

Potential conservation of biomass in the production of synthetic organics by Martin H. Bender

Abstract. *Hydrocarbon intermediates typical of the chemical industry are an inefficient route for the production of synthetic organics from biomass. This is demonstrated by stoichiometric calculations of mass losses of oxygen from biomass for various chemical reactions. As a result, the biomass required to meet the current US demand for synthetic organics would be more than three times the mass of current fossil fuel feedstocks. The mass losses can be avoided by converting biomass into oxygenated chemicals, not including fermentation of sugars into oxygenated alcohols. This alternative route would conserve about 50 percent of the biomass that would otherwise be required for the current mix of hydrocarbon processes across the synthetic organics industry. Oxygenated chemicals are surveyed briefly, including some considerations in finding oxygenated substitutes for hydrocarbon products.*

Introduction

Petrochemical feedstocks are used in industry to produce synthetic organics, such as plastics, synthetic fibers and rubber, solvents, lubricants, waxes, petrochemical coke, asphalt and road oil [1]. These organics can also be produced from renewable resources [2-5].

Synthetic organics are presently based on hydrocarbons mainly from petroleum and natural gas. If such organics were to be produced from renewable resources, most of the quantity would be derived from biomass [6]. In contrast to hydrocarbons, almost all biomass contains about 45 percent oxygen in addition to hydrogen and carbon, as roughly represented by the stoichiometry of the approximate, basic chemical formula of CH_2O for biomass.

Various economic feasibility studies have investigated the conversion of biomass into hydrocarbon intermediates of the current petrochemical industry [7,8]. However, this is an inefficient conversion of biomass into desired products because oxygen representing roughly half of the mass in biomass would be lost in oxygen-containing by-products such as water and carbon dioxide [8,9]. Moreover, empirical yields are short of theoretical yields [10].

In the long term, the chemical industry must be restructured to utilize processes that retain the oxygen in biomass during conversion of biomass into synthetic organics. In other words, this represents a conservation program of the oxygen in biomass as oxygenated chemicals. It is not premature to begin discussing long-term strategy since this restructuring will require much research to develop oxygenated chemicals as substitutes for current end-products and also large investment in many industrial facilities over more than a few decades.

This paper presents mass and energy balances for important chemical processes in the conversion of biomass into hydrocarbons. Then, the biomass required for the current national demand of synthetic organics is estimated for conventional hydrocarbon products and then for oxygenated chemicals. The paper lists some alternative chemical processes that avoid mass loss

of oxygen in the production of synthetic organics from biomass, including some considerations in finding oxygenated substitutes for hydrocarbon products.

Mass and energy balances

Biochemical processes involving the production of cellular biomass have substantial mass loss through by-products of carbon dioxide and water ([Table 1](#)). The first three reactions in [Table 1](#) normally appear in the literature without cellular biomass. For example, the balanced equation for anaerobic fermentation (incomplete digestion) is usually written: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$, in which case the stoichiometry of the equation gives an absolute maximum product yield of 51 percent for the ethanol (C_2H_5OH). However, with 8 percent of the glucose ($C_6H_{12}O_6$) being needed for growth and maintenance of the fermenting organism, the theoretical product yield drops to 47 percent [13].

Without cellular biomass in the chemical equation for methane generation (complete anaerobic digestion), the absolute maximum product yield would be 27 percent, but with 14 percent of the glucose needed for the digesting organism, the product yield drops to 23 percent ([Table 1](#)). Since there is no yield of product in aerobic respiration, it is not used to produce industrial hydrocarbons from biomass. However, it is included in [Table 1](#) because it is essentially the most efficient means of converting organic carbon compounds into biomass, as evident by the carbon balance in the table. It is also the means by which energy in carbohydrates is transferred to adenosine triphosphate, the chief chemical energy source for plant and animal cells, but with a substantial energy loss during the transfer ([Table 1](#)).

In contrast to aerobic respiration, there is little energy loss as heat in anaerobic fermentation and methane generation. Hence, they are theoretically efficient processes for producing useful fuels from carbohydrates. Methane (CH_4 , the main constituent of natural gas) is generated in biogas digesters utilized in India and China, and ethanol (part of gasohol) is commonly produced from grain or sugar crops by anaerobic fermentation in stills.

Polymerization is the process by which plants produce cellulose $(C_6H_{10}O_5)_n$ from glucose ([Table 1](#)). The reverse of this reaction, or hydrolysis of cellulose to release glucose, is the first industrial step in the biological conversion of biomass into synthetic organics [14]. Also, polysaccharides such as starch must be hydrated to release sugars for use as energy sources in living organisms. Dehydration of alcohols is one of the processes for producing olefins, such as ethylene ($H_2C=CH_2$). These processes incur little or no loss of energy, but dehydration involves considerable mass loss compared to polymerization and hydration.

General conversion efficiency

The conversion of biomass into synthetic organics often includes processes with large mass losses such as fermentation and dehydration. To determine the losses for the US synthetics

industry as a whole, Goldstein [10] divided the industry into 25 classes of products and tabulated the amount of lignocellulose that would be required for the production of each class. He found that the amount of oven-dry wood required to provide the lignocellulose for the entire synthetic industry would be four times the weight of these organics. This included the assumption that the lignocellulose was being fully utilized since the ratio of cellulose and lignin required for this industry was about 2:1, the same as their natural abundance in wood. Hence, the general efficiency for conversion of wood into these organics would be about 25 percent. Goldstein's study is the only one that has estimated this efficiency for the entire industry, and it still holds for current industry (I. Goldstein, personal communication, 9/27/99). The validity of some calculations by Goldstein for current technology is confirmed in the Appendix.

Use of this conversion efficiency in calculations below rests on two plausible assumptions. One is that other biomass besides wood would also have this conversion efficiency into these organics. The other is that it should be possible to structure the chemical industry of these organics so that its demand for cellulose, lignin and hemicellulose would match the natural abundance of these components in biomass, thus ensuring full utilization of these components. Wood and other cellulosic biomass consist almost entirely of these components [16].

Biomass demand

In 1995, the US consumed 132 million t of synthetic organics, an annual geometric increase of 3.1 percent since 1985, or 2.0 percent since 1970 [17] (all reported weights are oven-dry). Nearly two-thirds of this was in the petrochemical industries, and more than one-fifth was asphalt and road oil ([Table 2](#)). Within the petrochemical industries, the amount of plastics and synthetic fibers and rubber rose from 36 million t in 1992 to 41 million t in 1997, an annual geometric increase of 2.6 percent [18, 24].

Synthetic organics required 5.6 EJ (1 EJ = 10^{18} joules) of fossil fuel feedstocks ([Table 2](#)), or 7 percent of the 81 EJ of fossil fuels consumed by the US in 1995 [25]. Due to lack of recent data, this paper does not include the power required for producing synthetic organics.

The present US demand for synthetic organics would require 439 million t of biomass, or 3.3 times the mass of fossil fuel feedstocks currently consumed for synthetic organics ([Table 2](#), footnote a). Three-fourths of this is due to the above 25 percent conversion efficiency for the petrochemical industries ([Table 2](#)). Due to the gross energy content of biomass being slightly less than half of that for the current mix of fossil fuel feedstocks ([Table 2](#) footnotes), the total energy content of the required biomass feedstock would be about $(3.3)(0.5)$, or roughly 1.6 times that in current fossil fuel feedstocks, or more exactly, 8.8 EJ ([Table 2](#)).

Oxygenated chemicals

Mass losses of oxygen incurred by the conversion of biomass into hydrocarbons could be avoided by instead converting the biomass into oxygenated chemicals. Nearly half of the 50 most important industrial organic chemicals are oxygenated olefins [26,27]. Hence, it should be possible to restructure the organic chemical industry around oxygenated chemicals from biomass.

If this restructuring could be done efficiently without mismatch between the relative amount of products and the composition of biomass feedstock, then biomass required to provide the current US demand for each group of synthetic organics would be (million t): lubricants and waxes, 13; coke, 19; and tar, 77 ([Table 2](#)). The demand for the petrochemical industries in [Table 2](#) is crudely estimated by assuming that for any given oxygenated chemical end-product only hydrolysis of biomass and several subsequent oxygen-conserving processes would be needed to produce it. For three consecutive processes, this would give an average empirical mass conversion efficiency of $(1.11)(0.80)(0.95)(0.95)$, or 0.80 gram of oxygenated chemicals per gram of biomass ([Table 1](#), Appendix). Hence, the national biomass demand for the petrochemical industries would be $83/0.80$, or 104 million t ([Table 2](#)). The resulting total biomass demand for synthetic organics would be 213 million t, or almost half of the same demand met by biomass converted into hydrocarbons for synthetic organics ([Table 2](#)).

Oxygenated olefins could be obtained from cellulose and hemicellulose [26], and oxygenated aromatics such as phenolics from lignin [28]. For example, hydrolysis of biomass yields simple sugars such as glucose, mannose and xylose, which can be subjected to hydrogenation or acid catalysis, followed by other chemical reactions to yield a wide variety of oxygenated chemicals. Some of these processes have been practiced commercially for decades. However, fermentation of these sugars to various oxygenated alcohols should not be conducted because of the substantial mass loss of oxygen in carbon dioxide ([Table 1](#)). Instead, the alcohols must be obtained by chemical processes that do not incur large mass losses.

Also, pyrolysis would convert the entire biomass, mainly cellulose, hemicellulose and lignin, into various oxygenated olefins and aromatics [29]. For example, synthesis gas from gasification of biomass can be catalytically converted into methanol followed by oxidation to formaldehyde and other important industrial compounds [30].

In some cases, the difficult task will be to find oxygenated substitutes for current hydrocarbon-based products used by society. A substitute must have the properties for which the original product was utilized, or it must have a functional advantage. As an example of the former case, levulinic acid is a versatile chemical intermediate that at one time was obtained commercially by acid hydrolysis of wood, and it has been proposed that ethylene glycol could be replaced by levulinic acid salts as an automotive antifreeze [9]. An example of a functional advantage is crystallinity that can be controlled in optical isomers of natural chemicals to provide strength, elasticity and other properties [9]. In other words, an increased understanding of stereochemistry and polymer science could produce various sophisticated chemicals more easily from biomass than from fossil fuel feedstocks. Genetic engineering will also provide novel bio-based production of synthetic organics, such as biodegradable plastics, industrial lubricants, and feedstocks for soaps, detergents, drugs and pharmaceuticals [31,32].

Discussion

Previous studies of national biomass programs have regarded organics as a negligible demand compared to the current national demand for energy [e. g., 33]. This is because they compared the amount of end products in synthetic organics when instead they should have compared the initial amount of biomass required to make the end products. It would have been correct to consider only the end products if they were derived from fossil fuels with little mass loss. However, if these organics are to be produced from biomass by conventional hydrocarbon processes, then the accompanying mass losses must also be included in the comparison; i.e., the initial biomass must be considered. The result is that the biomass required to meet the current US demand for synthetic organics would be more than three times the mass of current fossil fuel feedstocks. The production of oxygenated chemicals instead of hydrocarbon products would reduce the required biomass by about half.

To reduce national demand for biomass in the future, coal could also be used as a feedstock for synthetic organics [34]. However, through processes such as pyrolysis, carbonization and hydrogenation, most conversion efficiencies of mass for coal across the range of synthetic organics will probably not be much better than those for biomass [35,36]. As the sole feedstock, if as much coal were required as biomass for the current national consumption of synthetic organics, or 8.8 EJ ([Table 2](#)), then this would represent an increase of 40 percent over the current consumption of coal in the US [25]. As with biomass, the conversion of coal into synthetic organics will involve large capital expenditures to install clean conversion technologies [35,36].

Conclusion

Production of the current demand of synthetic organics in the US by oxygenated chemicals would require only half of the biomass needed if the organics had been produced by hydrocarbons from biomass. This would be equivalent to conserving 50 percent of the biomass that would have been consumed in hydrocarbon processes for the production of synthetic organics. One stipulation is that oxygenated alcohols must be obtained by chemical processes other than fermentation of sugars, which entails considerable mass loss of oxygen in carbon dioxide.

Market forces currently dictate the economic structure of the petrochemical industry with regard to present resources, mainly fossil fuels, but are insensitive to the basic chemical composition of biomass resources [9,10]. Hence, there is a need for national policy on the development of the industry of synthetic organics from biomass and coal. in the existing petrochemical industry [9,10]. The will ensure that the structure of the industry for synthetic organics is efficiently developed to utilize biomass resources to their fullest extent.

Acknowledgments. The author thanks two reviewers for their contributions to this paper.

Appendix

In his comprehensive table on the lignocellulose required to provide the products of the entire US synthetics industry, Goldstein [10] did not specify the conversion efficiency for the hydrolysis of cellulose into sugars. Since hydrolysis is the initial step in the production of synthetic organics from biomass, his assumed value must be determined to verify that it still holds for current technology. It will be shown below that his assumed value was close to 80 percent. Although Goldstein regarded this as an optimistic efficiency in 1975 (footnote in his Table 2), it can now be achieved by technology currently available [15]. Hence, some particular results from his detailed table can be used in this paper for calculations on the current US synthetics industry.

Since Goldstein estimated a mass yield of 0.25 for polyethylene from cellulose, we will derive and compare an estimate of the mass yield for ethylene in order to determine his assumed conversion efficiency for hydrolysis. Ethylene can be obtained by hydration of cellulose into glucose followed by anaerobic fermentation into ethanol and then dehydration into ethylene. In the order of the three reactions, the overall theoretical mass yield of ethylene is $(1.11)(0.47)(0.61)$, or 0.32 gram per gram of cellulose in biomass ([Table 1](#)). In the same order, the overall empirical efficiency is $(80)(95)(95)$, or 0.72 [10,15]. Thus, the empirical mass yield of ethylene is 0.23 gram per gram of cellulose. Since this is similar to Goldstein's estimate for polyethylene, he also assumed an empirical efficiency close to 80 percent for hydrolysis of cellulose in the production of the other classes of synthetic organics that he surveyed.

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