

# **The Biomass Alternative**

## **A National Insurancy Policy to Protect the US Strategic Supply of Chemical Feedstocks**

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### **ABSTRACT**

Prospects for biomass commodity chemicals are currently unfavorable as a result of: generic deficiencies in fermentation processes with respect to generally low (below 5%) product concentrations and slow fermentation rates, and lack of a presently competitive advantage for renewable materials compared with depressed prices for crude oil. However, research can alter the first limitation, and Middle East politics, the second.

In the meantime, the continuation of a national research program on biomass conversion is strongly urged as a strategic insurance policy to protect the American organic chemicals industry against further disruptions in crude oil-based feedstocks.

**Index Entries:** Biomass utilization; chemical feedstocks; synthetic chemicals; ethanol; fermentation; national research policy.

### **INTRODUCTION**

#### **Historical Perspective**

Prior to the post-World War II boom in the chemical industry, many of the high volume chemical feedstocks were made from sugar substrates by fermentation. These included basic chemicals such as ethanol, from which ethylene and butadiene were made, butanol, acetone, and acetic acid.

However, low cost petroleum and natural gas became available in the early 1950s. As a result, the introduction of cheap petroleum feedstocks was more or less the death knell of the fermentation industry as people

knew it at that time. For the next thirty years, the chemical world became basically synonymous with producing petrochemicals from crude oil and natural gas-based feedstocks.

When the big energy crunch of 1973 occurred, many in the chemical process industry started to consider alternatives. Some reassessed the possibility of producing chemicals from *coal*, air, and water (again). Others opted to investigate a future of producing chemicals from *sunlight*, air, and water using photosynthesis to produce the basic carbohydrates needed as a source of energy and fixed carbon for these oxychemicals. For a decade, industry and academia, supported by Federal energy programs, explored ways to prepare cheap "biosugar" feedstocks from lignocellulose in the form of tree chips or agricultural residues, and to convert such renewable raw materials into chemicals or fuels.

Unfortunately for these programs, the softness in crude oil prices that occurred in the early 1980s brought an end, in most cases, to research programs aimed at using renewable resources as a basis for chemicals.

### National Insurance Policy Concept

Although the chemical industry has abandoned interest in renewable programs—at least for the moment—it is not to say that the same strategic shortfall in *cheap* petroleum feedstocks will not return. Indeed, James E. McNabb of Conoco, a leading petroleum refiner, pointed out that although OPEC is now operating at 60% of capacity, it will reach 80% of capacity early in the 1990s. Then, market power will shift from consumer to supplier, with a resulting trend toward raising prices again. As a consequence, he forecasts that although oil prices will remain in the low \$20s until 1990, they will rise to the mid-\$30s by 1995, and to \$50 per barrel by the year 2000 (1,2). In contrast, the cost of corn, a major biomass supply, is currently at \$1.50–\$2.00 per bushel—about where it was in 1970 (3–6).

Already, considerable pressure is being placed on the price of ethylene as a result of a strong demand for the plastics: polyethylene, polyvinyl chloride, and polystyrene (7). This pressure led to an increase in ethylene prices to 15.5 cents per pound in September, 1987, as production rose to above 95% of the average nameplate capacity of 35.2 billion pounds.

Price pressure on the other olefins has also been severe. The price of propylene reached 18 cents per pound in September, 1987, compared with 10 cents at the beginning of the year as a result of increased demand for polypropylene. Similarly, butadiene prices increased to 30 cents per pound from a low of 9 cents in October, 1986. Such trends may be bellwethers of future price increases, since tight supplies are expected to continue over the near future.

In addition, while the American chemical industry scrambled to reposition its businesses into more lucrative specialty chemical markets, the Saudi ministers repeatedly announced their intentions to invest heavily in commodity chemicals production. Already, Union Carbide, a leading

supplier of synthetic ethanol in this country, is having ethanol produced in Saudi Arabia on a toll basis (8). Nevertheless, E. C. Holmer, the recent president of Exxon Chemicals, sees no real threat in the commodity chemical capacity being built close to the Middle East wellheads (9). He points out that there is nothing cheap about petrochemical operations in remote Middle Eastern countries. Construction costs are tremendous and operating costs are very high, as are transportation charges for moving products to established markets. On the other hand, ethylene produced by the Saudi Basic Industries is based on its no-value, excess associated gas, which is otherwise flared. Since over half the cost-plus-return for ethylene is based on raw material costs, this is a formidable advantage; particularly, if the price of crude oil rises from the current \$15-\$20 per barrel to \$35 again or more.

In the meantime, it would be a nationally tragic waste of scientific momentum if some programs on biomass-based chemicals were not kept alive as a strategic insurance policy when and if the Middle East economic and political climate triggers another and potentially far worse crisis in petroleum feedstocks than in 1973.

### Study Outline

The ECUT (Energy Conservation and Utilization Technology) program of the US Department of Energy supports the development of new generic processes for converting renewable biomass into chemicals. As such, it is one of the last government programs specifically directed toward developing alternative routes to chemicals so as to relieve national dependence on foreign oil-based feedstocks.

This study was supported by the Jet Propulsion Laboratory of California Institute of Technology as part of its management of projects for the ECUT program. The study was aimed at helping to define a strategically relevant national plan for developing new processes to convert renewable resources to organic chemicals by indicating significant avenues for process research. The study consists of two parts: an assessment of present petrochemical products and their relationship to their generic feedstocks, and an extrapolation of this product position to a biomass feedstock economy based on technically demonstrated, albeit presently economically unfavorable, processes.

### The Data Base

Statistics on the production and sales of synthetic organic chemicals are compiled annually by the US International Trade Commission. This study relied heavily on 1985 data from this source (10) supplemented by information from the Chemical Marketing Reporter (11) and the Modern Plastics Encyclopaedia (12) and estimates by Bio En-Gene-Er Associates, Inc. (BEA) in compiling its database. The database was limited as a practical matter to products produced at annual rates over one million pounds.

The database that was developed contains information on production volume and value, sales volume and value, and the original feedstock and intermediates for each chemical. The sales data do not reflect the value of captive intermediates included in the production data. Also, the database does by no means include all organic chemicals produced in the United States. There are a number of reasons for this:

1. As noted, the study was limited to production levels over one million pounds. However, the aggregate amount of products produced at lesser volumes is estimated to be only a few percent of the production listed in the database.
2. Government statistics include only those compounds reported to be involved in commerce. As a result, many captive intermediates, such as adiponitrile and hexamethylenediamine, which are important precursors to nylon, are not included. For the same reason, the sales volume cited in the database are generally smaller than production volume as a result of captive use. As an example of this, ethylene dichloride, one of the most important of the ethylene derivatives, is produced at a rate of 12 billion annual pounds, but sales only amount to about 400 million pounds—the rest is used captively.
3. The government data base refers to “synthetic” organic chemicals and, hence, ignores many other types of products. Nevertheless, the purposes of this study are still served since the emphasis here is on replacing synthetic petrochemicals by biomass-based chemicals.

It should also be noted that the data are not mutually exclusive in that many compounds on the list are intermediates for others on the list, i.e., ethylene to ethylene oxide to ethylene glycol to 2-ethoxyethanol. Hence, the aggregate sum of all chemicals relates to a flow of materials and value through the industry rather than a sum of feedstock needs.

## SYNTHETIC PETROCHEMICALS

### Overall Position

About 390 organic chemicals were identified having production levels above one million pounds per year (MM PPY). These products comprised 316-billion pounds valued at the manufacturers' level of over \$110 billion in 1985 (Table 1). This amounts to a weight average value of \$0.35 per pound. The average is heavily skewed to the high volume chemicals.

Of the 390 chemicals, the top five, which had production levels over 10 billion pounds each, accounted for 25% of production and 9% of value. Similarly, the top 19 each exceeded 5 billion pounds and accounted for 55% of total production and 30% of value.

Table 1  
Synthetic Organic Chemicals  
1985 US Production

Production level Million PPY	No. of products	Total Production		Total Value	
		MM PPY	%	\$million	%
Over 10,000	5	78,276	24.8	\$10,070	8.9
5,000-10,000	14	94,650	30.0	24,164	21.4
1,000-5,000	40	82,623	26.1	36,733	32.5
500-1,000	43	29,557	9.4	17,106	15.1
250-500	48	17,719	5.6	13,282	11.8
100-250	53	8,315	2.6	6,757	6.0
Subtotal	203	311,140	98.5	108,113	95.7
50-100	38	2,643	0.8	1,905	1.7
10-50	79	1,895	0.6	2,112	1.9
1-10	70	290	0.1	815	0.7
Total	390	315,968	100.0	\$112,946	100.0

Over half of the products had production levels over 100 million pounds and accounted for 98% of total production and 96% of total value. Hence, from the standpoint of relevance to the national economy, the nationally funded research programs should be directed toward these high volume commodity chemicals rather than to the expensive lower volume specialty chemicals of current interest to industry.

### Price/Volume Relationship

Within product classes, price decreases as production volume increases. Generally, products like medicinal chemicals, fragrances, and flavors lie at the high value/low volume end of the scale. Plastic resins and elastomers are in the middle of the volume spread and priced above the primary petrochemical from which they are made. Fuels are on the bottom of the value spectrum (3).

Price/volume data from the database lie on a broad band as a result of the mixing of various industrial classes. The average price/volume relation for production classes can be obtained from the normalized data of Table 2. At present, commodity chemicals are priced under \$1.00 per pound.

### Primary Feedstocks and Derivatives

In order to structure the relationship of intermediates, each compound in the database was appraised as to the presently preferred method of manufacture, using standard texts on the subject (13-15) plus the collective experience of the BEA staff. The intermediates used to make each compound were identified and followed back the synthesis chain to the original "primary" feedstock. Primary feedstocks are defined here as

Table 2  
US Synthetic Organic Chemicals  
1985 Price/Volume Relationship  
400 Products

Production level Million PPY	Average Value \$/lb	Average Prod'n MM PPY
0.1-10	\$15.42	0.5
1-10	\$3.08	4.2
10-100	\$0.93	38.9
100-250	\$0.89	158.2
250-500	\$0.75	369.2
500-1000	\$0.57	686.2
1,000-5,000	\$0.44	2,092.7
5,000-10,000	\$0.26	6,781.5
Over 10,000	\$0.13	15,655.3

those materials first identified by name out of the petroleum mix in the refinery. Ethylene and propylene are examples. These feedstocks are normally made from refinery gases (16).

The data for all products were sorted by primary feedstock to show the derivatives from each feedstock and the combinations of feedstocks used. These results are summarized in Table 3, which categorizes production as to whether it refers to a primary feedstock, a derivative of a single primary, or a derivative of a combination of primaries.

Out of 316 billion pounds of synthetic organic chemicals, 96 billion, or 30%, is represented by the primary feedstocks; 140 billion, or 44%, by the derivatives of single primaries; and 79 billion pounds by derivatives of combinations of primary feedstocks.

It is interesting to note that the big five: the olefins, ethylene and propylene, and aromatics, benzene, toluene, and xylene (BTX) comprise 69 billion pounds, or 72% of all primary feedstocks, whereas these and their single derivatives account for 169 billion pounds, of 53%, of all chemicals. In addition, these strategic feedstocks are also involved in additional combinations. (Please note, however, that the data for combinations cannot be added because of duplications.) Therefore, any plan for relieving the pressure of foreign oil must take into account the alternatives of these feedstocks, particularly ethylene (Fig. 1).

### Primary Feedstock Combinations

In assessing the importance of feedstocks to the national chemical economy, it is also important to recognize the interaction of feedstocks in producing derivatives in addition to the importance of the feedstock alone. These data are summarized in Fig. 2. Considering the origin of derivatives, the importance of ethylene is overwhelming. Out of a total derivative

Table 3  
Interrelation among Major Feedstocks, Million Pounds per Year—1985

Primary feedstock	Derivatives with Other Feedstocks									
	Ethylene	Propylene	Buta <sup>a</sup>	Xylene	Benzene	Toluene	Cyane	CH4/SG	Natural	Total
Ethylene	29,847	76,703	5,178	7,703	29,204	2,900	0	8,056	1,706	140,884
Propylene	14,887	9,434	1,471	2,268	17,708	1,481	37	9,970	764	61,122
Butadiene & Butenes <sup>a</sup>	3,698	1,471	1,396	0	5,177	8	2,172	2,246	0	17,648
Subtotal	48,431	91,315	8,044	9,971	52,089	4,388	2,209	20,273	2,470	
Xylenes, m,o,p <sup>b</sup>	9,918	7,703	0	2,304	1,394	0	0	8,203	1,756	23,628
Benzene	9,390	29,204	5,177	1,394	2,569	0	0	7,102	4	63,157
Toulene	5,074	2,900	8	0	0	230	0	628	0	5,247
Cyclohexane <sup>c</sup>	1,657	0	2,172	0	0	0	3,554	37	0	5,800
Subtotal BTXC	26,038	39,807	7,357	3,698	3,963	230	3,554	15,970	1,760	
CH4/Synthesis Gas		8,056	2,246	8,203	7,102	628	37	26,989	190	63,421
Natural products		1,706	0	1,756	4	0	0	190	8,401	12,822
Total	74,470	140,884	17,648	23,628	63,157	5,247	5,800	63,421	12,822	
Ethane	5,631									
Propane	10,305									
n-Butane	2,214									
Isobutane	1,639									
n-pentane	107									
Hexane	482									
n-heptane	124									
Subtotal	20,503									
Pentenes	973									
Dicyclopentadiene	63									
Grand Total	96,010									

<sup>a</sup>Includes: Butadiene 2,340, 2-butenes 640, 1-butene 414, isobutylene 303.

<sup>b</sup>Includes p-xylene 4,779, xylenes 4,464, o-xylene 675.

<sup>c</sup>Included with aromatics because of tradeoff with benzene.

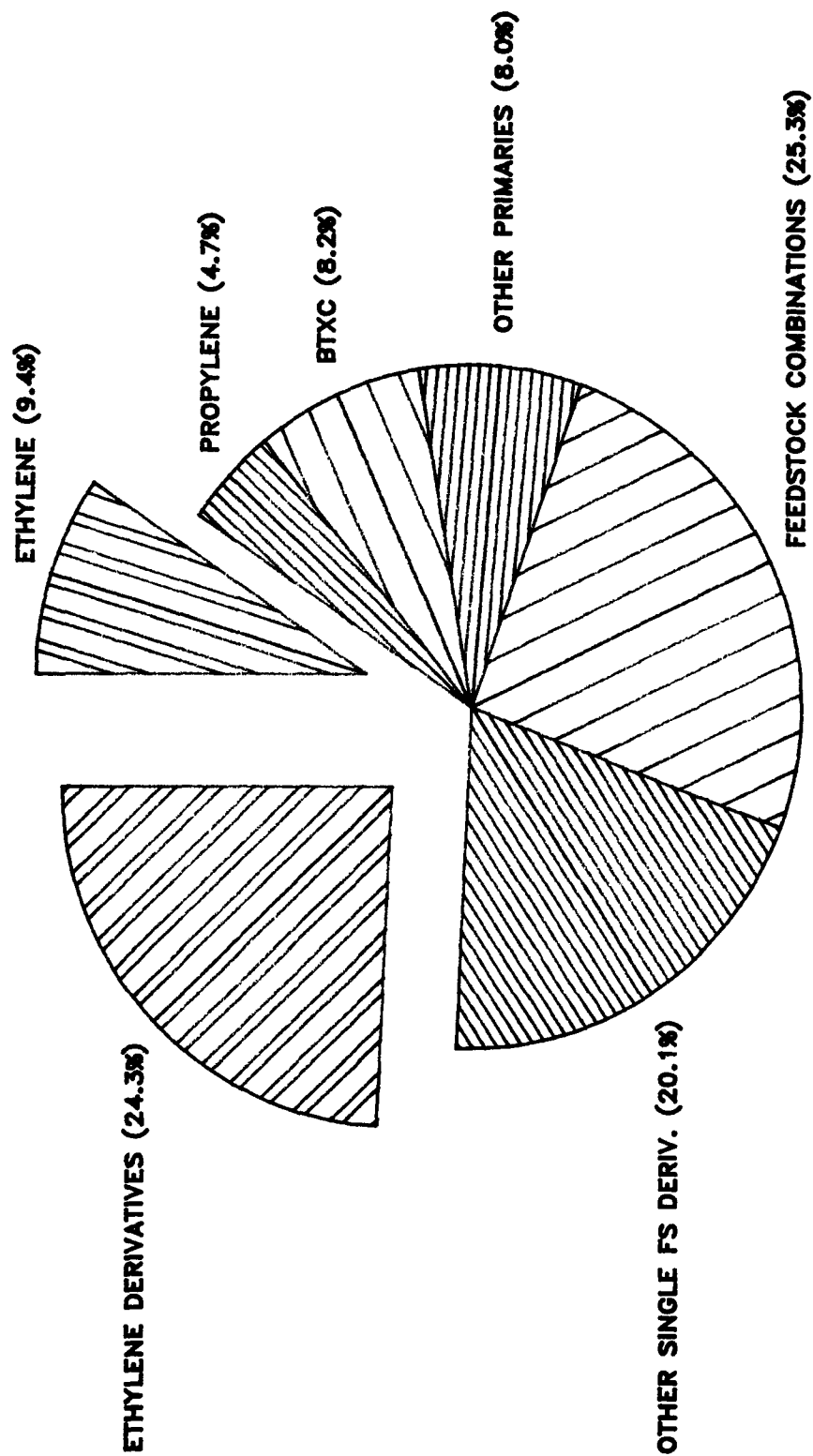


Fig. 1. US organic chemicals—1985. Feedstock origin of all products.

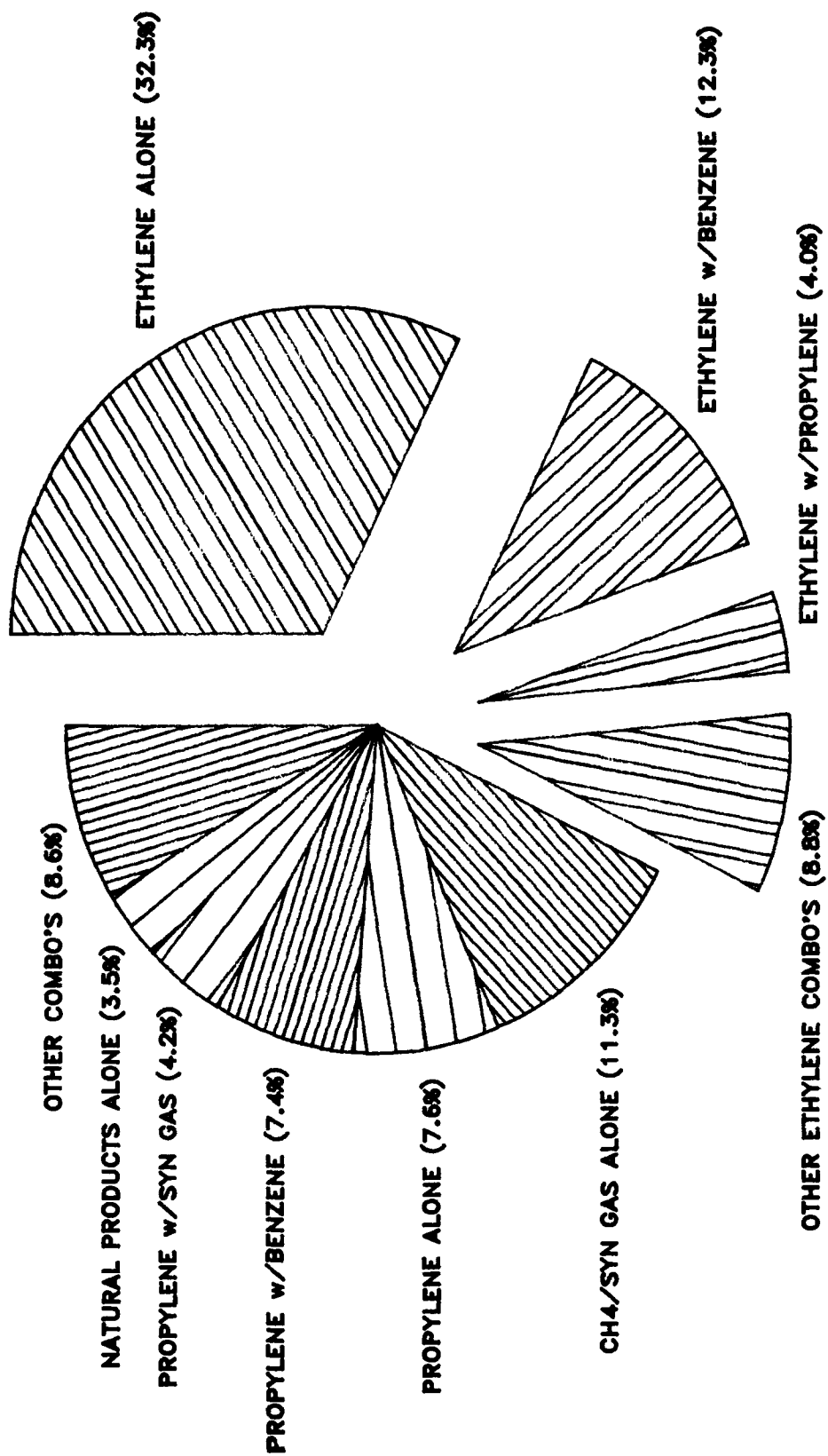


Fig. 2. US organic chemicals—1985. Feedstock origin of derivatives.

pool of 220 billion pounds, derivatives of ethylene alone account for one-third. Combinations of ethylene with benzene, propylene, synthesis gas, or butadiene also rank highly.

Derivatives of propylene alone or in combination with benzene, synthesis gas, or ethylene are second to ethylene derivatives in volume. Although a case can be made for concentrating research on a single feedstock, such as ethylene, it is also important to recognize the need for a broader feedstock mix in order to reach a balance of products for the overall economy.

## THE BIOMASS ALTERNATIVE

The second half of the study involved developing a scenario translating the petrochemical economy to a biomass economy. To do this the data base was reorganized relative to alternative routes of feedstocks or derivatives based on renewable resources.

### Biomass Supply

There are two basic renewable feedstocks in nature of interest here: starch and lignocellulose. In practical economics, starch in the United States refers almost exclusively to corn starch; lignocellulose refers to wood chips or, to a lesser extent, corn stover or cereal straws. Corn yields over recent crop years have amounted to 7–8 billion bushels, equivalent to 225–250 billion pounds of starch, or 250–275 billion pounds of sugar (5). In contrast, the annual *economically collectible* supply of lignocellulose amounts to almost 800 million dry tons, equivalent to 1.1 trillion pounds of polysaccharides (17–20). This lignocellulose supply is about equally divided between collectible residues of the major agricultural crops and annual available growth of American forests' net of commercial removals and mortality (21). Hence, the total available US biomass supply is roughly four times greater than the volume of petrochemicals now produced. This is not a very large surplus, considering that the entire US corn crop and forest growth is involved. One can conclude that other resources, such as coal, will be important adjuncts to the use of biomass.

### Conversion Process Scenario

Corn starch, certainly at present, and cellulose, potentially, can be hydrolyzed by acid or enzyme catalysts to produce a "biosugar syrup" amenable to further processing to chemicals. Two basic process modes are involved: fermentation or hydrogenolysis.

Lignocellulose can be gasified to produce synthesis gas (a mixture of carbon monoxide and hydrogen) in a similar manner to coal gasification. It can also be hydrogenated to produce a mixture of oxygenated aromatic compounds in like manner to coal hydrogenation.

As a plausible scenario it was assumed that all four basic processes would be employed in the "biomass alternative."

### Fermentation

Fermentation would be used to produce from biosugar:

1. **Ethanol** via the yeast *Saccharomyces cerevisiae* or bacterium *Zymomonis mobilis*. The commercial yeast system is relatively satisfactory with respect to product concentration in the beer but needs to be improved with respect to increasing fermentation rates (22,23). *Zymomonis* shows promise for outstanding performance if operating consistency can be demonstrated (24).
2. **Isopropanol, *n*-butanol, and acetone** via the bacterium *Clostridium acetobutylicum* and related species. The product concentration attainable in this system is severely limited by product feedback inhibition, which must be corrected (25,26). The recent innovations made by Battelle Memorial Institute in its *in situ* extractive fermentation process for butanol (27) appears to have the profound effect of increasing effective concentration of product to 140 g/L while maintaining actual concentration near the organism below 10 g/L, the threshold of inhibition. As a result, the selling price to yield a 30% pretax return on investment might be reduced from over \$1.25 per pound for butanol if produced now by the old Weizmann process to about 59 cents per pound. Further reductions appear attainable.
3. **Acetic Acid** via *Acetobacter suboxidans* from ethanol in a modernized version of the old vinegar process or directly from sugar via *Clostridium thermoaceticum*. The vinegar organism provides acceptable concentrations of acetic acid (10%) in the beer but requires a two-step fermentation by way of ethanol. As a result, theoretical yield is limited to two mols of acid per mol of glucose (28). The product concentration of the newer *Clostridium* system is severely limited by product feedback inhibition, although theoretical yield is three mols of acetate per mol of glucose (29,30).
4. **Fumaric acid or malic acid** via the fungus *Rhizopus arrhizus*. Both yield and product concentrations have been exceptional in laboratory studies but further demonstration at pilot scale is needed (31).

### Hydrogenolysis

Hydrogenolysis of glucose is the preferred route to commercial sorbitol. It was extensively studied years ago as a route to the polyhydric alcohols: glycerol, ethylene glycol, and propylene glycol (32,33). However, cheaper petroleum substrates redirected research to the synthetic routes.

More recent improvements to the catalyst system (34) could lead to a practical process for producing ethylene glycol.

Alternatively, glycerol could be produced directly by fermentation (35). The glycols can also be produced via fermentation to the respective alcohols followed by dehydration to the olefin and vapor phase oxidation to the oxide. Hydration of the oxide is the current commercial method. Hence, in this study, products from hydrogenolysis can be compiled separately of lumped under the alternative fermentation route.

### *Gasification*

Many studies of the gasification of biomass have been made over the past decade and earlier. In gasification part of the raw material is burned to provide energy for the endothermic gasification reactions. Unfortunately, biomass usually contains 50% moisture as received and 45% oxygen on a dry basis. Both place a severe thermodynamic handicap on the use of biomass compared with coal (36–38). On the positive side, biomass is usually sulfur-free, so that gas cleanup is easy and cheap to accomplish. Whether this attribute can overcome the basic composition shortcomings remains to be seen. In any event, synthesis gas from either biomass or coal could be teamed with the other conversion routes to spare the use of natural gas for this purpose.

### *Hydrogenation*

The production of aromatic compounds from coal or biomass has very early beginnings in the German Bergius process. This approach was further developed during the energy crisis of the early 1950s and 1970s (39). The process is embodied in the highly successful H-Coal process program. The so-called Lignol process is the biomass spinoff. The latter process has shown a 38 wt% yield of Kraft lignin to phenols consisting of: 2.5% phenol, 9.5% cresols, 12.5% ethyl phenol, 10.5% propyl phenol, and 2.6% xylene. It was expected that a commercial plant could produce 98 t/d of phenol, 70 t/d benzene, and 53 t/d fuel oil from 485 t/d Kraft lignin (40,41).

Coal provides a product slate of the preferred nonoxygenated aromatic compounds and would be a better raw material for this purpose if cost is comparable to biomass.

## **Biomass Potential**

The biomass-oriented database was compiled by applying the biomass process scenario to the need for chemicals. The data are sorted for all products and for each of the major feedstocks and their derivatives. The results are summarized in Table 4.

Biomass sources could account for almost all of the current petrochemicals except for 21 billion pounds of petroleum products that are predominantly C2–C7 alkanes. These petrochemicals would be replaced by biosugar as feedstocks for ethylene, and so on. Hence, bioproducts could constitute

Table 4  
The Biomass Alternative  
Interrelation among Potential Feedstocks,  
Million Pounds per Year—1985 Basis

	Primary feedstock	Derivatives with Other Feedstocks										Total
		Ethanol	Propanol	Butanol	Acetone	Acetate	Fumerate	Polyols	Syn Gas	Aromatics	Nat Prod	
Ethanol	5,352	103,351	8,717	79	535	4,850	0	272	1,819	37,695	1,483	158,800
Propanol	1,235	8,717	31,588	504	421	406	0	396	2,454	10,625	761	55,872
Butanol	716	79	504	3,693	0	179	3	357	1,898	48	0	6,761
Acetone	1,788	535	421	0	1,177	0	0	0	2,011	2,030	3	6,177
Acetic acid	2,917	4,850	406	179	0	0	0	103	0	28	63	5,630
Fumeric acid, etc.	923	0	0	3	0	0	1,051	0	0	158	4	1,216
Polyhydric alcohols	760	272	396	357	0	103	0	1,923	188	2,933	261	6,432
Subtotal	13,690	117,804	42,032	4,815	2,133	5,538	1,054	3,050	8,371	53,517	2,574	
Synthesis												
Gas	0	1,819	2,454	1,898	2,011	0	0	188	23,750	12,059	124	44,303
Aromatics	29,873	37,695	10,625	48	2,030	28	158	2,933	12,059	9,928	1,755	77,260
Subtotal	29,873	39,513	13,080	1,946	4,041	28	158	3,121	35,809	21,987	1,879	
Natural products	0	1,483	761	0	3	63	4	261	124	1,755	2,586	7,040
Petroleum products	21,549	0	0	0	0	0	0	0	0	0	0	0
Grand Total	65,112	158,800	55,872	6,761	6,177	5,630	1,216	6,432	44,303	77,260	7,040	

294 billion pounds of products, or 93% of the total; valued at roughly \$106 billion dollars. As shown in Fig. 3, this amount exceeds the 1985 personal purchase of new automobiles in the US and is 68% as large as clothing purchases. It represents 6.5% of the gross national product for goods and 2.5% of the total GNP for 1985.

### **Biomass Primary Feedstocks**

Since it was assumed that ethylene would be produced by dehydrating ethanol, it is understandable that ethanol would become the ranking biomass-based feedstock. Moreover, butadiene would also be produced from ethanol as it was during World War II by Publicker and Union Carbide in government plants to provide synthetic rubber for the war effort. Accordingly, ethanol would capture an even greater share of the total feedstocks than ethylene does for petrochemicals. It should be pointed out that the data for ethanol as a primary feedstock in Table 4 refer to the amount of ethanol now produced rather than that which would be needed to produce the derivatives that would be attributed to it.

### **Ethanol Derivatives**

As shown in Fig. 4, potential ethanol derivatives could account for a third of all organic chemicals, whereas propanol derivatives could account for another 10%.

A further breakdown of derivative combinations is shown in Figs. 5 and 6. Of all derivatives, those based on ethanol alone comprise the largest share. Derivatives of ethanol with aromatics are in a substantial second place. A dual research program on ethanol fermentation and lignocellulose hydrogenation would be required to achieve this position. Derivatives of propanol and synthesis gas, either alone or in combination with other primary feedstocks, also appear to be important.

## **CONCLUSIONS AND RECOMMENDATIONS**

Prospects for biomass commodity chemicals are currently unfavorable as a result of: generic deficiencies in the fermentation process, particularly with respect to generally low (below 5%) product concentrations and slow fermentation rates, and lack of a present competitive advantage for renewable materials compared with depressed prices for crude oil (42-47).

However, research can alter the first limitation and Middle East politics, the second.

In the meantime, a national research program on biomass conversion is strongly urged as a strategic insurance policy to protect the American organic chemicals industry against further disruptions in crude oil sup-

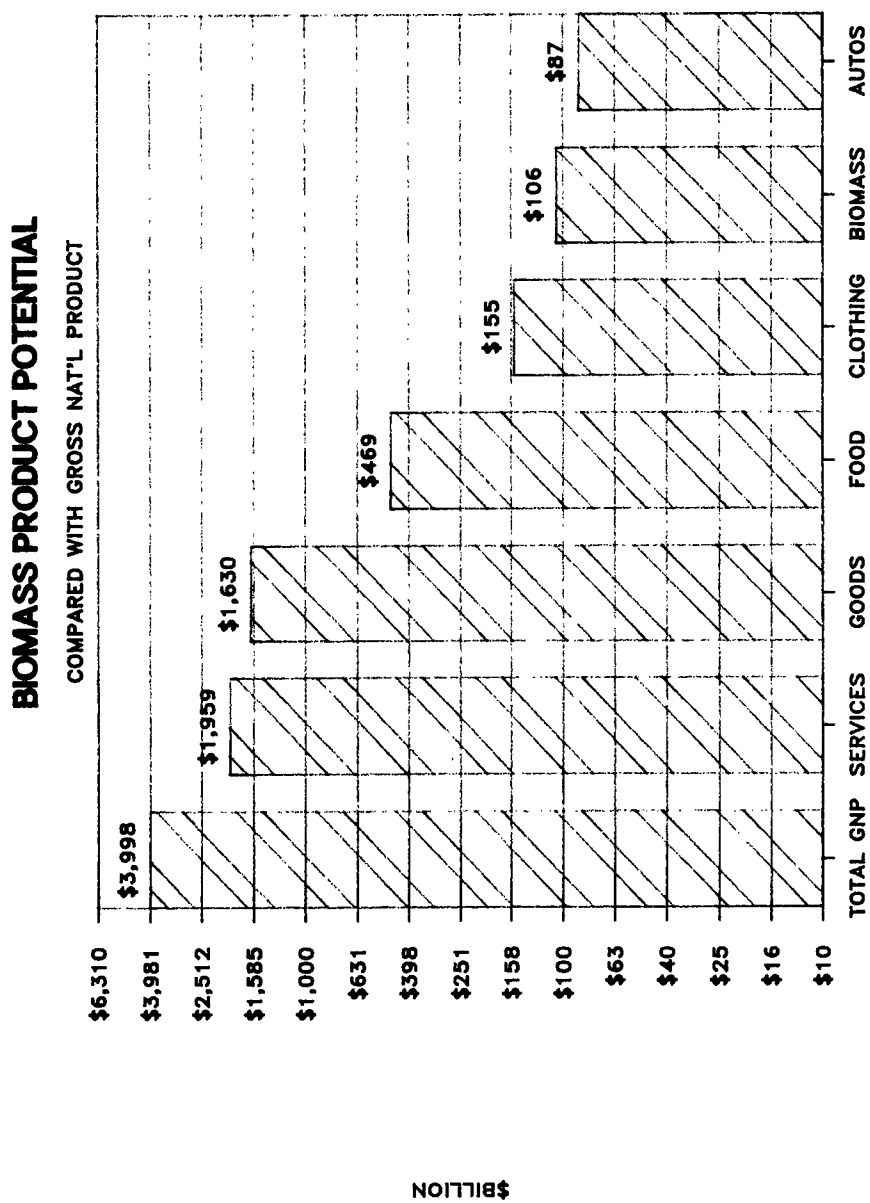


Fig. 3. Biomass product potential, compared with gross nat'l product.

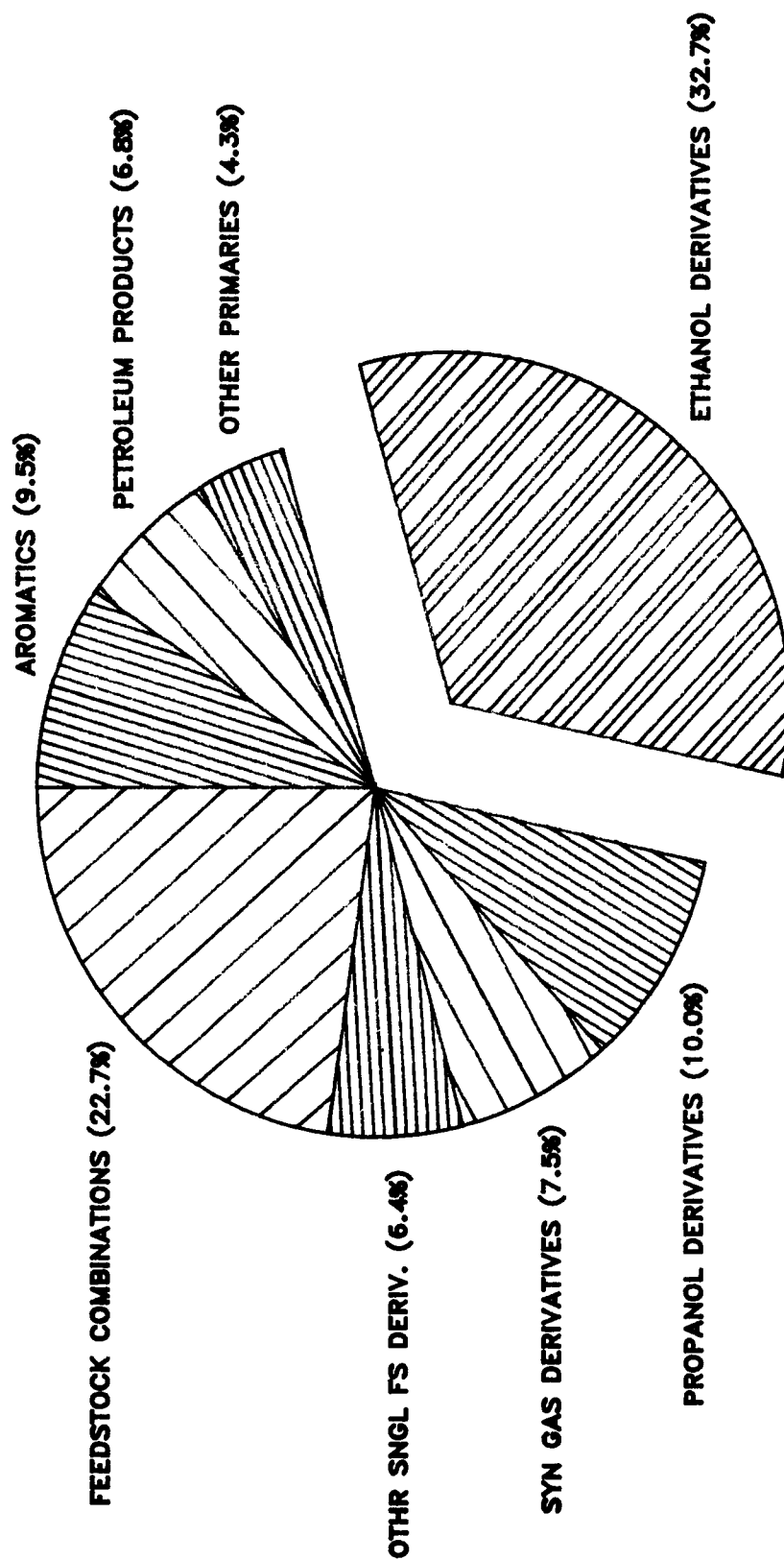


Fig. 4. The biomass alternative—potential origin of all products.

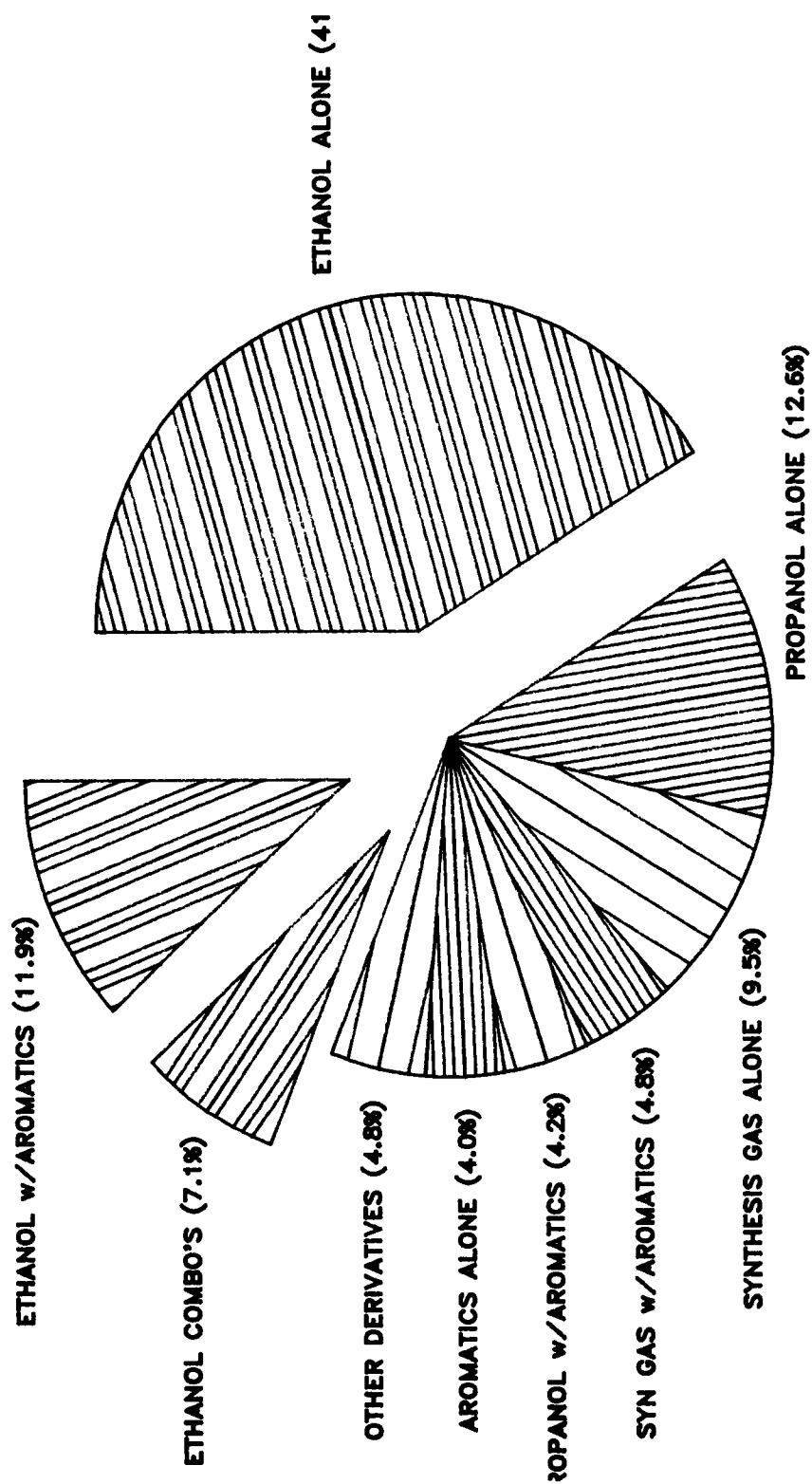


Fig. 5. Biomass-based organic chemicals—feedstock origin of derivatives.

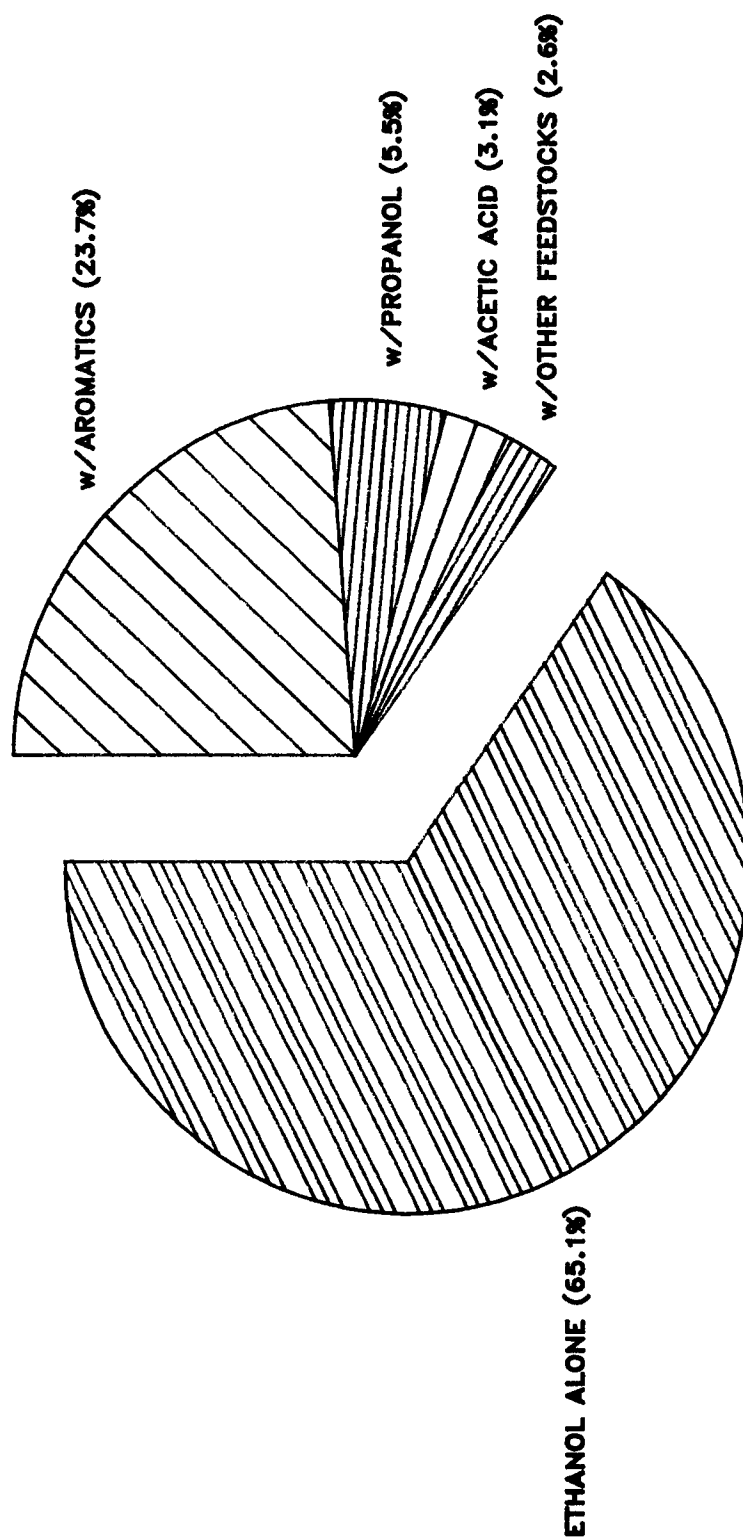


Fig. 6. Biomass-based organic chemicals—ethanol derivatives.

plies. Research should certainly feature fermentation programs related to ethanol and propanol. Concomitant research on lignin hydrogenation is also suggested as a means to broaden the potential bioproduct line.

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