

RENEWABLE FEEDSTOCKS FOR THE PRODUCTION OF CHEMICALS

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INTRODUCTION

Many similarities exist between biomass and crude oil when compared as chemical feedstocks. Both begin as complex multicomponent mixtures. Both must be fractionated into more easily managed building blocks before conversion to products. Both require methodology for the transformation of these building blocks into useful derivatives. Biomass differs from crude oil in that it offers a *renewable* and *sustainable* source of carbon in the form of polymeric (cellulose, starch, lignin, hemicellulose, protein) and monomeric (carbohydrates, oils, amino acids, plant extractives) components. These materials could be used to supply both direct replacements for existing petrochemical raw materials and new building blocks for chemical production. Renewables could become much more important over the next 20 years should recent projections on oil production prove correct.¹

Renewable carbon is produced at a huge rate in the biosphere; about 77×10^9 tons is fixed annually, an amount that has led several projections to conclude that biomass could supply almost all domestic organic chemical needs.² Cellulose alone has an annual production of about 100×10^9 tons.³ Since 7-8% of crude oil consumption in the U. S. is used for chemicals production, incorporation of biomass as a raw material could also result in important global environmental benefits associated with a decrease in crude oil use.⁴ Moreover, the infrastructure for a biomass to chemicals industry is already starting to emerge. Currently, almost 30 billion lb/yr of chemical products are made from or contain some type of renewable component.⁵ However, the large majority of these products use renewables with little or no conversion of the structures originally found in nature. Selective and efficient separation and transformation technology for renewables significantly lags that for petrochemicals thus limiting the amount of discrete chemicals produced from biomass. Research at the National Renewable Energy Laboratory (NREL) is directed toward developing the tools necessary to make biomass as valuable a feedstock for chemicals production as crude oil.⁶

ADVANTAGES AND DISADVANTAGES OF BIOMASS AS A CHEMICAL FEEDSTOCK

The rationale for using biomass as a chemical feedstock is illustrated by several important advantages it exhibits when compared to petrochemicals.

- A huge array of diverse materials, frequently stereochemically and enantiomerically defined, is available from biomass giving the user many new structural features to exploit.
- Many products of the chemical industry are oxygenated. There are few general ways to add oxygen to crude oil derived hydrocarbons, and many of them require the use of toxic reagents in stoichiometric amounts resulting in severe waste disposal problems.⁷ Biomass is already highly oxygenated, and could be used to avoid problems with oxidation.
- Increased use of biomass would extend the lifetime of diminishing crude oil supplies.^{8,9}
- The use of biomass could be a way to mitigate the buildup of CO_2 in the atmosphere because the use of biomass as a feedstock results in no net increase in atmospheric CO_2 content.¹⁰
- A chemicals industry incorporating a significant percentage of renewable materials is secure because the feedstock supplies are domestic.
- Biomass is a more flexible feedstock than is crude oil. Crude oil is formed and its composition set by geological forces. With the advent of genetic engineering, the tailoring of certain plants to produce high levels of specific chemicals is possible.

However, several disadvantages have also been described.

- Existing economic circumstances are an important issue. A renewables based industry must be compared to the existing petrochemical industry because the products from both serve the same marketplace. The petrochemical industry

is huge and highly efficient in all stages of operation. Much of its capital investment is paid off. The mechanisms and operation of its processes are well understood and give single products of high purity. The biomass industry is still developing processes that possess these features.

- Many of the biomass sources being considered as chemical feedstocks have traditionally been used as sources of food. The justification for diverting part of this resource to chemical production has been questioned. Biomass also requires space to grow, and the environmental impact of large scale biomass plantations has been examined.^{11,12}
- Biomass is necessarily seasonal, leading to peaks and valleys in the supply of feedstock. The chemical producer using biomass needs a regular day to day supply, and must be assured that the material used at the beginning of the year will be the same quality as that used at the end of the year.
- The wide range of materials that comprise biomass could be a detriment if new processes need to be developed for each feedstock. The building blocks extracted from biomass are foreign to traditional chemical producers and must be demonstrated to function similarly to existing building blocks.

BIOMASS VS. PETROCHEMICAL REFINING

Conversion technology for biomass lags significantly behind that for petrochemicals leading to a divergence of the two industries and an understanding of the economic differences. The number of products from the petrochemical industry is much greater, and the variety of possible routes to a given product is more diverse than for biomass. To illustrate the effect of conversion technology differences, consider how biomass usually fits in the context of petrochemical refining (Figure 1).¹³

The top half of Figure 1 is an abbreviated schematic of the petrochemical industry. Refining proceeds from naturally occurring, but nonrenewable resources such as coal, oil, or natural gas, through the simplest building blocks that can be extracted, to primary chemicals, and finally, to the many products and intermediates made by the chemical industry. Conversion processes for the petrochemical refinery are nicely self-contained, and move smoothly in a "horizontal" sense (as Figure 1 is drawn) from raw materials to products.

A similar diagram can be prepared starting from renewable feedstocks (bottom half of Figure 1). The flow of materials is exactly analogous to a petrochemical refinery. The indigenous resources are lignocellulosics, grains, sugar crops, oil crops, etc., from which one again extracts smaller building blocks, and converts them into a slate of intermediates and products. However, the biomass refinery has fewer "horizontal" processes available to it for the selective conversion of biomass to chemicals. Typically, renewable raw materials proceed only a short distance horizontally (for example, from lignocellulosics to cellulose), and then move in a vertical manner to place a biomass derived building block into the petrochemical realm, i. e., components available from biomass are converted into hydrocarbons (e.g., glucose might be converted to benzene or similar). The remaining horizontal movement to end products is then carried out in the petrochemical refinery.

There is some sense to this approach. It is direct; one simply develops technology to convert renewables into building blocks already recognized by the chemical industry. The infrastructure is in place, and the technology is well developed to make these building blocks into products of importance.

This most common use of renewables (structural duplication of existing petrochemical products) is known as *direct substitution*. However, given the current supply and cost scenarios for crude oil, this use for biomass is almost always less economically favorable because of the additional chemical manipulations necessary to make biomass building blocks replicate existing petrochemical building blocks. The lack of a wide range of useful synthetic techniques unique for transforming renewables results in an uneconomical force fit of a new feedstock into an existing industry. An alternative approach known as *indirect substitution* results in a much greater "horizontal" movement through the biomass refinery. The key to this approach is a recognition that the best opportunities for use of biomass result from duplicating *properties* of existing petrochemicals rather than *structures*.

For several years, we have been studying the new synthetic methodology necessary to make indirect substitution practical and use the unique structural features and physical properties inherent in biomass derived feedstocks. We are investigating materials that can be obtained easily and in high yield from renewable feedstocks, how they are efficiently converted to new products, and determining how the properties of these new products resemble those of petrochemical derivatives.

SEPARATION: CLEAN FRACTIONATION OF LIGNOCELLULOSICS

The processes outlined in Figure 1 indicate that an efficient separation of renewable feedstocks into their individual components is necessary. To address this issue, we have developed a new refining process for wood, known as Clean Fractionation.¹⁴ This process is carried out by treating wood with a ternary mixture of methyl isobutyl ketone (MIBK), ethanol, and water, present in proportions to maintain a single phase at all temperatures of the separation process (Figure 2). The process selectively separates the wood components by dissolving the lignin and hemicellulose. The cellulose is obtained as a solid while the soluble component is further fractionated by adding H₂O, resulting in a phase separation. The lignin is found in the organic phase and can be isolated by solvent evaporation. The hemicellulose is obtained as a dilute aqueous solution.

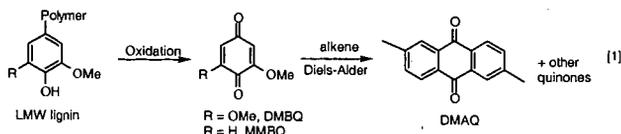
This process provides several benefits not realized by conventional wood separation technology. The single phase nature of the solution allows greater control over the lignin isolation step, and more complete lignin removal during the fractionation. At the completion of the run, the organic phase containing the lignin remains homogeneous even after phase separation. Since the solvent mixture remains as a single phase until additional water or MIBK is added, the lignin isolation step is more controlled and minimizes aggregation of lignin particles and redeposition on the cellulose.

This process offers a direct analogy to the petroleum refining process in that it efficiently converts wood into its individual constituents. Greater than 95-98% of the cellulose present in the starting feedstock is isolated after fractionation with little cross-contamination by other components. In addition, the process is self-contained, and much more environmentally friendly when compared to existing separation (kraft or sulfite) processes. Up to 99% of the solvents used for separation can be recovered and recycled resulting in reduction of downstream environmental processing of effluent. The cellulose is also more easily purified using environmentally benign processing (chlorine free bleaching) than cellulose from other wood fractionation processes.

We have investigated the use of each of these components for the production of chemicals. Some components are obtained from the Clean Fractionation process, while others are obtained from other sources. Results of these studies are described in the following sections.

LIGNIN CONVERSION: PREPARATION OF PULPING CATALYSTS

Anthraquinone (AQ) is a well known additive in the pulp and paper industry. AQ improves the performance of alkaline pulping operations while protecting the cellulose product from degradation reactions that normally occur. However, AQ is not widely used by the pulp and paper industry because of cost. We developed a process for the synthesis of an AQ-containing catalyst mixture (equation 1).¹⁵



This process is an excellent example of indirect substitution. The process starts from lignin, and through a two step chemical process yields a mixture of quinones, including dimethylantraquinone. This new catalyst mixture has been demonstrated to promote pulping at least as effectively as AQ itself. In certain instances, we have observed the activity of the catalyst mixture to be 2 times as high as AQ. Pulp prepared with the catalyst exhibits properties equivalent to pulp produced using conventional methodology. The process could also address the economic issues of AQ. If certain yield and performance targets are met, this process would be one of the least expensive methods for catalyst production known.

However, a single technical issue still exists in the first step of the process, oxidation of the lignin. While the oxidation occurs, its yield is, as yet, too low to make the overall process economically viable. Success in the first step requires that the polymeric lignin starting material, which is a heterogeneous mixture of dozens of different substructural units, be converted efficiently into a *single* material using a *single* reagent. Solution of this problem would complete the list of requirements

necessary for positioning this process as a new, commercially viable approach to pulping catalysts.

CELLULOSE CONVERSION: LEVULINIC ACID AS A PLATFORM CHEMICAL

A huge amount of waste cellulose is produced annually in the U. S. as paper sludge in pulping operations or as waste paper delivered to landfills. Several years ago, a process was developed by Biofine Corporation to convert this cellulose into levulinic acid (LA, 4-oxopentanoic acid), a material that can be used as a "platform chemical." Platform chemicals are materials that currently may have only a small market, but could be expanded to a large market if other chemicals could be produced from the platform. For a platform to be successful, it must be made cheaply enough so that its derivatives are also inexpensive. LA from the Biofine process is projected to cost as little as \$0.04 - \$0.10/lb depending on the scale of the operation. We have investigated the use of this inexpensive LA for the production of two derivatives: methyltetrahydrofuran (MTHF), a fuel additive with a huge potential market, and delta-amino levulinic acid (DALA) a broad spectrum herbicide/pesticide with a projected market of 200 - 400 million pounds/year. Our results indicate that both derivatives can be produced efficiently from LA.

A new catalytic process for MTHF production developed under this project by workers at the Pacific Northwest National Laboratory gives a 49% mass yield (66% of theoretical) in a single step. Mass yields as high as 60% (81% theoretical) are obtained with improved reactor systems. In addition, a three step process for the conversion of LA to DALA that is a significant improvement over known approaches to DALA has been developed. Each DALA process step proceeds in high (>80%) yield and affords DALA (as the hydrochloride salt) in greater than 99% purity, giving a process that is a significant improvement over other reported DALA syntheses¹⁶ and could be commercially viable.

HEMICELLULOSE CONVERSION: ISOLATION OF XYLOSE AND ARABINOSE FROM CORN FIBER FOR POLYOLS PRODUCTION

Corn fiber is an exceedingly abundant (annual production of 10 billion pounds) and inexpensive renewable feedstock available as a byproduct of the corn wet milling industry. The most abundant component is hemicellulose, which makes up about 60% of the weight of the corn fiber.¹⁷ Xylose and arabinose make up about 60-70% of the weight of the hemicellulose¹⁸ and represent an enormous potential feedstock stream for the production of chemicals. The key to the use of corn fiber as a source of xylose and arabinose is the ability to cleanly separate those materials from the remaining components in the fiber. The literature reports several methods for corn fiber fractionation using both acidic and basic media.¹⁹ However, none give an effective selectivity for the desired C5 sugars.

We have developed a separation for corn fiber that gives a stream enriched with xylose and arabinose. While this fraction is probably not yet of sufficient purity for use in chemicals production, the process has significantly reduced the number of components in the original corn fiber. The process employed exhibits mass balances typically around 75 - 85%; select runs are as high as 90%. The process achieves an isolation of C5 sugars in 30-35% yield as a dilute aqueous solution; select runs have given sugar yields as high as 40%, corresponding to recovery of almost 90% of the C5 sugars present in corn fiber. We observe that some of the sugars are still present in an oligosaccharide form, and it is important to note that our yields assume that the oligosaccharide component is all C5 sugar. Evidence has been obtained to support this assumption. If the sugar solution is further hydrolyzed after isolation, the oligosaccharide component disappears while the xylose/arabinose concentration increases. More recent work has resulted in a significant improvement in the amount of monomeric C5 sugar isolated.

The first product targets intended for manufacture from these sugars have also been identified. New catalytic transformations being carried out in partnership with Michigan State University indicates that these sugars can be selectively transformed into C2 and C3 fragments (i. e., ethylene glycol and propylene glycol).

CONCLUSIONS

These transformations of lignin, cellulose, and hemicellulose demonstrate how renewables can be used as starting templates for chemical synthesis. In considering ways to increase the use of renewables for production of chemicals, new techniques in organic synthesis, environmentally friendly processing, and catalysis, will be of great importance. Combining the use of renewable materials as sources of chemical

feedstocks with new technology will lead to processes as efficient as those currently used for the conversion of petrochemicals.

ACKNOWLEDGEMENTS

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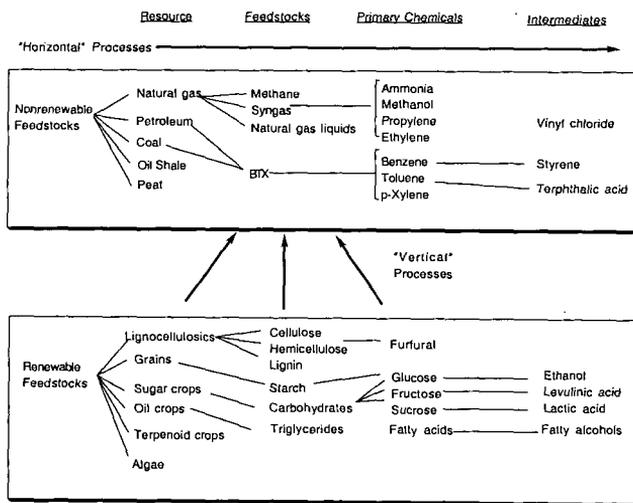


Figure 1 - Comparison of Petrochemical and Biomass Refining

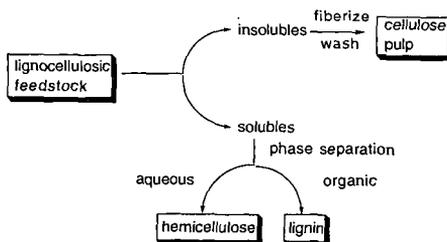


Figure 2 - Schematic of the Clean Fractionation Process