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Biomass as a Source of Chemical Feedstocks: An Economic Evaluation

B. O. Palsson, S. Fathi-Afshar, D. F. Rudd, E. N. Lightfoot

Summary. It is suggested that the raw materials and technology exist for basing a major fraction of the U.S. chemical industry on four fermentation products, used in the proper portions: ethanol, isopropanol, *n*-butanol, and 2,3-butanediol. The primary route for introduction of these materials is dehydration of the alcohols and diols to olefins, which would cause little disruption of the existing industry downstream from the olefins. The proposed substitution has the advantages that it would provide a smooth transition toward renewable feedstocks, while decreasing dependence on fossil sources of organic material and use of toxic materials. However, to make these materials attractive as feedstocks or intermediates in chemical production, their current prices must be substantially reduced. Even with the optimum mix, their large-scale utilization will only occur at about 20 to 40 percent of their estimated chemical prices.

The chemical industry provides the synthetic materials used by industrial societies today. Its operations can be viewed as a continuum of chemical transformations, starting from basic raw materials and yielding finished products. The raw materials used currently by the industry are mostly hydrocarbons, derived from natural gas and crude oil, and synthesis gas, derived from coal. At present, the industry consumes a significant fraction of these commodities, and its consumption is expected to increase in the future.

Fermentation-derived fuels and chemicals have recently received much attention as a result of drastic price increases for oil and gas and forecasts of future shortages. Here we will not discuss biomass-derived fuels, but note that there is serious doubt about the adequacy of supply for this very large use. Instead, we will concentrate on biomass as an alternative source of chemical feedstocks. We believe that this is the more promising use of biomass, both because the supply of raw materials is unlikely to be limiting and because chemical feedstocks generally command a higher price than fuel. As a rule, the chemical value of a reactive compound is about three times its fuel value.

Our approach is to seek effective points of entry into the chemical industry, diagrammed in Fig. 1a. Shown in a schematic way is the progression from relatively low-cost raw materials at the left to much more valuable consumer products at the right. Figure 1b shows current production and prices for 14 of the largest volume intermediates at their approximate position in the progression. Greatly facilitating our task is the remarkable flexibility of the industry, which stems basically from the fact that there are many alternative routes to a given product. This has led the industry to a continuous search for the most economical feedstocks, and all we need to do is join the search process.

There are several good reasons for believing that biomass is an attractive source of organic materials on a long-term basis. Perhaps most important is the fact that biomass production can be sustained indefinitely in many different regions of the world and in both terrestrial and aquatic environments. For many countries then, and not least the United States, there is a prospect for decreased dependence on imports from expensive and frequently insecure sources. There are also potentially important social and ecological benefits.

1) Biomass production is relatively labor-intensive and can employ unskilled and semiskilled workers, who are currently in surplus, not only in developing countries but also in many industrialized ones.

2) Producing facilities would tend to be small relative to petrochemical complexes and could be dispersed, at least to some extent, according to social needs.

3) In addition to conserving nonrenewable resources, use of biomass would have ecological benefits. For example, carbon dioxide is abstracted from the atmosphere through photosynthesis, heat release to the environment is reduced, and formation of toxicants such as benzene can frequently be eliminated from process sequences.

4) It may be possible to upgrade municipal, industrial, and agricultural wastes, which can no longer be discarded without expensive processing; their negative economic value can have a significant effect on process costs.

These benefits are particularly important because, as we will see, the strictly economic advantages of biomass-based processes are still doubtful.

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Problem Selection and Scope of the Analysis

Promising approaches to increased utilization of biomass by the chemical industry range from gasification, yielding carbon monoxide and hydrogen, through pyrolysis reactions, to a wide variety of fermentations. We have chosen to concentrate on fermentations, primarily to narrow the scope of our analysis, but also because of the basic natures of biomass production and processing technologies.

Characteristically, biomass can be economically gathered only from a restricted geographic radius, in amounts that are small compared to those available from more concentrated raw materials such as coal. Since the economics of scale work strongly to the advantage of large gasification units, biomass sources are at a heavy disadvantage here.

On the other hand, even very large fermentations can be supplied effectively, and the facilities can be dispersed without great economic penalties. Moreover, fermentation has a long history of industrial success. It was the chief source of chemicals and solvents up to the 1940's, when the competition from inexpensive oil, coupled with a highly developed petrochemical technology, forced the industry to concentrate on pharmaceuticals and other complex molecules.

Fermentation technology has continued to evolve in these specialty applications, and microbial physiology has become a fast-growing and increasingly impressive branch of science. These factors, coupled with the increasingly high prices and doubtful availability of petroleum products, suggest that we take a hard look at the potential of fermentation. Critical to the success of such an endeavor is a clear measure of market requirements.

Table 1. Top 15 organic chemicals produced in the United States in 1979. Production and price values are from (*8*) and (*9*), respectively.

Chemical	Production (billion pounds per year)	Price (cents per pound)	Price (dollars per mole)
Ethylene	29.19	24	6.73
Propylene	14.30	20	8.42
Benzene	12.72	22	17.58
Toluene	11.86	19	17.51
Ethylene dichloride	11.82	22	21.77
Ethylbenzene	8.53	31	32.90
Vinyl chloride	7.54	22	13.75
Styrene	7.48	40	41.66
Methanol	7.41	7	2.28
Terephthalic acid	7.26		
Xylene	6.89	19	20.17
Formaldehyde	6.45	7	2.00
Ethylene oxide	5.28	39	17.18
Ethylene glycol	4.60	35	21.72
Butadiene	3.55	32	17.58

We concentrate here on characterizing the financial constraints within which a fermentation-based chemical industry must evolve if it is to become economically viable. We therefore choose not to consider the technology of fermentation in our analysis at all. Instead, we attempt to estimate the degree of market acceptance for fermentation products as a function of selling price, and we seek ways to maximize this acceptance. We thus provide a measure of the economic challenge facing fermentation technologies and at the same time hope to stimulate others to seek more effective entries into the chemical market.

It is clear at the outset that we face two major difficulties:

1) Since there are limited outlets for such high-value chemicals as alcohols, major market penetration requires chemical transformations to species acceptable by the chemical industry as intermediates. This generally means entering the diagram of Fig. 1a toward the left, where unit prices are typically lower.

2) Because the present industry is highly interactive, mainly through by-product production, large-scale introduction of a single chemical compound can cause substantial imbalances and result in a lowered acceptable price for the new chemical. As previously observed (*1*), direct price comparisons are not always meaningful.

We attempt to lessen the impact of these factors by seeking as attractive transformations as possible and by using a mix of fermentation products.

In other respects, our analysis is similar to that of Fathi-Afshar and Rudd (*1*) and has the same basis. We use the linear model of the chemical industry of Rudd *et al.* (*2*), which includes about 300 of the most important currently used chemical processes.

Here a computer is programmed to

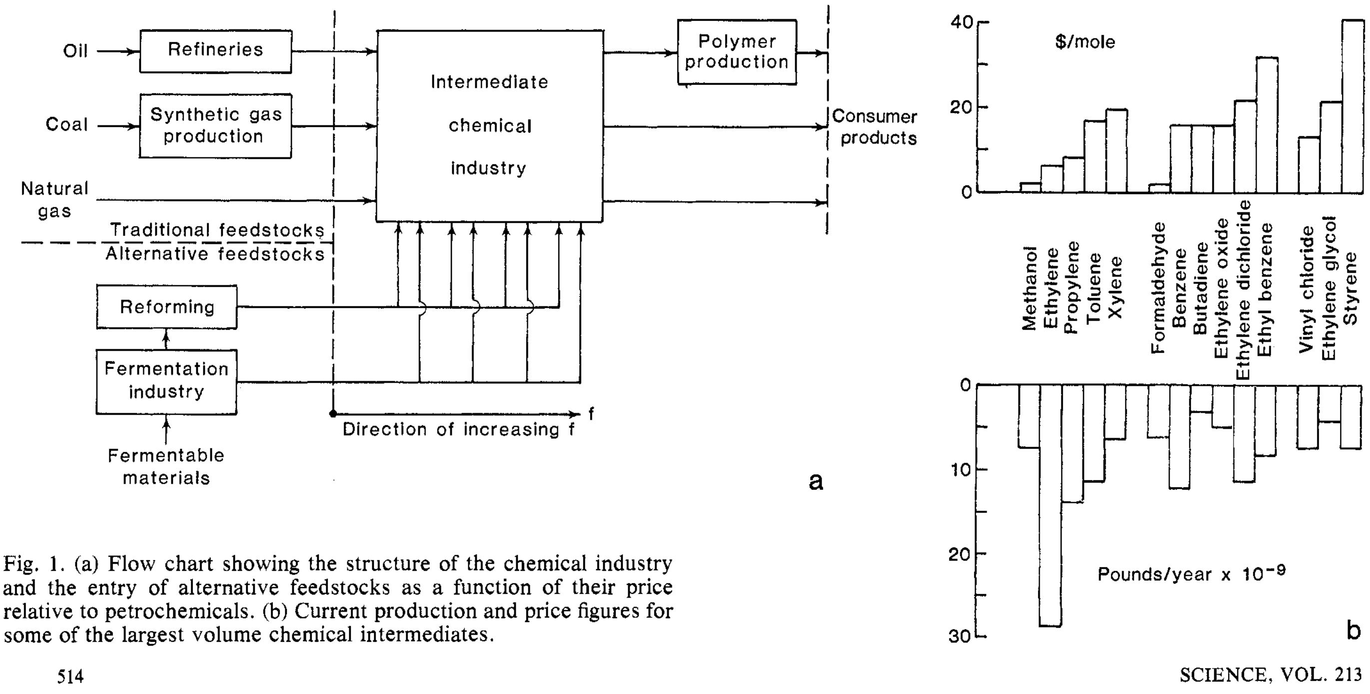


Fig. 1. (a) Flow chart showing the structure of the chemical industry and the entry of alternative feedstocks as a function of their price relative to petrochemicals. (b) Current production and price figures for some of the largest volume chemical intermediates.

select the technology that best meets the projected demands of the economy for end products. This model has already been used extensively by the chemical industry for long-range planning and was developed in a joint project by the National Science Foundation, Exxon Chemical Company, and the University of Wisconsin. A detailed description of the technique is given in (*2*).

Our reference frame is the industry as it is predicted to look in 1985, and the prices of fermentation products are expressed relative to projected chemical prices. That is, the penetration of each fermentation product into the 1985 chemical market is estimated as a function of f, where f is the price of the fermentation product under investigation divided by the projected chemical price of the corresponding petroleum-derived compound in 1985. We first analyze the acceptability of selected fermentation products by using only the processes included in the model. Then we consider the effects of adding new transformations to fermentation products, such as alcohol and diol dehydrations, to permit new entry points. We also look into the production of other intermediates from fermentation-derived chemicals.

Acceptance of Selected Fermentation Products by Existing Technology

Since a very wide variety of chemicals can be produced by fermentation processes, we must find some reasonable means for limiting the number considered. Here we confine our attention to markets of 1 billion pounds per year or higher, and under these circumstances we need only seek substitutes for very large volume feedstocks, basically those shown in Fig. 1 and listed in Table 1. These include only linear aliphatics of one to four carbon atoms and two basic aromatics, toluene and xylenes. The aromatics are primarily converted into only a few compounds, of which the most important is styrene. We will not further consider one-carbon compounds, as they can be most simply produced by gasification and the most promising raw materials for them are coals and related fossil fuels.

Promising fermentation products in the two- to four-carbon range include ethanol, acetic acid, acetone, isopropanol, *n*-butanol, and 2,3-butanediol, and we begin with these. Means by which these materials can be introduced into the intermediate chemical industry through existing processes are shown in Table 2. Promising new routes are discussed below.

Ethanol has already been discussed (*1*); here we need only put the results in perspective. Although ethanol finds a considerable market even at current chemical prices, it does not have a great impact until its price is reduced fivefold. At this point it becomes attractive for the production of ethylene by dehydration, a reversal of the present process for petrochemical ethanol. The very large price penalty required to open up this market results partly from process interaction. All of the propylene currently produced by the intermediate chemical industry is a by-product of ethylene production. To open the ethylene market for dehydration of biomass ethanol, the industry has to select an alternative, less economical route to ethylene with more propylene by-product. This constraint on ethylene production results in a higher price penalty for biomass ethanol than there would be if it only competed with ethylene production. As shown in the next section, this situation can be relieved by offering biomass-derived propylene in appropriate proportions to ethylene.

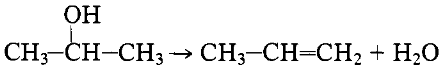
Market estimates for the other five products turn up no major surprises and suggest no truly large-scale markets. They do show that biomass acetic acid, acetone, isopropanol, and, to a lesser extent, *n*-butanol can take over existing markets from their petrochemical counterparts at relatively modest price reductions; markets of the order of 1 billion to 3 billion pounds per year open this way. However, 2,3-butanediol cannot be utilized by current technologies and does not find markets at any price. We now turn to seeking new entries and focus on the most important present intermediates.

Enhancement of Acceptance Through Dehydration Reactions

Since short-chain linear olefins and aromatics are the primary feedstocks of the present chemical industry, their production from fermentation products is an attractive route to our goal. The fermentation alcohols listed above can be dehydrated to yield these short-chain olefins. Furthermore, the 2,3-butanediol dehydration product, butadiene, can be dimerized to yield the important aromatic intermediate styrene. These reactions are the dehydration of ethanol to ethylene

$$CH_3{-}CH_2OH \rightarrow H_2C{=}CH_2 + H_2O$$

dehydration of isopropanol to propylene

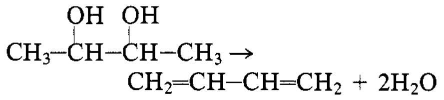


$$CH_3{-}\overset{OH}{CH}{-}CH_3 \rightarrow CH_3{-}CH{=}CH_2 + H_2O$$

dehydration of *n*-butanol to *n*-butylene

$$CH_3{-}CH_2{-}CH_2{-}CH_2OH \rightarrow CH_3{-}CH_2{-}CH{=}CH_2 + H_2O$$

dehydration of 2,3-butanediol to butadiene



$$CH_3{-}\overset{OH}{CH}{-}\overset{OH}{CH}{-}CH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + 2H_2O$$

and dimerization of butadiene to styrene (Diels-Alder reaction)

$$2CH_2{=}CH{-}CH{=}CH_2 \rightarrow C_6H_5{-}CH{=}CH_2$$

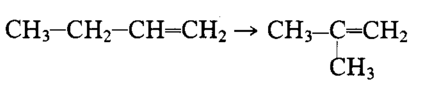
Except for ethanol, the dehydrations shown above have not been carried out on an industrial scale. In fact, the hydration of propylene to isopropanol in the 1920's is generally considered the beginning of petrochemical production. The dehydrations of the alcohols other than ethanol have been described (*3–5*) and take place under conditions similar to

Table 2. Utilization of fermentation feedstocks by the model industry in 1985 with present technologies.

Chemical	Amount (million pounds per year) at f value								
	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2
Ethanol*	1690	1690	1690	1690	1690	1690	2350	6540	55050
Acetic acid†	0	0	0	3400	3400	3400	3400	3400	3400
Isopropanol‡	2160	2160	2160	2160	2580	2580	2580	2580	2580
Acetone§	380	380	1370	1530	1530	1530	1530	1530	1530
n-Butanol‖	670	670	670	670	670	670	670	670	670
2,3-Butanediol¶	0	0	0	0	0	0	0	0	0

*The effects of price reduction on the model industry are discussed in (*1*). †At $f = 0.7$, fermentation-derived acetic acid is preferred over acetic acid synthesized from methanol and carbon monoxide; this will reduce consumption of methane, the precursor for methanol. ‡At $f = 1$, the isopropanol feedstock is preferred over isopropanol derived from hydration of propylene; at $f = 0.6$, acetone synthesized from isopropanol is favored over feedstock acetone. §At $f = 1$, acetone feedstock is preferred over acetone that is a by-product of phenol production by air oxidation of cumene (less phenol is made from cumene); at $f = 0.8$, hydrogen peroxide from isopropanol with acetone as a by-product becomes unattractive, and hydrogen peroxide via anthraquinone is favored; at $f = 0.7$, no phenol is derived from air oxidation of cumene. ‖At $f = 1$, *n*-butanol feedstock is preferred over *n*-butanol from propylene. ¶Since 2,3-butanediol is not produced commercially there is no price projection available for it; our price for 2,3-butanediol will be the same as for ethanol.

those for ethanol dehydration; therefore we assume that the cost data available for ethanol dehydration apply to the other processes as well. (For a typical dehydration the processing cost is minor compared to the raw material cost, and thus even large errors in our assumption will not affect the overall cost much.) The dimerization of butadiene has been described (*6*), as has the isomerization of *n*-butylene to isobutylene (*7*)



$$CH_3{-}CH_2{-}CH{=}CH_2 \rightarrow CH_3{-}\underset{\overset{|}{CH_3}}{C}{=}CH_2$$

which we will discuss later.

The impact of biomass isopropanol dehydration on the model industry is shown in some detail in Table 3. While reducing the price of biomass isopropanol, we keep biomass ethanol available at half of the 1985 projected price. We do this in order to observe the interaction effect between ethylene and propylene production. Previously, biomass ethanol available at $f = 1/2$ was not utilized for acetaldehyde production, but it becomes attractive when $f = 0.35$ for isopropanol. The dehydration of isopropanol becomes attractive at $f = 0.6$, and the propylene produced is used for acrylonitrile production. As the price reduction is continued, the dehydration route is increasingly utilized (Table 3), and at $f = 0.35$ isopropanol becomes the main source of propylene. This will force ethylene production to an ethane-based process with less propylene by-product. At this point isopropanol is utilized at the rate of 19 billion pounds per year.

Table 4 shows the main changes in the model industry's feedstock consumption when the price level of isopropanol is held at $f = 0.35$ and that of biomass ethanol is reduced from $f = 0.5$ to $f = 0.35$. The ethane-based ethylene process is forced out of the model, and both ethylene and propylene are made entirely from biomass sources. The rate of ethanol utilization is 69 billion pounds per year at a price level of $f = 0.35$, compared to 55 billion pounds per year at $f = 0.2$, when only ethanol dehydration was available. At this point, biomass ethanol and isopropanol are the two largest feedstocks utilized by the industry at 69 billion and 25.5 billion pounds per year, respectively.

The effects of price reduction for 2,3-butanediol are much simpler. Butadiene produced by its dehydration at $f = 0.6$ is preferred over that derived by conventional routes, from *n*-butane and *n*-butylene, so that it becomes the sole supplier of butadiene. When the price level of 2,3-butanediol reaches $f = 0.25$, its dimerization to styrene becomes economical and 40 percent of the styrene produced is obtained by this route. Dimerization of butadiene cannot totally take over the styrene market because of the very attractive hydrogen peroxide process that yields styrene from ethylbenzene with the valuable by-product propylene oxide.

Dehydration of *n*-butanol is not accepted at any price unless it is isomerized to yield a mixture of *n*-butylene and isobutylene. This is because the separation of mixed butylenes from refineries, to obtain isobutylene for polymer production, yields *n*-butylene as a by-product. Dehydration of *n*-butanol followed by isomerization is accepted as the sole supplier of four-carbon monoolefins in the model industry when the price level of *n*-butanol is at $f = 0.17$.

The changes in feedstock consumption brought about at different price levels for fermentation products are summarized in Table 5. The values in Table 5 show that biomass-derived feedstocks can be the major supplier of chemicals to the model industry. The utilization of other traditional feedstocks is substantially reduced and in some cases has vanished. The perturbation in aromatic feedstocks is not substantial, but would be greater if benzene utilization were taxed because of the toxic nature of this material.

Discussion

The analysis above demonstrates the technical feasibility of basing the U.S. chemical industry largely on indigenous renewable raw materials, but it also suggests that large-scale shifts of this type

Table 3. Utilization of isopropanol by the model industry in 1985; *f* for ethanol is 0.5.

Feedstock or process	Amount (million pounds per year) at *f* for isopropanol							
	1.0	0.9	0.8	0.7	0.6*	0.5†	0.4‡	0.35§
Acetone	370	370	330	330	0	0	0	0
Ethane	2,780	2,780	2,780	2,780	2,780	2,710	2,050	20,000
Ethanol	1,690	1,690	1,690	1,690	1,690	1,690	1,690	2,350
Isopropanol	2,160	2,160	2,220	2,220	5,480	5,710	7,000	18,750
n-Butanol	670	670	670	670	670	470	0	0
Propylene (refinery grade)	4,700	4,700	4,700	4,700	4,700	4,700	4,700	0
Propane	86,630	86,630	86,630	86,630	84,140	84,080	83,930	38,830
Acetaldehyde								
From ethylene	550	550	550	550	550	550	550	0
From ethanol	0	0	0	0	0	0	0	550
Acrylic acid								
From propylene	0	0	0	0	0	0	400	400
From carbonylation of acetylene	400	400	400	400	400	400	0	0
Acrylonitrile								
From ammoxidation of propylene	320	320	320	320	1,710	1,710	1,710	1,710
From cyanation/oxidation of ethylene	1,390	1,390	1,390	1,390	0	0	0	0
Acetone, from hydrogenation of isopropanol	0	0	0	0	330	330	40	40
Ethylene								
From pyrolysis of ethane	0	0	0	0	0	0	0	13,800
From pyrolysis of propane	37,300	37,300	37,300	37,300	36,250	36,220	36,150	16,450
Hydrogen cyanide, from ammoxidation of methane	1,280	1,280	1,280	1,280	440	440	440	440
n-Butanol, from propylene	0	0	0	0	0	200	670	670
Hydrogen peroxide, from isopropanol	470	470	490	490	490	490	630	630
Propylene, from dehydration of isopropanol	0	0	0	0	1,920	2,070	2,930	10,725

*At $f = 0.6$, dehydration of isopropanol becomes feasible. Acetone is derived from isopropanol. Acrylonitrile is made from propylene and ammonia; HCN production then goes down because acrylonitrile was made from ethylene and HCN. †At $f = 0.5$, propylene becomes attractive for production of *n*-butanol. ‡At $f = 0.4$, all hydrogen peroxide is made from isopropanol; the increased acetone by-product drives the direct process from isopropanol to acetone out of the model. Acrylic acid is made by oxidation of propylene. §At $f = 0.35$, acetaldehyde from ethanol becomes attractive, and it is no longer made from ethylene. All the propylene used by the model industry is derived from isopropanol; this leads to the production of ethylene from ethane rather than propane.

Table 4. Utilization by the model industry of isopropanol and ethanol in 1985; f for isopropanol is 0.35.

Feedstock	Amount (million pounds per year) at f for ethanol	
	0.5	0.35*
Ethane	20,000	2,050
Ethanol	2,350	69,150
Isopropanol	18,750	25,550
Propane	38,800	0

*At f = 0.35, dehydration of ethanol becomes attractive and replaces ethylene from ethane. Note that the quantity of ethanol used is considerably higher than in Table 2. Ethylene based on propane is forced out of the model industry, and the propylene by-product is obtained from dehydration of isopropanol.

are not imminent on the basis of strictly economic criteria. It is therefore important to decide whether social factors justify fostering the development of a major biochemical industry and, if so, to elaborate an effective economic strategy for doing so.

We believe that this discussion can be put into perspective by comparing the characteristics of a biochemical industry and one required to produce chemicals from coal, as by-products of synthetic liquid fuels production. Such a comparison is in many ways favorable to fermentation.

1) Both approaches would reduce our dependence on foreign energy sources, but fermentation would put only a small pressure on fossil reserves of raw material.

2) A fermentation-based industry would employ simpler technologies and relatively larger numbers of semiskilled workers.

3) Fermentation would be most economical in relatively small, dispersed units, since transportation of thinly distributed raw materials would be a major cost. Synthetic fuel plants, on the other hand, must be large installations, putting a heavy pressure on the environment in their vicinity.

4) By-products of a fermentation industry can be beneficial if returned as fertilizer to the source of raw materials, whereas by-products of synthetic fuel production tend to be toxic and to present health and environmental hazards.

Direct economic comparisons are beyond the scope of our present discussion. However, coal-based synthetic fuels cannot currently compete with petroleum-derived products in the market, and subsidies are also required for their development.

It should also be noted that the infrastructure for a fermentation industry is already at hand. Applied microbiology is a vigorous and dynamic area of technology, with an impressive scientific base in both biochemistry and microbial physiology. Well-staffed laboratories exist in universities, industry, and government-operated facilities. In addition, the major oil companies have developed considerable expertise in large-scale fermentation technology. [For example, in a process being developed by Gulf Oil Company, cellulose is converted to ethanol (*7*).]

It appears that rapid development does not require an elaborate government-directed research program—only the economic incentive of a profitable outlet for products. Such an incentive can be provided in many ways, each with its own social and economic impact. One could, for example, select a production level suitable for development of a pilot industry and subsidize one or two corresponding processes sufficiently to stimulate it. An example could be an industry employing 2,3-butanediol. Alternatively, one could subsidize employment in a region that is not now self-supporting—for example, by developing hydrolysis of wood to fermentable sugars in northern Michigan or Appalachia. Here the decrease in cost of federal aid to the underemployed labor force would offset at least part of the subsidy and lead to a healthier social situation. Penalties for production of toxic intermediates such as benzene would tend to make butadiene the preferred source of styrene and favor the development of a 2,3-butanediol fermentation industry.

Taking all these factors into account, we believe that the immediate development of a biochemical industry, at least on a pilot scale, is desirable. At the same time, it must be recognized that historically developments in the energy industry have critically affected chemicals, while the reverse has not been true. Therefore, if a coal-based synthetic fuels industry becomes a major supplier of energy needs, it will create by-products of significant chemical value that would compete with biomass-derived products.

Table 5. Changes in feedstock consumption by the model industry.

Feedstock*	Feedstock consumption (million pounds per year)	
	Without fermentation-derived feedstocks	With fermentation-derived feedstocks†
2,3-Butanediol	0	17,000
Butylene	1,670	0
Butadiene	3,150	0
n-Butanol	0	2,400
Ethane	2,800	2,300
Ethanol	75	69,150
Gas oil	16,000	0
Fuel oil (high sulfur)	200	0
Isopropanol	0	25,550
n-Butane	3,400	2,600
Naphtha	2,450	1,150
Oxygen	18,100	11,300
Propylene (refinery grade)	4,700	0
Propane	83,800	0
Benzene	12,500	11,950
Toluene	10,300	8,250

*At this point acetone is made from isopropanol and acetic acid from *n*-butylene, so we do not further explore these feedstocks. †Here f = 0.35 for ethanol, 0.35 for isopropanol, 0.25 for 2,3-butanediol, and 0.17 for *n*-butanol.

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