

ECONOMICALLY SOUND BIOBASED ALTERNATIVES TO PETROCHEMICALS USE OF CARBOHYDRATES AS RAW MATERIAL FOR CHEMICAL INDUSTRY

GEETANJLI DHAWAN

Associate Professor, Head of the Department, Department of Zoology and Environment Studies, Arya P. G. College,
Panipat, Haryana, India

ABSTRACT

Chemical industry today is dependent on fossil raw material like coal, oil and natural gas although they are depleting and irreplaceable. By 2040, they would become so expensive that bio feed stocks will be an economically competitive alternative. The limitation in today scenario for transition to a more bio based production system is hampered by a variety of obstacles including the cost and technology to transform bio based raw material into product with industrial application profile. Compared to coal, oil and natural gas, terrestrial biomass is considerably more complex constituting sugar hydroxyl and amino acid, lipid and biopolymer such as cellulose, hemi cellulose, chitin, starch, lignin and protein. Among these, the most important class of organic compounds in terms of volume produce i.e. carbohydrates are worked out in the present study as they represent roughly 75% of annually renewable biomass of about 200 billion tonnes but only a minor fraction (4%) is used by man, the rest decay and recycle along natural pathways. Thus, carbohydrates are the industrially and economically viable organic chemical that would replace those derived from petrochemical sources and would constitute the major bio feed stocks aside from there traditional use for food, lumber, paper and heat.

KEYWORDS: Bio feed stocks, Chemical Industry, Terrestrial Biomass, Bio based Production System

INTRODUCTION

- The present over-reliance of chemical industry on fossil raw materials has its foreseeable limits as they are **depleting and irreplaceable**.¹
- The prevailing issue is: **“When will fossil raw materials have become so expensive that biofeedstocks are an economically competitive alternative ?”** for 2040at the latest²
- The most important class of organic compounds in terms of volume produced are **carbohydrates** as they represent roughly **75% of the annually renewable biomass** of about 200 billion tones. Of these, only a minor fraction (ca. 4%) is used by man, the rest decays and recycles along naturalpathways.³

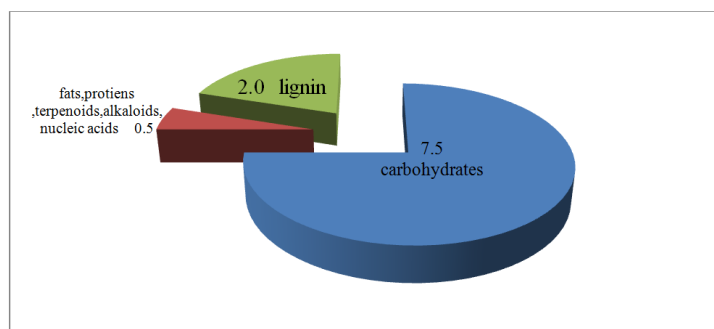


Figure 1

Obstacles in Transition to a More Bio based Production System

- Although well developed process technology⁴ but basically different from already existing industrial application profiles.
- Considerably more complex compared to coal, oil and natural gas.

Reason: It lies in the inherently **different structure** of carbohydrates and fossil raw materials. Our fossil resources are hydrocarbons, distinctly hydrophobic, oxygen –free, and lacking functional groups; annually renewables are carbohydrates, over functionalized with hydroxyl groups and pronouncedly hydrophilic.

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

Availability of Mono-, di- and Polysaccharides

Table 1

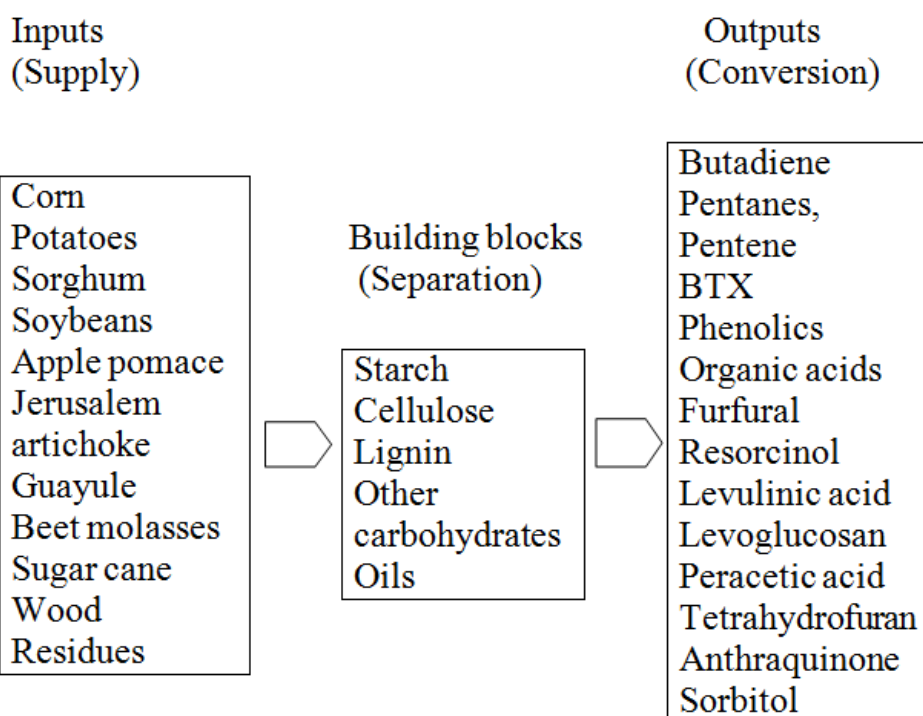
		World Production ^a (metric t/year)	Price ^b (/kg)
Sugars	Sucrose	130.000.000	0.30
	D-Glucose	5.000.000	0.60
	Lactose	340.000	0.60
	D-Fructose	100.000	1.00
	Isomaltulose	80.000	2.00
	Maltose	3.000	3.00
	D-Xylose	25.000	4.50
	L-Sorbose	60.000	7.50
Sugar Alcohols	D-Sorbitol	650.000	1.80
	D-Xylitol	30.000	5.00
	D- Mannitol	30.000	8.00
Sugar derived Acids	D-Gluconic acid	60.000	1.40
	L-Lactic acid	>100.000	1.75
	Citric acid	500.000	2.50
	L-Tartaric acid	35.000	6.00
Amino Acids	L-Lysine	40.000	5.50
	L-Glutamic acid	500.000	7.00

Basic Chemicals	Aniline	1.300.000	0.95
	Acetaldehyde	900.000	1.15
	Adipic acid	1.500.000	1.70
Solvents	Methanol		0.15
	Toluene		0.25
	Acetone		0.55
	Cellulose	25.000.000	0.44
Polymers ⁵	Lignin	6.500.000	0.07
	Levulinic acid	3.200.000	0.18
Others ⁶	α -pinene		5.50
	β -pinene		6.38

A Reliable data are only available for the world production of sucrose, the figure given referring to the crop cycle 2007/2008.

^bPrices given are those attainable in early 2008 for bulk delivery of crystalline material(where applicable) based on pricing information from sugar industry(sugars) and the Chemical Market Reporter 2008(acids, basic chemicals, and solvents).

MATERIALS AND METHODS



CLEAN FRACTIONATION PROCESS

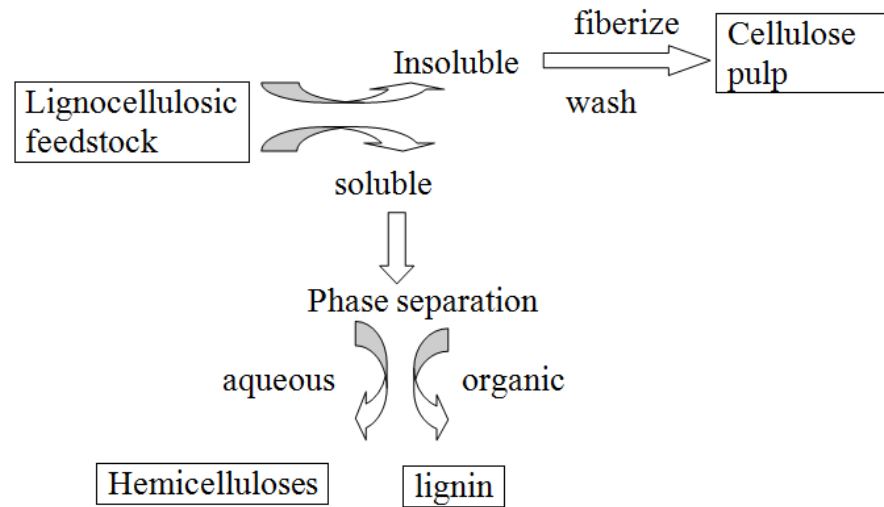


Figure 2: Clean Fractionation Process

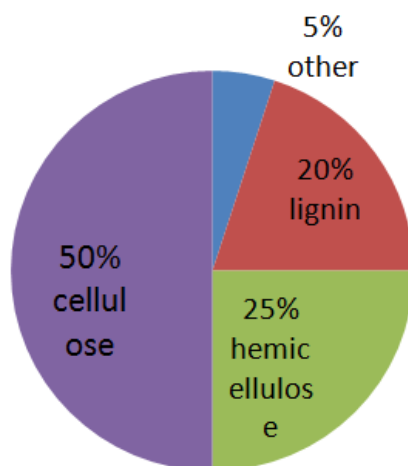


Figure 3: Biomass Feedstock (Wood)

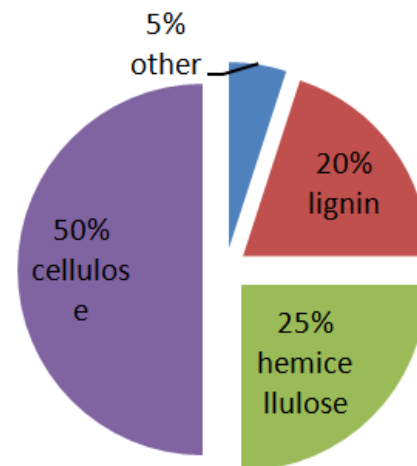
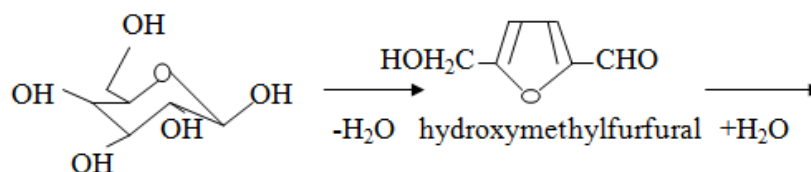


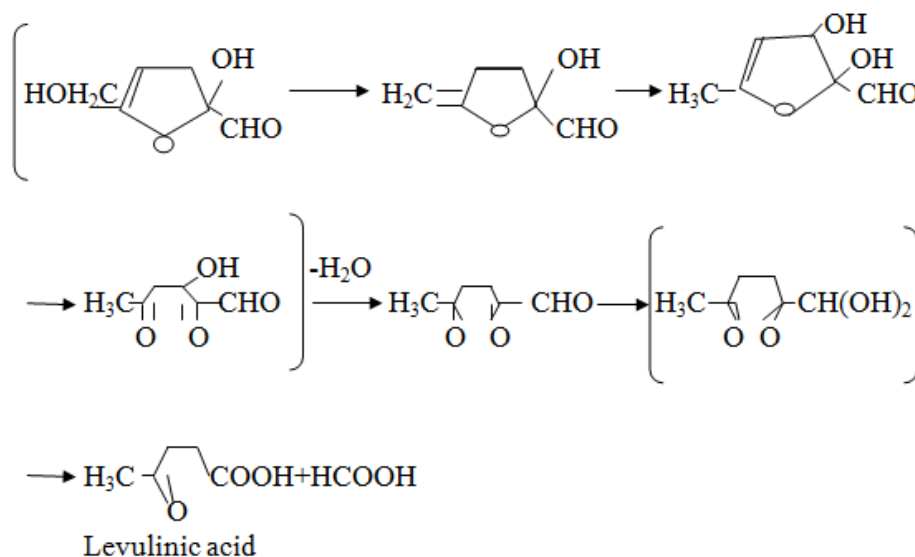
Figure 4: Fractionated Product

- >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 FORMATION⁷



Any c6 containing feedstock:
Paper, paper sludge, ag fibers,
wood, etc.



RESULTS AND DISCUSSIONS

Advantages to Biomass Feedstocks

- Lowered demand for diminishing crude oil supplies
- Sustainability
- Recycling of CO₂
- Lessened dependence on politically unstable nations for feedstock supply.⁸
- New types of complexity in building blocks
- Flexibility through biotechnology/bioprocessing as a growth industry⁹

Is Levulinic Acid a Viable Primary Chemical Building Block

Table 2

Sl. No.		
1	Primary building blocks: C ₂ H ₄ , C ₃ H ₆ , BTX, etc	Primary building block: levulinic acid
2	Their preparation from raw materials (petrochemicals) is simple, one step, and high yielding	Its preparation from raw materials (carbohydrates) is simple, one step and high yielding
3	They are inexpensive	It is inexpensive

4	Unit operations using these materials lead to a large family of chemical products	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

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 derivative relatively easy, but economically bad
- Duplication of properties: biomass is used to duplicate desirable marketplace propertie relatively difficult, but much greater economic opportunity

CONCLUSIONS

Carbohydrates represent 75% of annually renewable biomass though only 4% is being used by humans. These, being the industrially and economically viable organic chemicals, would replace the fuels derived from petrochemical sources. In the near future, these would constitute the major bio feedstocks that would be economically competitive alternatives to petrochemicals besides their traditional use as food and lumber. Major advantages to biomass feed stocks include lessen dependence on politically unstable nature for feedstock supply and their flexibility through bio processing as a growth industry. Levilinic acid is viable primary chemical building block. A new carbohydrate based unit for chemical industry would be possible by developing a family of chemicals from cheap levilinic acid.

REFERENCES

1. Okkerse, C.; van Bekkum, H. "From Fossil to Green", *Green Chem.* **1999**, 107-114.
2. Campbell, C. J.; Laherrere, J. H. "The End of Cheap Oil", *Sci. American*, March **1998**, 60-65.
3. Lichtenthaler, F. W. "Unsaturated O- and N-Heterocycles from Carbohydrate Feedstocks", *Acc. Chem. Res.* **2002**, 35, 728-737;
4. Lichtenthaler, F. W. "Carbohydrates as Organic Raw Materials", *Ullmann's Encyclop. Industrial Chem.*, 6th Ed. **2002**, 6, 262-273.

5. M. Bols, "Carbohydrate Building Blocks", Wiley-Interscience, New York (1996)
6. F. Lichtenthaler and S. Mondel, *Pure Appl. Chem.*, **1997**, 69, 1853.
7. For useful preparative procedures, see: *Methods Carbohydr. Chem.* **1963**, 2, 318-325; 326-328; 405-408; 427-430.
8. Gandi, A. "Furans in Polymer Chemistry", *Prog. Polym. Sci.* **1997**, 22, 1203-1279.
9. L. R. Lynd, C. E. Wyman, T. U. Gerngross, *Biotechnol. Prog.* **1999**, 15, 777

