Chapter 1

Chemicals and Materials from Renewable Resources

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Abstract: A symposium entitled "Chemicals and Materials from Renewable Resources" was held as part of the ACS National Meeting in August, 1999. This introductory chapter attempts to show that a good case can be made for the use of renewables as chemical feedstocks. While economic considerations certainly play a role, greater use of renewables is primarily prevented by a lack of technology development. The breadth of technology available for high yield, selective manipulation of renewable raw materials pales in comparison to that available in the petrochemical industry. It is hoped that the papers collected in this monograph will introduce the reader to new technology available for the use of renewables, and serve as a catalyst for broader coordination of efforts in this developing field.

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The Case for Renewables

The symposium on which this book is based is certainly not the first to describe the concept of using renewables as chemical feedstocks. Well into the 20th century, renewable feedstocks supplied a significant portion of the nation's chemical needs. The chemurgy movement of the 1930s, led by such notables as William Hale and Henry Ford, promoted the use of farm products as a source of chemicals, with the belief that "*anything that can be made from a hydrocarbon could be made from a carbohydrate" (1)*. It is only in the period of time between 1920 and 1950 that we have witnessed the transition to a nonrenewables based economy *(2)*.

A vast amount of renewable carbon is produced in the biosphere; about $77x10^9$ tons is fixed annually, an amount that could supply almost all domestic organic chemical needs, currently about 7 - 8% of our total nonrenewables consumption *(3)*. When measured in energy terms, the amount of carbon synthesized is equivalent to about ten times the world consumption *(4)*. Cellulose, the most abundant organic chemical on earth, has an annual production of about $100x10^9$ tons. Lignin production by the pulp and paper industry is 30 - $50x10^6$ tons/year *(5)*. Yet our chemical feedstock supply is overwhelmingly dominated by nonrenewable carbon. Some of the largest industrial users of renewable feedstocks are the pulp and paper industry and the corn wet milling industry. However, the pulp and paper industry devotes only a small part of its production to chemicals, while the corn wet milling industry is focused largely on starch and its commercial derivatives, ethanol and corn syrup. Given such a plentiful potential source of chemicals and products, what are the barriers that stand between the promise of renewables and their wider use by the chemical industry?

Several advantages are frequently associated with renewables:

- The use of biomass has been suggested as a way to mitigate the buildup of greenhouse CO_2 in the atmosphere *(6)*. Since biomass uses CO_2 for growth through photosynthesis, the use of biomass as a feedstock results in no net increase in atmospheric CO_2 content when the products break down in the environment *(7)*.
- It is generally acknowledged that increased use of biomass would extend the lifetime of the available crude oil supplies. The Royal Dutch/Shell group has developed several scenarios for the impact of biomass on chemicals and fuel production. One scenario projects a biomass market in the first half of the 21st century of $150 billion/year, with up to 30% of worldwide chemical and fuel needs supplied by renewable feedstocks in the same time period *(8,9)*.
- A chemical industry incorporating a significant percentage of renewable materials is more secure because the feedstock supplies are domestic, leading to a lessened dependence on international "hot spots". The 1991 and 1996 events between Iraq and the U. S. and the immediate response of the oil

futures market is a graphic example of the hazards associated with dependence on politically unstable regions for crude oil supplies.

- Biomass is a more flexible feedstock than is crude oil. Crude oil is formed and its composition set by geological forces. The diversity of building blocks from biomass offers a great opportunity for the production of a range of chemicals as wide as that available from nonrenewables. With the advent of genetic engineering, the tailoring of certain plants to produce high levels of specific chemicals is also possible.
- Building blocks isolated from crude oil are not oxygenated, yet many of the final products of the chemical industry are. Biomass derived materials are often highly oxygenated. There are few general ways to add oxygen to hydrocarbons, and many of them require the use of toxic reagents (chromium, lead, etc) in stoichiometric amounts resulting in severe waste disposal problems *(10)*.

Moreover, increased use of renewable feedstocks could address other, broader issues:

Feedstock Needs Globally - Recent work has attempted to model when world oil production will peak *(11)*. This work, based on methodology developed in the 1950s for predicting U. S. oil production, projects that global production will begin to decline sometime in the next 5 - 10 years. The earlier work accurately predicted the decline in domestic oil production that occurred in the mid 1970s. Demand will not decrease in line with production. U.S. energy consumption has increased by more than 28 percent (about 21 quadrillion btu) during the last 25 years, but more than half of the overall energy growth of the last 25 years (about 11 quadrillion btu) has occurred during the last 6 years *(12)*. Other feedstock sources will be needed.

Domestic Energy Consumption - The U. S. annually consumes about 94 quads of energy *(12,13)*. Of this 94 quads, 35 are used by industry, and almost 8 quads are used in the production of chemicals and paper. This is a significant energy target, and one that could be addressed by a greater use of renewables.

These potential benefits would seem to indicate that renewables hold promise as a feedstock complementary to those used by the chemical industry. *Why isn't renewable carbon in its many forms (cellulose, lignin, monomeric and oligomeric carbohydrates, oils, terpenes, etc.) more widely used as a chemical feedstock?*

An answer to this question must begin with an economic comparison. Certainly the primary driver for greater domestic use of renewable feedstocks is cost because it will be the chemical industry that needs to be convinced of the value of renewables. That argument is only won by favorable economics. As shown in several studies, not all renewables-based materials are reasonable targets for biomass based processes, primarily for economic reasons *(14)*.

However, a number of polymeric (cellulose, lignin) and monomeric (carbohydrates: glucose, xylose; other materials: levulinic acid) materials are available at production costs that make them comparable to many nonrenewable raw materials *(15)*. Strong cost competition would exist from the simpler nonrenewable building blocks; it is difficult to beat ethylene at $0.16/lb. However, many examples exist of low cost, readily available renewable building blocks that could be incorporated into the domestic feedstock supply stream. A cost argument is not sufficient to render renewables unattractive as feedstocks. Table I summarizes some sales or production costs of a few typical renewable building blocks (depending on the source, the costs are current as of 1995-1999).

Table I - Costs of Some Selected Renewable Feedstocks

Material	$/kg	$/lb	Cost Type	Source
Polymers				
Cellulose	0.44 - 1.10	0.20 - 0.50	Production	3
Lignin	0.07 - 0.13	0.03 - 0.06	Production	Fuel value
Carbohydrates				
glucose	0.60 - 1.10	0.27 - 0.50	Sales	1
	0.13 – 0.26	0.06 – 0.12	Production	3
xylose/arabinose	0.07 – 0.13	0.03 – 0.06	Production	3
sucrose	0.40	0.18	Sales	2
lactose	0.65	0.30	Sales	2
	0.50 – 1.50	0.23 – 0.68	Sales	1
fructose	0.90	0.41	Sales	1
sorbitol	1.60	0.73	Sales	1
Other				
Levulinic acid	0.18 – 0.26	0.08 – 0.12	Production	3

1. M. Bols, "Carbohydrate Building Blocks", Wiley-Interscience, New York (1996)
2. F. Lichtenthaler and S. Mondel, *Pure Appl. Chem.*, **1997**, *69*, 1853.
3. Range of estimates from discussions with various industrial sources.

One must also examine possible barriers in the overall production of chemicals. However, there are some interesting similarities between the renewables and petrochemical industries. Both face the same three general issues for producing chemicals. First is an issue of supply. Both industries need to know the source of their feedstock, its lifetime, and methods for its removal from the structures in which it is found. Second, both industries must face issues of separation by determining what components are present in the feedstock and how these components are separated from one another. Finally, both industries face the issue of conversion. Once the building blocks are removed from the feedstock, they must be converted to products. Of these three areas, issues of supply and separation are generally understood for both renewables and petrochemical refining.

Technology Development Issues

Thus, we are left to examine the differences in issues of conversion. What stands between the concept and realization of a vibrant renewables to chemicals industry is *technology development*. The world understands and can manipulate existing nonrenewable feedstocks. In contrast, the level of technology development for similar manipulation of renewables lags far behind. Where nonrenewables particularly excel in comparison to renewables is that understanding of nonrenewables is much greater at a *molecular* level. The nonrenewables industry has gained amazing control over the behavior of their primary building blocks. Efficient functionalization and rearrangement of their primary building blocks is a cornerstone of the industry. And importantly, these transformations are achieved selectively (i. e., without the formation of unwanted byproducts) and in very high yield (i. e., all of the starting feedstock is converted into the next product) *(16)*.

In contrast, the analogous use of renewables suffers from a much narrower range of discrete building blocks, fewer methods to convert those building blocks to other materials, a lack of fundamental understanding of how to convert starting raw materials (lignin, carbohydrates, oil crops, protein, biomass polymers, etc.) into single products in high yield, and a lack of information about the properties and performance available from those products. We are faced with the puzzle of possessing an almost limitless source of raw material in the United States, while being unable to effectively convert it to a wide range of useful products.

It was in this context that the symposium was organized. The hope was to attract participants that could speak to this technology gap, and describe new research that would address the shortcomings renewables currently face. What are the new building blocks available from renewables? What properties do they exhibit? How does one selectively transform biomass polymers into single products? What is known about the mechanisms of these transformations? What new methodologies hold promise for improving the utility of renewables? How can synthesis introduce desirable structural features into renewable building blocks? How can the structural features inherent to renewable building blocks most effectively be used?

As a result, a broad range of topics was covered at this symposium, reflecting the diversity that currently exists in this field. Yet the symposium could have been much broader: a truly comprehensive symposium on renewables could have included topics such as agricultural practices, new genetic engineering techniques for plants, biofuels, modern separation techniques, marketing, engineering of renewables-based processes, education, and a wide range of other related disciplines. But to keep the program manageable, the organizers decided to focus as closely as possible on new building blocks and materials that can be derived from renewables. We were particularly interested in papers that improved understanding of renewables at the *molecular* level. When phenomena are defined and understood at a molecular level, control of processes is a result. Process control and understanding allow for the effective design of molecular structure for function, for example, the production of a new polymeric material, or new commodity chemical with new properties.

Overview of Papers

In the following chapters the reader will find: 1) overview material; 2) novel monomeric building blocks; 3) biochemical processes; and 4) new polymeric materials. Even with a program limited to these four topics, the organizers received some comments of concern regarding the content of this symposium, since it seemed to lack a clear focus. This is certainly a danger. However, at this stage in the development of the renewables industry, we felt the intent should be to provide a sampling of several areas, with focus on specific topics of interest to be used in future symposia.

Part 1 - Overview material

The first paper in the book is included as an important contrast to any unwarranted renewables fervor. The contribution by Gerngross describes the need for careful life cycle analyses and shows how renewables should not automatically be assumed to be good, just because they are "green". The production of PHAs in comparison to polystyrene is used as an example. The following chapter by McLaren presents a general vision for renewables, based on the Vision 2020 process being used by the U. S. Department of Energy.

Part 2 - New chemicals and intermediates. Chemical processes and mechanism.

This section describes several new building blocks available from renewables, and how those building blocks can be converted by chemical processes into other materials. The contributions by Moens and Olson describe new uses for levulinic acid, an important renewable building block available inexpensively from cellulosic wastes *(17)*. Kiely's paper on carbohydrate diacids describes approaches to selective glucose oxidation, the preparation of new polymers made from oxidized glucose, and where these materials might find use in the chemical industry. Witczak overviews uses of levoglucosenone, an interesting renewable building block available from starch pyrolysis. The paper describes some of the important structural details that control its reactivity, and presents the chemical details and the utility of new technology. The paper by Gandini reports the author's work in converting furans, available from renewable feedstocks, into new polymeric materials. Gravitis discusses how furfural and levoglucosan can be prepared and isolated from biomass as novel renewable building blocks using new tandem catalysis technology. The contribution from Brown describes recent work in biomass pretreatment technology to improve the production of levoglucosan, a building block that is on the verge of becoming a large scale fine chemical intermediate.

Part 3 - Bioprocesses/Biotechnology

The use of biotechnology to convert fermentable sugars into chemicals is certainly one of the most rapidly growing areas of the chemistry of renewables. Frost's paper describes work carried out on understanding and tailoring components of the shikimic acid cascade, and how this work will lead to a wide range of chemicals from one of the key intermediates, dihydroshikimate. The contribution from Baker describes approaches to and properties of new polylactides, of particular current importance with the planned commercialization of a polylactic acid process by Cargill Dow Polymers. Finally, Nghiem's paper presents details on the development of a bioprocess for producing succinic acid, and how it has gone from a laboratory scale program to planned commercial development.

Part 4 - New Materials from Renewables

Two papers point to the use of renewables in the production of interesting polymeric materials based on renewables. The contribution from Kelley describes a model compound study on the reactivity of pyrolysis oils, and how this information can be used in the formulation of new renewables based adhesives. Glasser describes the use of steam explosion technology to facilitate the simultaneous production of lignin and cellulose esters, useful in the production of thermoplastic structural polymers from wood.

Conclusions

It is hoped that the reader will view this collection of diverse topics as a starting point to stimulate greater interest in the field. Obviously, a key component for fully developing this field will be the willingness of funding agencies to support such work. As pointed out by Lichtenthaler:

"The prospects are promising, if one is prepared to generously invest into basic research...research can be planned, results cannot (!). Thus, the only other thing then needed is patience - patience until the "fruits" from renewables, in upgraded, value added form, can be harvested."*(18)*.

As workers in the field, we hope someone is listening.

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