecular aromatics does not depend on the reaction temperature, but rather the ratio of lignin over cellulose plus hemicellulose [$R = \text{lignin} / (\text{cellulose} + \text{hemicellulose})$]. The temperature dependence of the process is: observable hydrolysis occurs at a temperature higher than 190°C, and black tar formation was observed at a temperature higher than 280°C. For $R \geq 0.5$, the yield of lactic acid and phenolic compounds increased for higher R . The oxygen content of the products formed from lignin decreased significantly; meanwhile, small organic acids

have higher oxygen content than that of cellulose and hemicellulose. All these results from our reported reactions suggest a novel reaction mechanism, which is the intermolecular oxygen transfer between lignin and carbohydrates.

There are no over oxidation products (such as carbon dioxide) or over reduction products (such as cyclohexanols) observed. This suggests that the oxygen transfer between lignin and carbohydrates does not proceed via free oxygen atoms. Some chemicals in black liquor extract oxygen from lignin to form an active oxygen carrier. Meanwhile, lignin is depolymerized into small molecular aromatics with reduced-oxygen content. The fragments with oxygen attached to benzene rings are hydrolyzed into phenols, the rest of the lignin are converted to phenyl oligomers. The active oxygen carrier can oxidize sulfides into sulfates, and carbohydrates into organic acids. The formation of lactic acid may occur through an oxygen transfer from lignin, followed by a retro-aldol reaction reported in the literature (2).

Our results confirm that a quantitative conversion of carbohydrates into simple organic acid products and lignin into small molecular aromatics is feasible. The small molecular aromatics are easily converted into substituted benzene products via a hydrocracking reaction. This result is better or at least the same as the proposed one-step conversion of isolated lignin into aromatics or liquid fuels (12). In conclusion, this method is an successful example of the third generation technology of biorefining. It is the potential technology for replacing fossil oil with lignocelluloses: organic chemicals, such as small organic acids and phenols, and liquid fuels, such as substituted benzene products and esters of organic acids.

Another example of the third generation technology of biorefining has been reported this year (28). Tunsten carbide and noble metal modified tunsten carbides were used in this study. Hemicellulose and cellulose are converted into ethylene glycol and other diols. Meanwhile, some lignin is hydrogenated into phenols. Due to the interruption caused by hydrogenation, the oxygen transfer is inhibited. The authors observed that small-molecule alcohols promote the yields of

phenols. This promotion may be caused by oxygen transfer from lignin to alcohols, with the alcohol oxidized into organic acids. The leaching of metals from catalysts and the oxidation of the catalyst metals were concluded to be responsible for the catalytic activity loss. It is possible to solve the catalytic activity loss due to metal oxidation, if the metal chosen has both a stable high oxidation state and a lower oxidation state.

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