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Hybrid Thermochemical/Biological Processing

Putting the Cart Before the Horse?

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Abstract

The conventional view of biorefineries is that lignocellulosic plant material will be fractionated into cellulose, hemicellulose, lignin, and terpenes before these components are biochemically converted into market products. Occasionally, these plants include a thermochemical step at the end of the process to convert recalcitrant plant components or mixed waste streams into heat to meet thermal energy demands elsewhere in the facility. However, another possibility for converting high-fiber plant materials is to start by thermochemically processing it into a uniform intermediate product that can be biologically converted into a bio-based product. This alternative route to bio-based products is known as hybrid thermochemical/biological processing. There are two distinct approaches to hybrid processing: (a) gasification followed by fermentation of the resulting gaseous mixture of carbon monoxide (CO), hydrogen (H_2), and carbon dioxide (CO_2) and (b) fast pyrolysis followed by hydrolysis and/or fermentation of the anhydrosugars found in the resulting bio-oil. This article explores this “cart before the horse” approach to biorefineries.

Index Entries: Biochemical processing; biorefinery; gasification; lignocellulose; pyrolysis; thermochemical processing.

Introduction

The Biomass Research and Development Technical Advisory Committee (2002) of the US Departments of Energy and Agriculture defines a biorefinery as: “A processing and conversion facility that (a) efficiently separates its biomass raw material into individual components and (b) converts these components into marketplace products, including biofuels, biopower, and conventional and new bioproducts” *(1)*. In the conventional view of a biorefinery, the separated components are monosaccharides and lignin. This separation involves physical and chemical pretreatments and enzymatic hydrolysis. The carbohydrate fractions are then biologically

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converted into ethanol and other bio-based products. Lignin may be burned for process heat, gasified to syngas, or processed into bio-based products. Thus, biological treatments are followed by high-temperature thermochemical treatments. An alternative approach is to subject biomass to thermochemical treatments that yield a uniform intermediate product, which can then be biologically converted into a bio-based product. There are two distinct approaches to hybrid processing:

1. Fast pyrolysis followed by hydrolysis and/or fermentation of the anhydrosugars found in the resulting bio-oil.
2. Gasification followed by fermentation of the resulting gaseous mixture of carbon monoxide (CO), hydrogen (H_2), and carbon dioxide (CO_2).

Bio-Oil Fermentation

Fast pyrolysis is the rapid thermal decomposition of organic compounds in the absence of oxygen to produce liquids, gases, and char *(2)*. Bio-oil from fast pyrolysis is a low-viscosity, dark-brown fluid with up to 15–20% water, which contrasts with the black, tarry liquid resulting from slow pyrolysis or gasification *(3)*. The bio-oil is a mixture of many compounds, although most can be classified as acids, aldehydes, sugars, anhydrosugars, and furans, derived from the carbohydrate fraction and phenolic compounds, aromatic acids, and aldehydes, derived from the lignin fraction. The higher heating values of pyrolysis liquids range between 17 MJ/kg and 20 MJ/kg with liquid densities of about 1280.0 kg/m^3. Assuming conversion of 72% of the biomass feedstock to liquid on a weight basis, yield of pyrolysis oil is about 560 L/t (dry) biomass.

Bio-oil fermentation is based on the observation that under rapid pyrolytic conditions, pure cellulose yields levoglucosan, an anhydrosugar with the same empirical formula as the monomeric building block of cellulose: $C_6H_{10}O_5$ *(4)*. Anhydrosugar is a sugar from which one or more molecules of water have been removed, resulting in the formation of an internal acetal structure (*see* Fig. 1). On the other hand, addition of a small amount of alkali inhibits the formation of levoglucosan and promotes the formation of hydroxyacetaldehyde and for slower heating rates and lower temperatures char rather than liquids is preferentially formed. These multiple reaction pathways for pyrolysis of cellulose are illustrated in Fig. 2 *(2)*.

Scott and coworkers *(5)* at the University of Waterloo in Ontario, Canada recognized that alkali in biomass catalyzed the char-forming pathway. If these cations are removed by soaking the feedstock in dilute acid before pyrolysis, the lignocellulose is depolymerized to anhydrosugars, primarily levoglucosan, at very high yields. Levoglucosan is readily hydrolyzed to glucose. Brown and his collaborators *(6)* evaluated the effect of alkali removal on the pyrolytic products of cornstover. Three pretreatments were evaluated: acid hydrolysis, washing in dilute nitric acid, and

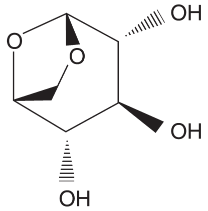

Fig. 1. Chemical structure for levoglucosan (1,6-anhydro-β-D-glucose).

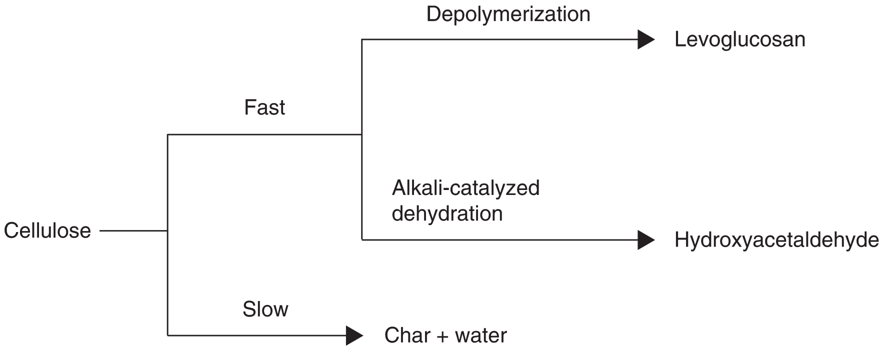

Fig. 2. Reaction pathways in fast pyrolysis.

washing in dilute nitric acid with the addition of $(NH_4)_2SO_4$ as a pyrolytic catalyst. All three acid treatments were able to substantially increase the yield of anhydrosugars, as shown in Table 1. Acid hydrolysis of this anhydrosugar yielded 5% solutions of glucose and other simple sugars.

The resulting glucose solutions can be fermented, as demonstrated by Prosen et al. *(7)*. However, the resulting substrate derived from the bio-oil contains fermentation inhibitors that must be removed or neutralized by chemical or biological methods. Chemical methods that have been evaluated on bio-oil derived substrate include solvent extraction, hydrophilic extraction, and adsorption extraction *(8)*. Khiyami *(9)* explored the use of biofilms of *Pseudomonas putida* and *Streptomyces setonii* to remove toxins from bio-oil.

One manifestation of a biorefinery based on fermentation of bio-oil is illustrated in Fig. 3. Fibrous biomass is pretreated with dilute acid to simultaneously remove alkali and hydrolyzes the hemicellulose fraction to pentose. The remaining fraction, containing cellulose and lignin, is pyrolyzed at 500°C to yield char, gas, and bio-oil. The bio-oil is separated into pyrolytic lignin and levoglucosan-rich aqueous phase. The char, gas, and lignin are burned to generate steam for distillation and other process heat requirements of the plant while the levoglucosan is hydrolyzed to hexose. The pentose and hexose are fermented to ethanol.

Table 1
Products (maf wt%) of Pyrolysis for Different Pretreatments of Cornstover

	No pretreatment	Acid hydrolysis	Demineralization	Demineralization with catalyst
Pyrolysis products (wt%)				
Char	15.8	13.2	13.2	15.9
Water	2.57	10.6	10.4	7.96
Organics	59.1	67.2	68.5	67.7
Gases	22.6	9.02	7.88	8.44
Organics (wt%)				
Anhydrosugars	2.75	22.3	23.4	28.1
Aldehydes	14.4	7.6	3.7	4.6
Carboxylic acids	6.0	1.5	1.3	1.1
Acetol	4.53	Trace	Trace	Trace
Pyrolytic lignin	33.40	16.89	17.74	20.08

maf: moisture, ash-free basis. From ref. *6*.

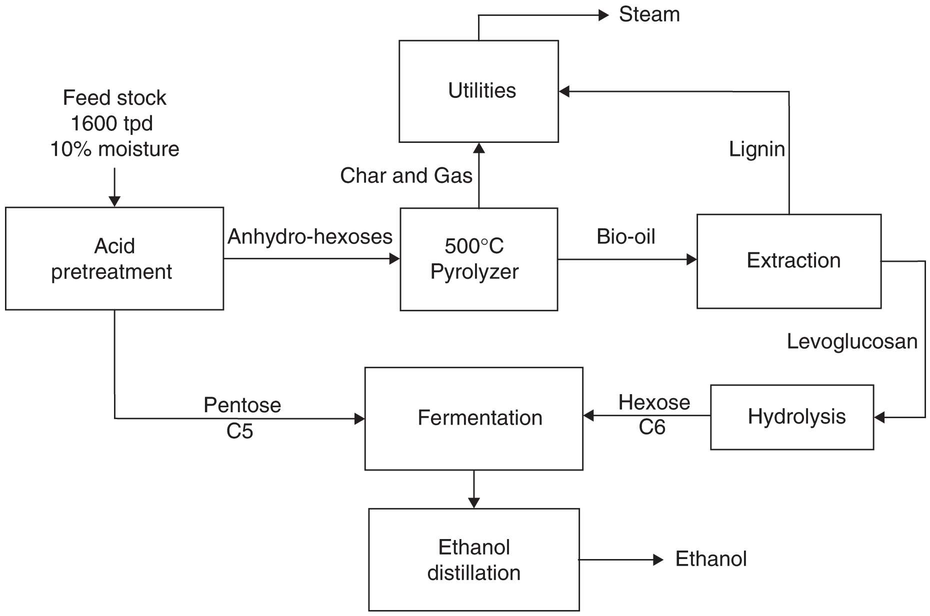

Fig. 3. Schematic of cellulosic biomass-to-ethanol based on fast pyrolysis *(10)*.

So and Brown *(10)* compared the cost of producing 95 million L/yr ethanol bio-oil fermentation, acid hydrolysis, and enzymatic hydrolysis. As summarized in Table 2, total capital investment for a plant based on fermentation of bio-oil was estimated to be $69 million, whereas the annual operating cost was about $39.2 million, resulting in an ethanol production cost of $0.42/L. This is about 23% higher than ethanol from plants based on acid hydrolysis and enzymatic hydrolysis of biomass, but well within

Table 2
Comparing Production Cost of Ethanol From Cellulosic Biomass for Three Conversion Technologies[a]

	Fast pyrolysis	SSF[b]	Acid hydrolysis
Annual ethanol output	95 million L	95 million L	95 million L
Annual biomass input	240×10^6 kg	244×10^6 kg	238×10^6 kg
Total capital	\$69 million	\$64 million	\$67 million
Raw materials (\$46/t)	\$11.1 million	\$11.3 million	\$11.0 million
Labor, utilities,[c] and maintenance	\$6.18 million	\$0.9 million	\$2.13 million
Indirect costs	\$8.07 million	\$7.13 million	\$7.21 million
Annual capital charges	\$13.8 million	\$12.8 million	\$13.3 million
Annual operating costs	\$39.2 million	\$32.1 million	\$33.7 million
Production cost of ethanol	\$0.42/L	\$0.34/L	\$0.35/L

From ref. *10*.
[a] 1997 US\$.
[b] Simultaneous saccharification and fermentation (enzymatic hydrolysis).
[c] Includes credit for steam generation for SSF and acid hydrolysis processes.

the uncertainty of the analysis (33%). The presence of lignin, hemicellulose, and various inorganic compounds in fibrous biomass results in more than a hundred chemical products, many of them not only unsuitable as a carbon and energy source for fermentations, but that are actually toxic to the microorganisms to be cultivated. Improved selectivity of pyrolytic reactions will be important in achieving high yields of fermentable carbohydrate. Understanding reaction pathways will be the key to success in this endeavor.

Syngas Fermentation

Gasification is the high temperature (750–850°C) conversion of solid, carbonaceous fuels into flammable gas mixtures, sometimes known as synthesis gas or syngas, consisting of CO, H_2, CO_2, methane (CH_4), nitrogen (N_2), and smaller quantities of higher hydrocarbons. A number of microorganisms are able to utilize these gaseous compounds as substrates for growth and production. These include autotrophs, which use C_1 compounds as their sole source of carbon and hydrogen as their energy source and unicarbonotrophs, which use C_1 compounds as their sole source of both carbon and energy. Among the fermentation products are carboxylic acids, alcohols, esters, and hydrogen. In a comprehensive review on the prospects for ethanol from cellulosic biomass, Lynd *(11)* noted that syngas fermentation represents an "end run" with respect to acid or enzymatic hydrolysis of biomass because it avoids the costly and complicated steps of extracting monosaccharide from lignocellulose. It also has the potential for being more energy efficient because it effectively utilizes all the constituents of the feedstock, whether cellulose, hemicellulose, lignin, starch, oil, or protein.

Syngas fermentation also has advantages compared with the use of inorganic catalyst in the production of synthetic fuels *(12)*. Most catalysts used in the petrochemical industry are readily poisoned by sulfur-bearing gases whereas syngas-consuming anaerobes are sulfur tolerant. In conventional catalytic processing, the CO/H_2 ratio of the syngas is critical to commercial operations whereas biological catalysts are not sensitive to this ratio; indeed, the water-gas shift reaction is implicit in the metabolism of autotrophic and unicarbonotrophic anaerobes. Gas-phase catalysts typically use temperatures of several hundreds of degree Centigrade and at least 10 atm whereas syngas fermentation proceeds at near ambient conditions. Finally, biological catalysts tend to be more product specific than inorganic catalysts.

Nevertheless, as described by Grethlein and Jain *(12)*, syngas fermentation has several barriers to overcome before it can be commercialized. Among these are relatively low rates of growth and production by anaerobes, difficulties in maintaining anaerobic fermentations, product inhibition by acids and alcohols, and difficulties in transferring relatively insoluble CO and H_2 from the gas phase to the liquid phase, whereby the anaerobes can utilize the gas. Of these, mass-transfer limitations probably represent the main bottleneck to commercializing this technology. However, studies by Worden and coworkers *(13)* give encouragement that the use of nontoxic surfactants and novel dispersion devices can enhance mass transfer through the generation of microbubbles to carry syngas into bioreactors.

Our syngas studies have focused on the coproduction of hydrogen and polyhydroxyalkonoates (PHA) from CO using the purple nonsulfur bacteria *Rhodospirillum rubrum* under dark reaction conditions *(14)*. PHAs are a class of polymers that are both bio-based and biodegradable with many applications in the production of plastic utensils and disposable medical supplies *(15)*.

Figure 4 illustrates the laboratory-scale system assembled to study syngas fermentation at Iowa State University. It consists of a 5.0 kg/h fluidized bed gasifier, a hot gas filter to remove particulate, a tar removal system based on activated carbon, and stirred tank reactor that serves as a syngas bioreactor. The system allows fermentation to be studied using realistic syngas mixtures derived from switchgrass, waste seed corn, and distiller's dried grains or artificial syngas when the gasifier is not operating. Typical gas composition from air-blown gasification with this system is 10 vol (%) H_2, 18 vol (%) CO, 5.6 vol (%) CH_4, 17 vol (%) CO_2, and 46 vol (%) N_2, with the balance being light hydrocarbons.

Figure 5 summarizes our studies to date. The stirred tank reactor used in our studies is only able to convert about 40% of the CO bubbled through it. This reflects a limitation in gas-to-liquid exchange rather than a theoretical limit. Indeed, *R. rubrum* consumes CO so quickly that it cannot be

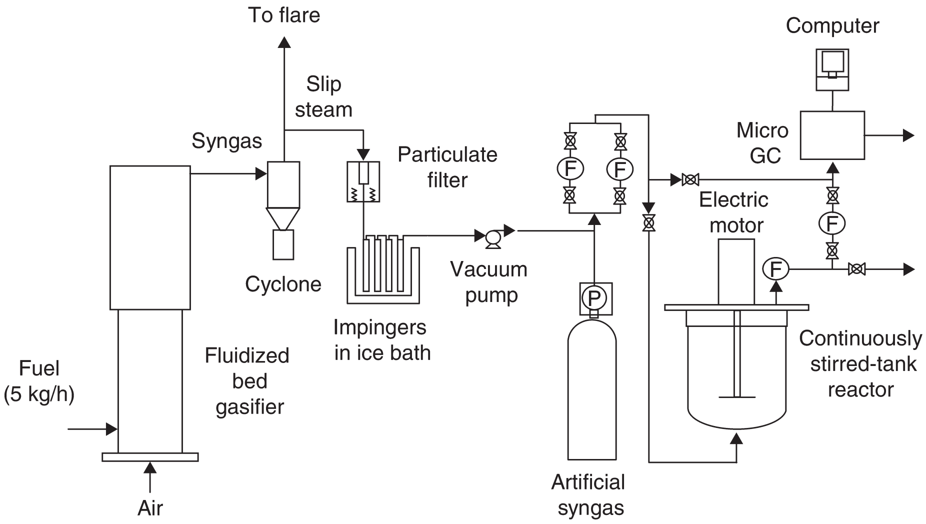

Fig. 4. Laboratory system for studying syngas fermentation.

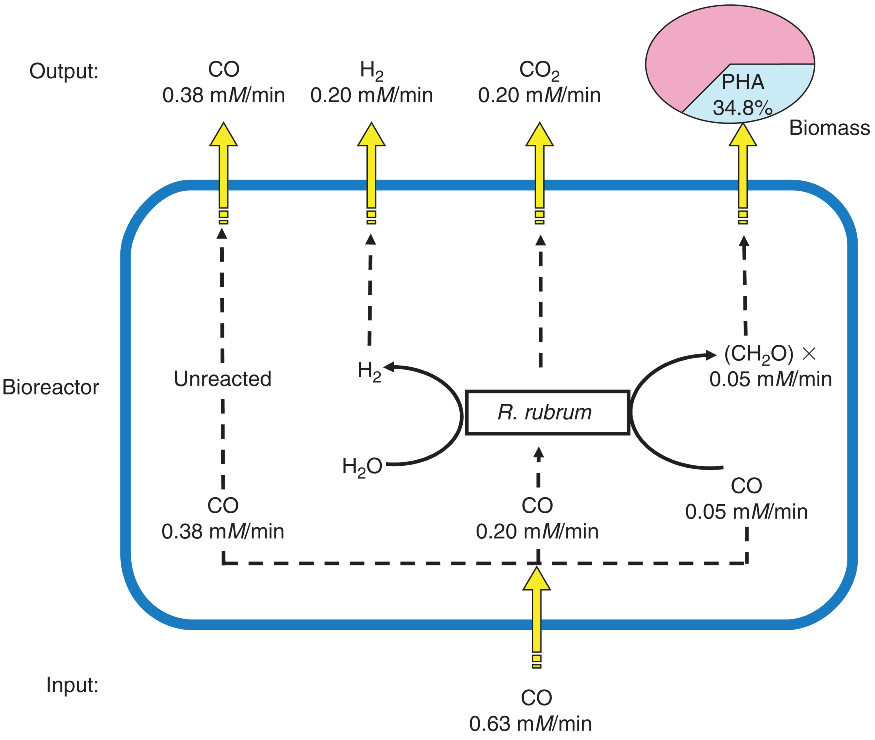

Fig. 5. Summary of results obtained from fermentation of syngas by *R. rubrum*.

detected in the liquid phase. Of the CO fermented, 20% is converted into cell mass and 80% is used in biologically mediated water-gas shift reaction to produce (extracellular) hydrogen. Of the cell mass, 35% is PHA. A biorefinery based on syngas fermentation to hydrogen and PHA is illustrated

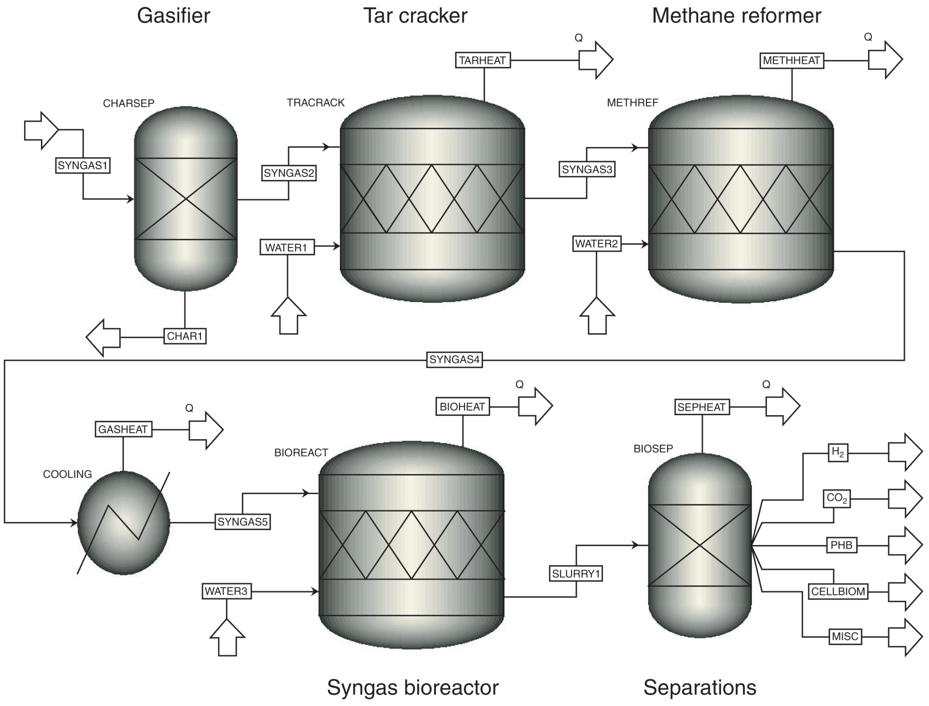

Fig. 6. Conceptual schematic of biorefinery to produce hydrogen and PHA coproducts from fibrous biomass.

in Fig. 6. Biomass is gasified in oxygen followed by additional steps to remove tar and methane from the syngas. No inorganic contaminant removal is thought necessary because the organisms are tolerant to sulfur and chlorine. The gas is cooled and passed through a bioreactor wherein CO is dissolved in the fermentation media and taken up by *R. rubrum*.

We have performed a preliminary economic assessment on this biorefinery concept, assuming 20 tons per day (tpd) of PHA and 55 tpd of hydrogen. The capital costs, detailed in Table 3, are estimated to be \$103 million. The operating costs for this plant, shown in Table 4, yields a production cost of \$2.80/kg of PHA assuming a credit for coproduct hydrogen equal to \$1.90/kg, which is based on the US Department of Energy's long-term target price for this fuel. This PHA production cost compares favorably with the production cost of PHA from glucose, which may be as much as \$5–7/kg.

Conclusions

Thermochemical processing of biomass to produce substrates suitable for fermentation is a relatively new approach to bio-based products. The syngas route, by transforming all plant constituents into CO and H_2, is attractive for its efficient use of biomass. The fast pyrolysis route, by yielding a storable carbohydrate-rich liquid, allows the processing of solid

Table 3
Estimated Capital Costs for Biorefinery to Produce Hydrogen and PHA Coproducts From Fibrous Biomass

Gasifier	$18.6 million	Estimated from: Larson and Svenningsson *(16)*
Fermenter	$59.1 million	Estimated as 25% of total cost of an ethanol plant
Separation equipment	$25.3 million	Estimated as 30% of total costs of a fermentation plant
Grassroots capital	$103 million	–

Table 4
Estimated Operating Costs for Biorefinery to Produce Hydrogen and PHA Coproducts From Fibrous Biomass

Annual H_2 output	18.1×10^6 kg	Based on 20% CO to cell mass; 35% cell mass to PHA
Annual PHA output	6.5×10^6 kg	
Annual input	210.0×10^6 kg	90% capacity factor
Total Capital	$119 million	–
Raw materials	$12.6 million	Purchased at $0.06/kg
Credit for H_2	$34.3 million	Assumed to sell for $1.90/kg
Labor, utilities, and maintenance	$15.6 million	–
Indirect costs	$10.4 million	–
Annual capital charges	$13.9 million	10% interest, 20 yr
Annual operating costs	$18.2 million	–
PHA production costs	$2.80/kg	–

biomass to be decoupled from fermentation and offers prospects for distributed processing of widely dispersed biomass resources. Both have an advantage over cellulose hydrolysis in that they are able to process a wider variety of feedstocks, although this is especially true for the gasification route. Based on the current state-of-the-art, the syngas fermentation route has an advantage over the bio-oil fermentation approach owing to the larger amount of nonfermentable compounds in the bio-oil.

Compared with acid and enzymatic hydrolysis, relatively few resources have been devoted to developing hybrid thermochemical/biological routes to bio-based products. The reason for this circumstance is easy to understand: the original feedstocks of the fermentation industry were naturally occurring sugars and starches that were easily hydrolyzed to sugar. The fact that starch and cellulose are both polymers of glucose encouraged similar approaches to depolymerizing these two carbohydrates. In fact, cellulose is not only more recalcitrant than starch but it is imbedded in a matrix of lignin, which makes the process of releasing sugar from lignocellulose much more difficult than for starch. Considering these difficulties, hybrid thermochemical/biological approaches to bio-based products deserves increased attention.

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