The Use of Renewable Feedstocks for the Production of Chemicals and Materials - A Brief Overview of Concepts

Joseph J. Bozell
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

Visions

"The U.S. is the Saudi Arabia of carbohydrates."

David Morris, Institute for Local Self Reliance

"Moving from an economy based on geology to one based on biology."

USDA

"Changes that will have effects comparable to those of the Industrial Revolution… are now beginning."

Phillip Abelson, Science

DOE Strategic Goals for the Use of Renewable Feedstocks

- Dramatically reduce, or even end, dependence on foreign oil (a *displacement* and *energy* component)
- Spur the creation of a domestic bioindustry (an *enabling* and *economic* component)
- Integration of chemicals with fuels will simultaneously address both goals.

The Biorefinery is Flexible

Inputs (Supply)

Corn
Potatoes
Sorghum
Soybeans
Apple pomace
Jerusalem artichoke
Guayule
Beet molasses
Sugar cane
Wood
Residues

→

Building blocks (Separation)

Starch
Cellulose
Lignin
Other Carbohydrates
Oils

→

Outputs (Conversion)

Butadiene
Pentanes, pentene
BTX
Phenolics
Organic acids
Furfural
Resorcinol
Levulinic acid
Levoglucosan
Peracetic acid
Tetrahydrofuran
Anthraquinone
Sorbitol

Advantages to Biomass Feedstocks

- Lowered demand for diminishing crude oil supplies
- Sustainability
- Recycling of CO_2
- Lessened dependence on politically unstable nations for feedstock supply
- New types of complexity in building blocks
- Flexibility through biotechnology/bioprocessing as a growth industry

Projected Raw Material Costs

	Oil	Natural Gas	Coal	Corn	Lignocellulosics
$/dry tonne	**129** ($17.5/barrel) **94** ($12.7/barrel) **44** ($6/barrel)	**122** ($2.50/1000 scf)	**33**	**98** (kernels, $2.50/bushel) **19** (stover)	**44** (poplar, switchgrass)
$/GJ	**3.1** ($17.5/barrel) **2.3** ($12.7/barrel) **1.2** ($6/barrel)	**2.3**	**1.0**	**5.0** (kernels, $2.50/bushel) **1.0** (stover)	**2.3** (poplar, switchgrass)

L. R. Lynd, C. E. Wyman, T. U. Gerngross, *Biotechnol. Prog.*, **1999**, *15*, 777

Feedstock/Building Block Costs

Material	$/kg	$/lb	Source
Polymers			
Cellulose	0.44 - 1.10	0.20 - 0.50	Industrial sources
Lignin	0.07 - 0.13	0.03 - 0.06	Fuel value
Carbohydrates			
glucose	0.60 - 1.10	0.27 - 0.50	1
	0.13 - 0.26	0.06 - 0.12	NCGA estimate
xylose/arabinose	0.07 - 0.13	0.03 - 0.06	NCGA estimate
sucrose	0.40	0.18	2
lactose	0.65	0.30	2
	0.50 - 1.50	0.23 - 0.68	1
maltose	2.69	1.23	2
fructose	0.90	0.41	1
sorbitol	1.60	0.73	1
Other			
Levulinic acid	0.18 - 0.26	0.08 - 0.12	Industrial sources
α-pinene	5.50	2.50	Chemical Marketing Reporter
β-pinene	6.38	2.90	Chemical Marketing Reporter

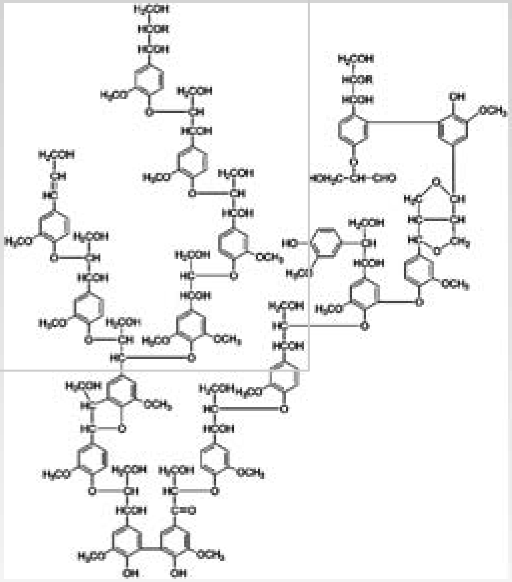
[1] M. Bols, "Carbohydrate Building Blocks", Wiley-Interscience, New York (1996)
[2] F. Lichtenthaler and S. Mondel, *Pure Appl. Chem.*, **1997**, *69*, 1853.

Meeting the organic chemical needs of North America from petrochemical raw materials

Chemical	Annual production (10^9 lb)	Location/source/ year	Include in evaluation?
Ethylene	61.4	NA/CEH/2001	x
Propylene	32.7	NA/CEH/1998	x
Ethylene dichloride	30.3	NA/CEH/2002	No Š from ethylene
Benzene	20.4	NA/CEH/2002	x Š first evaluation only
Vinyl chloride	16.9	NA/CEH/2002	No Š from ethylene
Ethylbenzene	15.9	NA/CEH/2002	No Š from benzene
Styrene	14.0	NA/CEH/2000	No Š from benzene
Methanol	9.77	NA/CEH/2001	x
Xylene	13.8	NA/CEH/1999	x Š first evaluation only
Formaldehyde	11.4	NA/CEH/2003	x
Terephthalic acid	11.1	NA/CEH/1999	No Š from xylene
Ethylene oxide	10.5	NA/CEH/2002	x
Toluene	11.1	NA/CEH/2002	x - first evaluation only
Cumene	7.37	NA/CEH/2001	No Š from benzene
Ethylene glycol	8.44	NA/CEH/2002	x
Acetic acid	4.23	NA/CEH/2002	x
Phenol	5.09	NA/CEH/2001	x - first evaluation only
Propylene oxide	4.08	NA/CEH/2001	x
Butadiene	4.37	NA/CEH/2002	x
Isobutylene	1.54	NA/CEH/2001	x
Acrylonitrile	3.47	NA/CEH/2000	x
Vinyl acetate	3.38	NA/CEH/1999	No Š from acetic acid
Acetone	3.13	NA/CEH/2001	x
Butyraldehyde	3.01	NA/CEH/2001	x
Cyclohexane	2.52	NA/CEH/2001	x
Adipic acid	1.88	NA/CEH/2001	x
Nitrobenzene	2.38	US/CEH/2001	No Š from benzene
Bisphenol A	1.96	NA/CEH/1999	No Š from acetone

Production of aromatics from lignin

Aromatic	Production (10^9 lb)
Benzene	20.4
Xylene	13.8
Terephthalic acid	11.1
Toluene	11.1
Phenol	5.09
Total	**61.5**



QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.

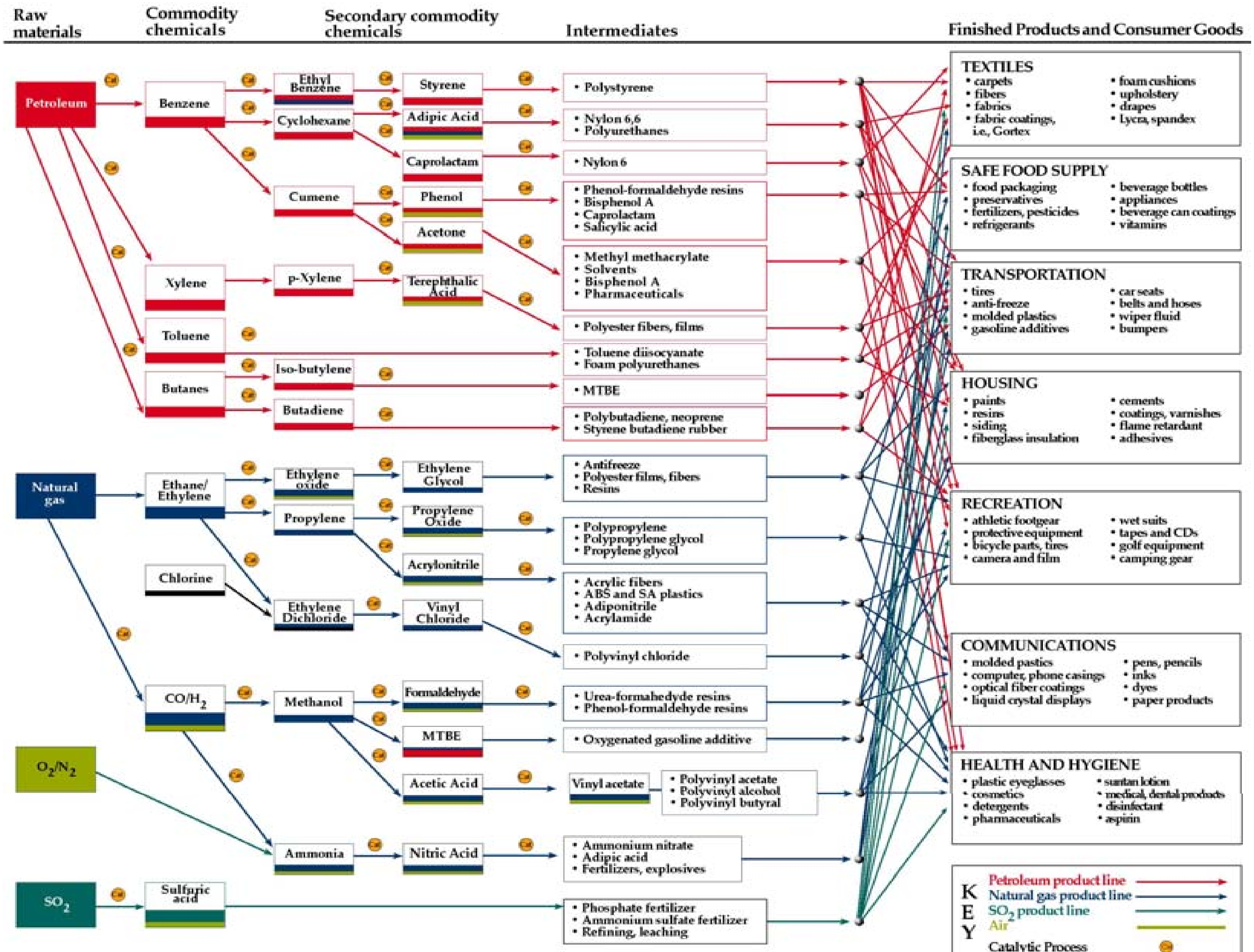
Aromatic	Lignin required (10^9 lb)
BTX	90.7
Terephthalic acid	12.7
Phenol	9.75
Total	**113**

Impact of products on fuel production

- $(113 \times 10^9$ lb$)(1/0.25) = 453 \times 10^9$ lb lignocellulosic feedstock required,
- $(453 \times 10^9$ lb lignocellulosic feedstock$)(0.75) = 339 \times 10^9$ lb of sugar available
- $(339 \times 10^9$ lb of sugar as glucose$)(92/180) = 174 \times 10^9$ lb of EtOH possible
- $(174 \times 10^9$ lb of EtOH$)(454$g/lb$)(1$ml$/0.816$ g$)(1$l$/1000$ml$)(0.264$ gal/l$) = 25.5 \times 10^9$ gal EtOH possible

- U. S. gasoline consumption: 136×10^9 gal/yr (EIA)
- Making products in the biorefinery that meet the current aromatic organic chemical needs of the U. S. could enable EtOH production equivalent to almost 19% of our current supply.
- *What is the impact on fuel supplies if the biorefinery makes products?* Significant, and potentially very large

Schematic of the Chemical Industry



Key Issues in Chemical Production

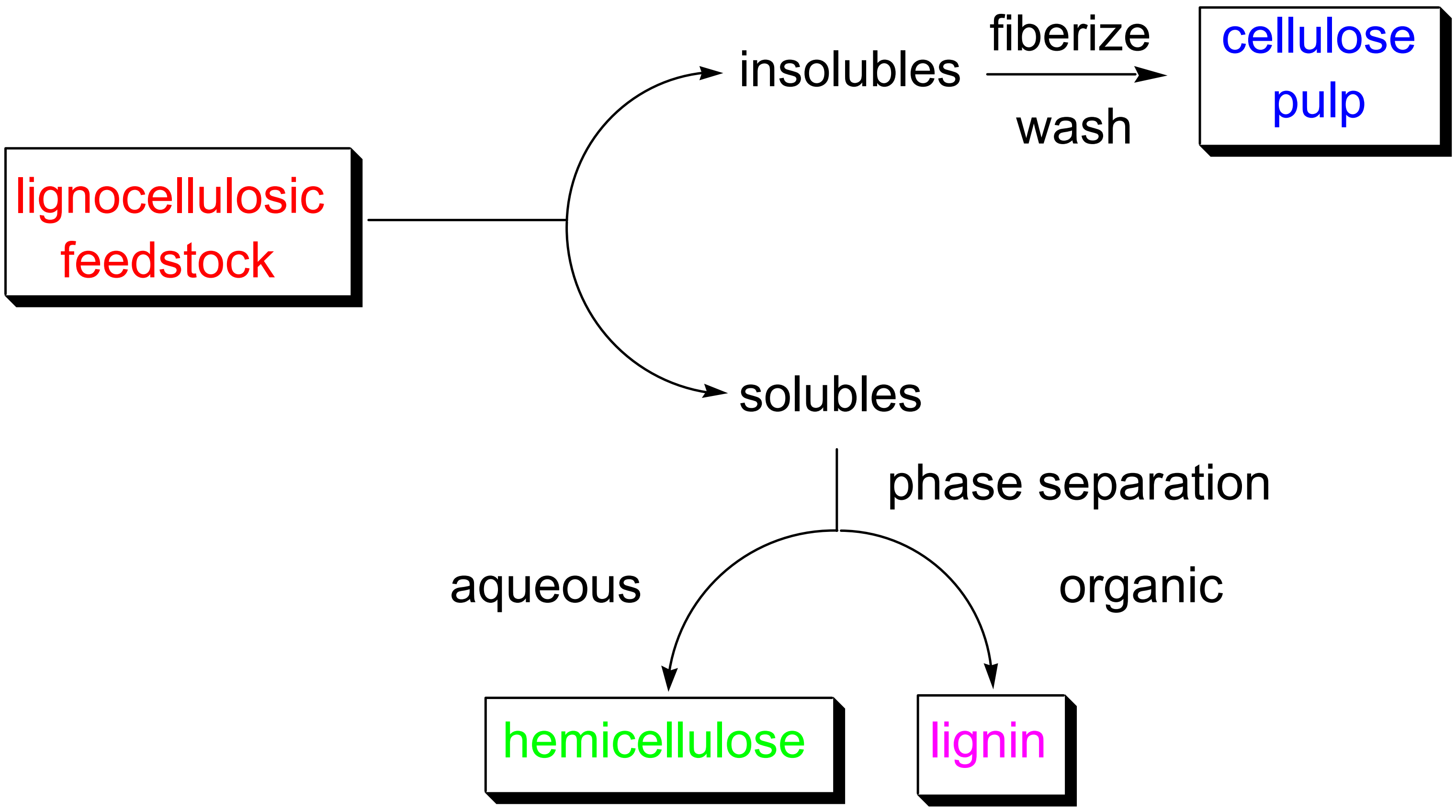
- *Supply*: Where does the starting feedstock come from? How much is there? How long will it last? How is it obtained?
- *Separation*: What are the primary components of the feedstock? How is one component obtained apart from the others?
- *Conversion*: How are the components transformed into products? Which processes are most useful? What products are most useful?

How Will Biomass be Incorporated?

- Duplication of products and structures: biomass is used to prepare known petrochemical derivatives…relatively easy, but economically bad

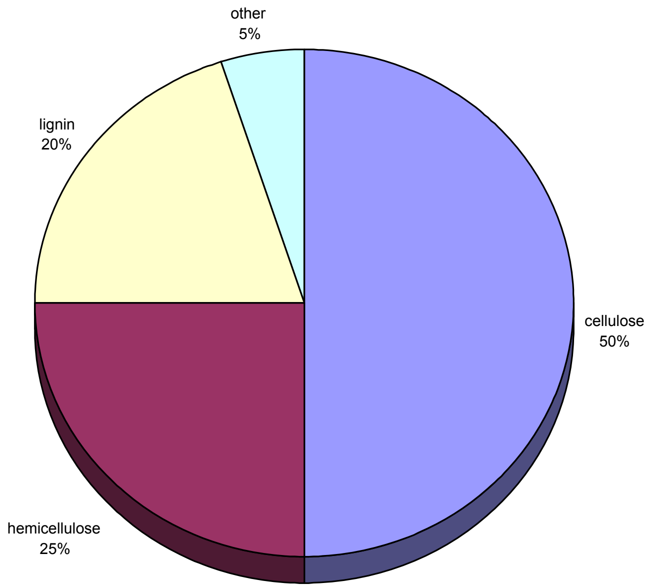
- Duplication of properties: biomass is used to duplicate desirable marketplace properties…relatively difficult, but much greater economic opportunity

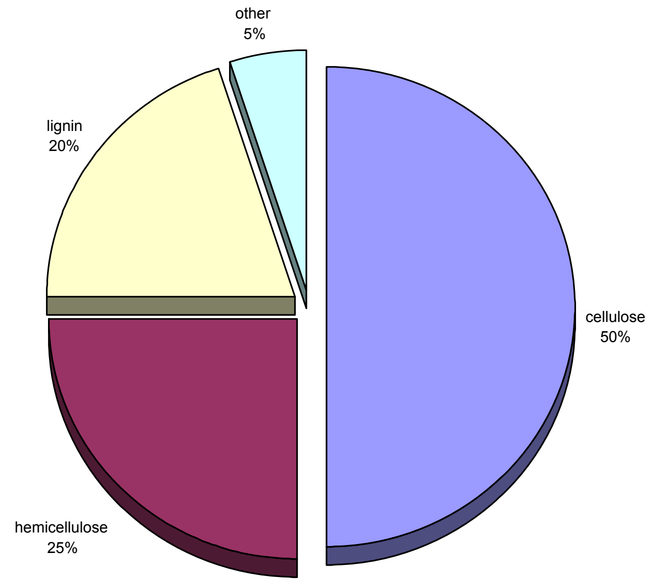
The NREL Clean Fractionation Process



Typical Clean Fractionation Result

Biomass Feedstock (wood)

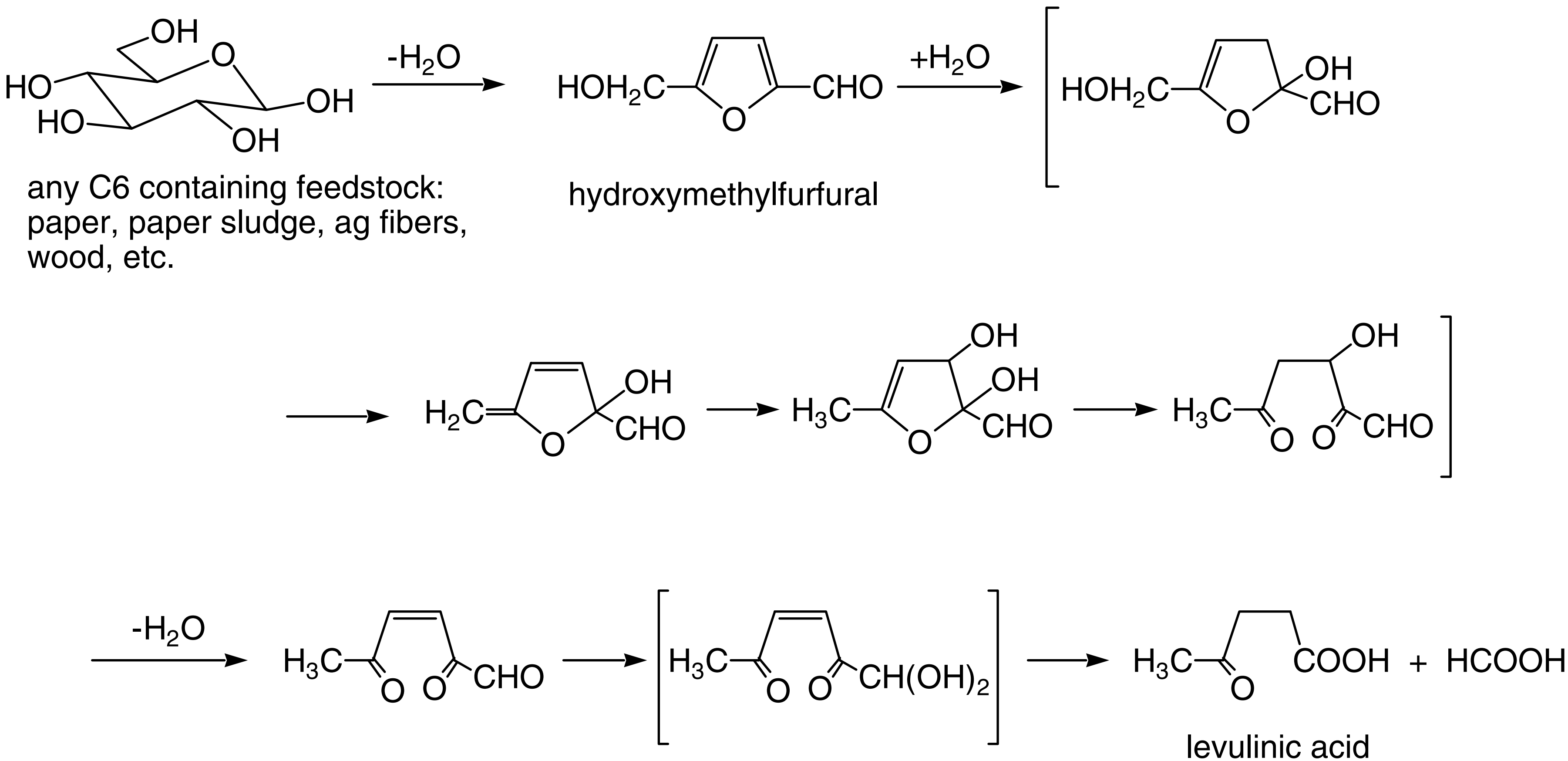




Fractionated Product

- **U. S. patent 5,730,837**
- **>95% recovery of each fraction with <5% cross contamination**
- **Separate, isolable cellulose, lignin, and hemicellulose fractions**
- **Successful with a wide range of biomass raw materials**
- **Useful as a “front end” for a forest biorefinery**
- **Economically viable**

Mechanism of Levulinic Acid Formation



J. Horvat, B. Klaic, B. Metelko, V. Sunjic, *Tetrahedron Lett.*, **1985**, *26*, 2111

Cost: $4.00 - 6.00/lb
Difficult separation

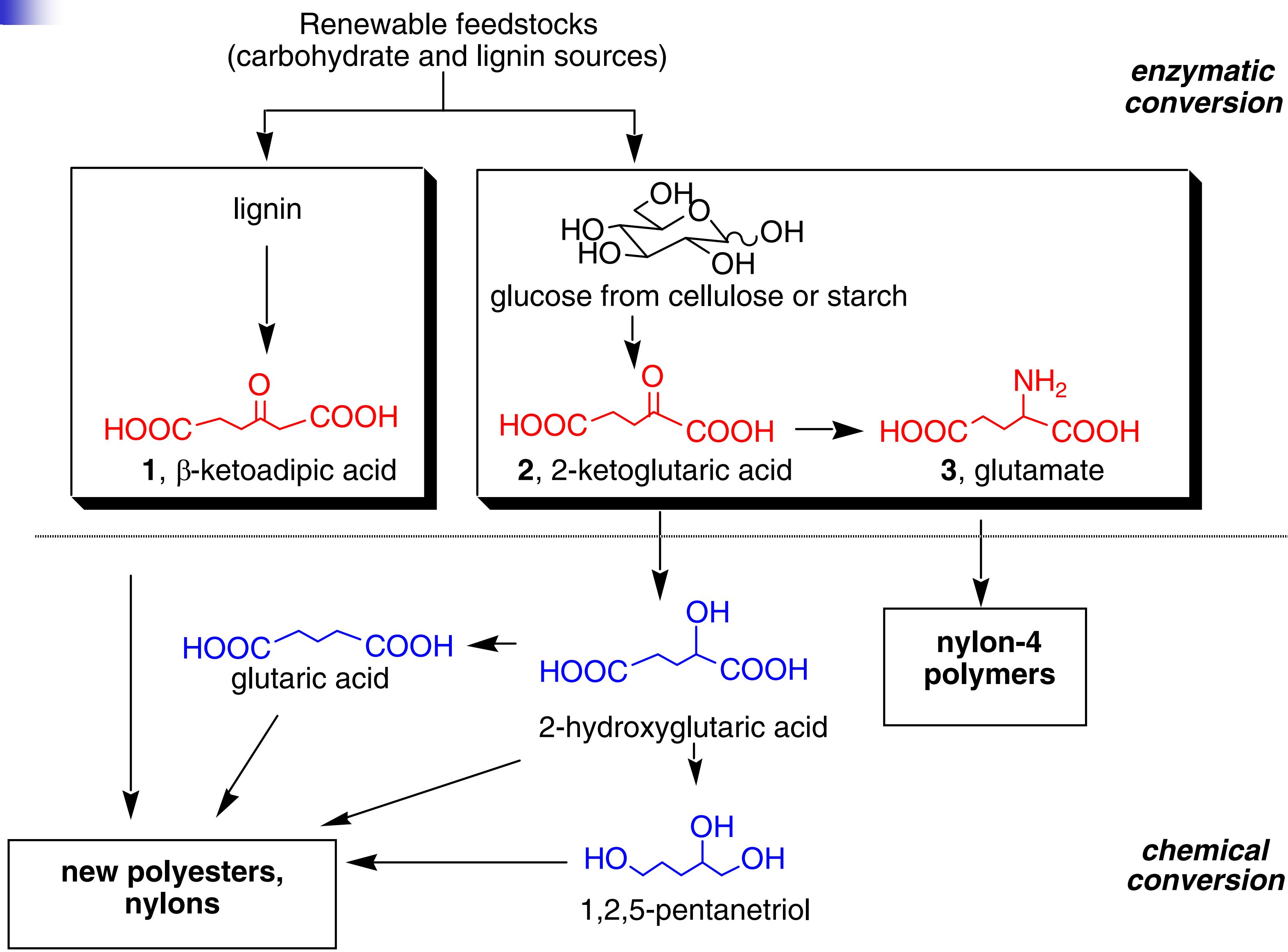
Is Levulinic Acid a Viable Primary Chemical Building Block?

- Primary building blocks: C_2H_4, C_3H_6, BTX, etc.
- Their preparation from raw materials (petrochemicals) is simple, one step, and high yielding
- They are inexpensive
- Unit operations using these materials lead to a large family of chemical products

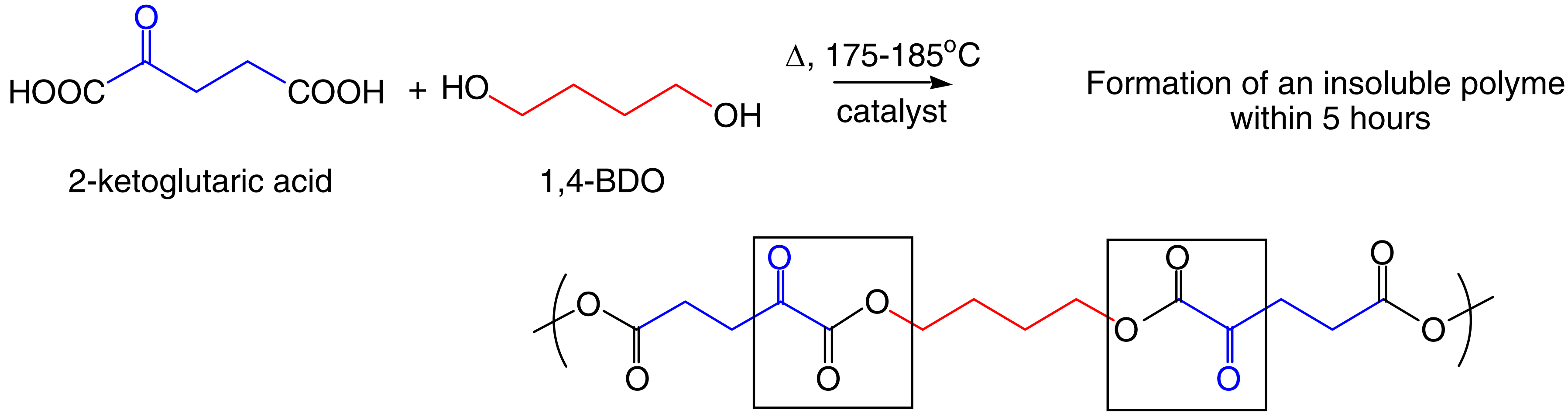
- Primary building block: levulinic acid
- Its preparation from raw materials (carbohydrates) is simple, one step and high yielding
- It is inexpensive
- *There are no unit operations based on levulinic acid that lead to a large family of chemical products*

Thus, developing a family of chemicals from cheap levulinic acid would lead to a new carbohydrate based unit op for the chemical industry!

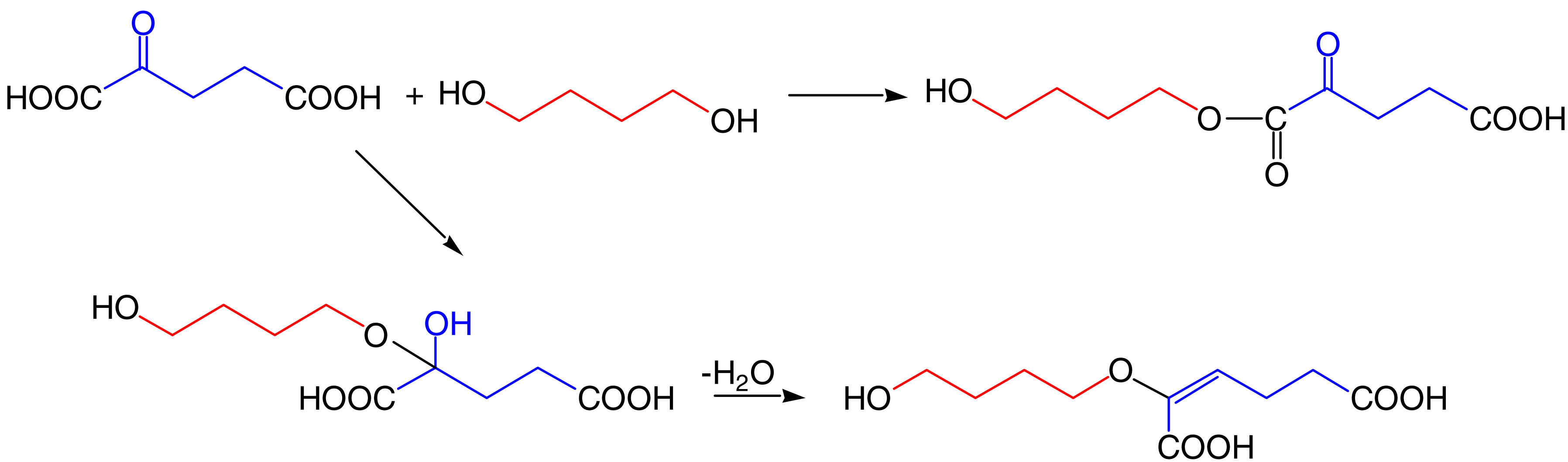
Reaction Matrix



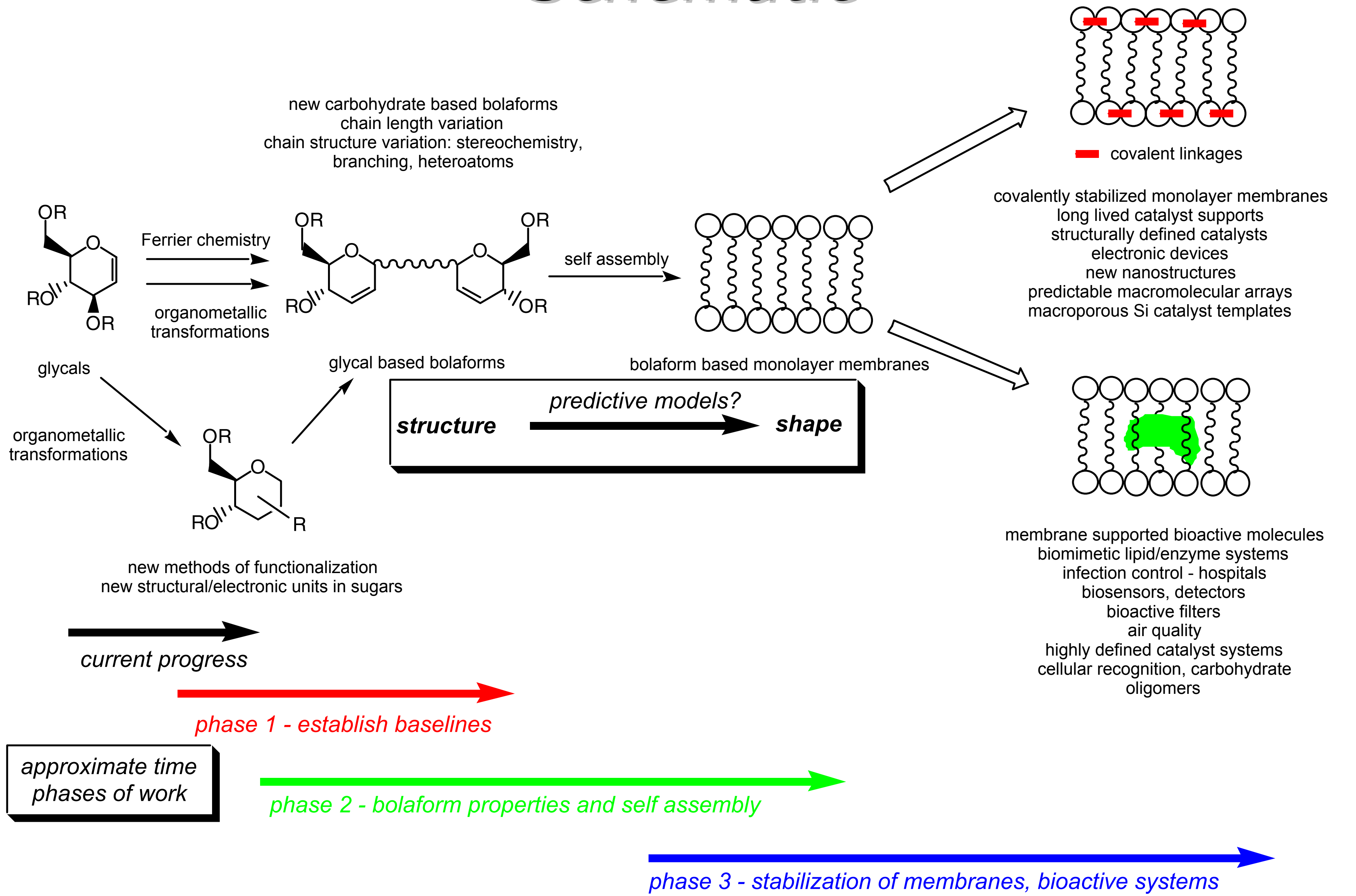
Renewables Based Polyesters – 2



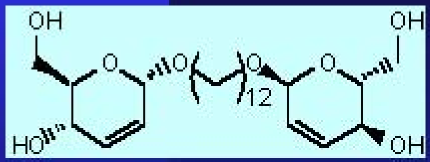
Possible initially formed units?

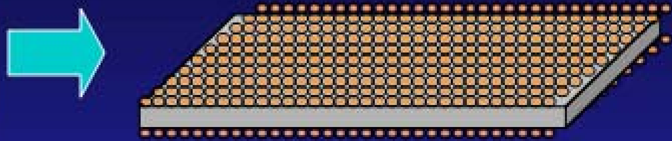


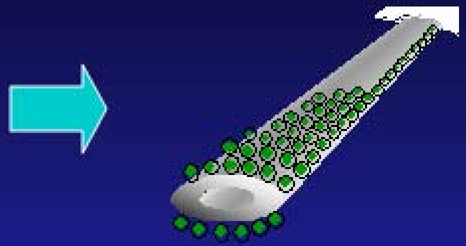
Glycal Based Bolaform Research Schematic



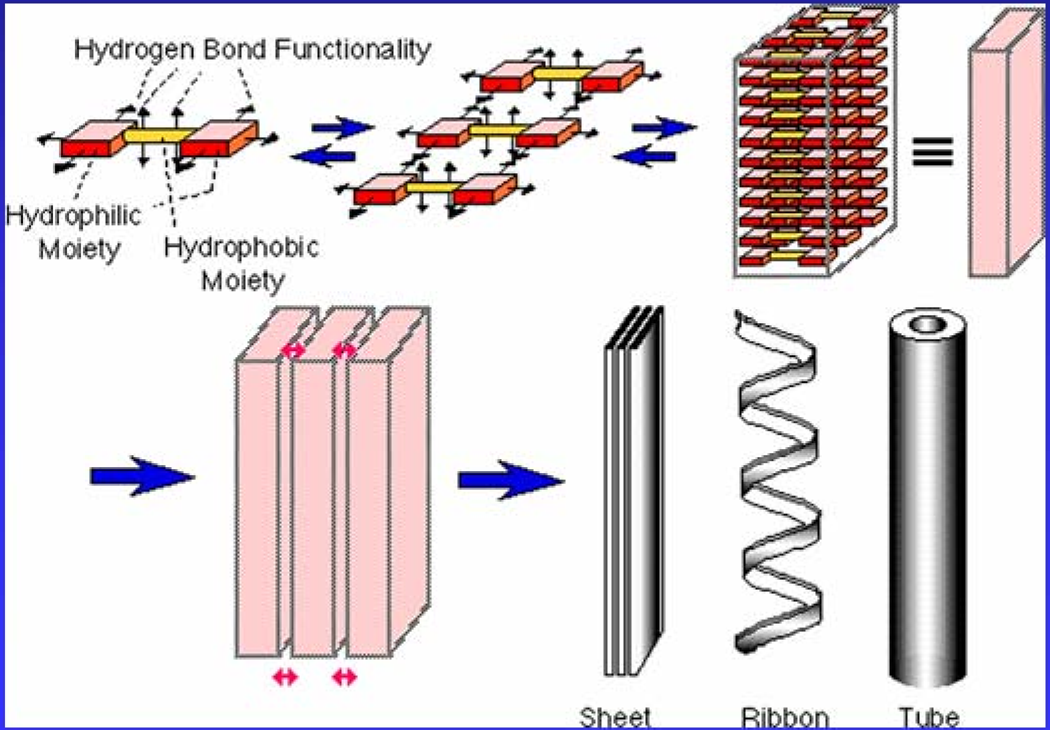
Hypothetical assembly process







Single molecule *Multimolecular array* *Large scale folding to tubes*



T. Shimizu, *Macromol. Rapid Commun.* **2002**, *23*, 311