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Review and Analysis of Renewable Feedstocks for the Production of Commodity Chemicals

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ABSTRACT

Several biomass feedstocks were analyzed for their suitability in chemicals production by industry. Feedstocks included dedicated feedstock crops, industrial residuals, and conventional food crops. The factors that were examined included price of raw materials, degree of raw material preprocessing necessary, storage requirements, potential fermentable sugar yield, opportunities for waste minimization, level of technology base, crop hardiness, and land usage. The following conclusions were made: (1) the US has great potential for controlling the direction of a biomass-based chemicals industry because domestic supplies of raw feedstock materials are in excess of what is required for the production of many commodity chemicals, and (2) of the representative feedstocks that were analyzed, cellulosic industrial residuals and fermentable sugar-containing industrial residuals were the most promising prospects.

Index Entries: Feedstocks; biomass; renewable; commodity chemicals; cellulose; molasses.

INTRODUCTION

The United States has vast supplies of diverse renewable resources that are available for conversion to a generic feedstock intermediate (fermentable sugars) that can be biologically converted to many different commodity chemicals. For example, the US Department of Agriculture has projected that US feed grain (corn, sorghum, oats, barley) production

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will increase by 14% to 249 million t in 1992/1993, and the domestic share of the world market will increase by 3% (to 56%) during 1993 (*1*). The US sugar industry projects a 1993 production of 7,500,000 t of raw sugar, which is a 4.2% increase over 1992 (*2*). Hawaii alone produced approx 800,000 t of raw sugar and 220,000 t of molasses in 1990 from the sugar-cane industry in that state (*3*).

This article will demonstrate that the most promising feedstock raw materials are: (1) immediate prospects: sugar-containing wastes (such as molasses), and (2) long-term prospects: cellulosic waste/coproduct materials (such as waste paper, forestry/milling residuals, corn stover, and sugar-cane residuals). The utilization of cellulosic materials for production of a multitude of chemicals is supported by a recent study in which the conclusion was made that the prospects for producing fuel ethanol from cellulosic materials were promising, provided dedicated research efforts were continued (*4*). Lynd et al. (*4*) proposed that conversion of cellulosic feedstocks to ethanol harbors the promise of technological improvements with regard to preprocessing of feedstock material, bioprocessing stages of conversion, and product recovery. The fruition of these improvements will require aggressive research efforts for approx 10 more years.

The fact that the US has significant production control over the raw materials represents an obvious opportunity for the US to be a leader in global-scale biomass-based chemicals production. In fact, in 1987, the New Farm and Forest Products Task Force of the USDA recommended that finding new uses for existing crops and developing unique crops "must become a national priority" in order to realize the "full economic potential which agriculture and forestry hold" for the US (*5*). There are other important reasons why biomass represents an attractive feedstock. Utilization of biomass feedstocks can expand the options of the chemicals industry (which is currently based on petroleum feedstocks) by increasing feedstock flexibility (*see* discussion *below*) and by broadening the spectrum of potential chemical products (*6*). Biobased chemicals production may provide acceptable answers to the current problems that the petroleum-based chemicals industry faces in terms of hazardous intermediates, waste generation, and external pressure (public and political) to protect the environment (*7,8*). With increasing emphasis on the importance of preserving the integrity of the environment and the resulting increase in protective legislation (and cost to industry), the potential benefits of developing alternative feedstock technologies cannot be overstated.

The adoption of any industrial process that relies on a primary raw material necessitates that the raw material be: (1) available in sufficient (if not excessive) quantities to supply the demand for end product, and (2) relatively inexpensive, since raw material costs make up a large portion (up to 70%) of total production costs of high-volume chemicals. Current data indicate that biomass-based raw feedstock materials are produced in the United States in quantities great enough to supply raw materials for the production of several commodity chemicals (*9*). There is also great potential for new dedicated production of biomass crops based on the vast amount of available cropland in the US (*5,10*). This is a strong advantage for the US with regard to future competitiveness in a global biomass-based chemicals industry. Much of the feedstock material available is inexpensive and would be ideal for production of chemicals.

Biomass-based feedstock materials for utilization in production of chemicals can be obtained from a large variety of resources that include dedicated feedstock crops (e.g., silviculture or short-rotation tree crops), waste materials (e.g., food processing wastes), and conventional food crops (e.g., corn) (*9,11*). Although these raw materials contain many different chemical components (i.e., carbohydrates, proteins, lipids, lignin, minerals), what is of primary importance to bioconversion technologies are those chemical constituents found in feedstock materials that can be converted (by feedstock preprocessing) to fermentable sugars, e.g., glucose (Fig. 1). Such chemical constituents include starch, cellulose, other polysaccharides, and free sugars. The fermentable sugars derived from feedstock preprocessing could be utilized in microbial fermentations to form valuable chemical products, e.g., organic acids and neutral solvents. Fermentable sugars are not the only components derived from biomass that might be used to produce chemicals biologically; however, sugars are ideal as generic feedstock intermediates because they are easily converted by biocatalysts into many different chemicals (*9*). In general, this is true for such sugars as glucose, sucrose, and fructose, which are readily derived from biomass.

Because many of the raw materials can be processed into a generic feedstock material (fermentable sugars), biomass-based chemicals production has the potential to be very flexible with respect to the choice of feedstock. For example, if the supply of one feedstock raw material inadvertently drops below demand level, then another raw material can easily act as a substitute. Increasing the variety of feedstock choices will have a positive influence on the work force that will benefit from chemicals production from biomass because a greater variety of beneficiaries (including farmers, foresters, and feedstock processors) will be affected. US farm and ranch operations have exhibited decreased economic efficiency in the last 2 yr; expanding markets for farm-derived commodities represent an excellent opportunity for improving economic returns to farm communities (*12*).

RESULTS AND DISCUSSION

In the last 10 yr, approx 50 different sources of renewable biomass have been suggested for use as alternative feedstocks for the production of valued chemicals (*9*). Sixteen of these 50 possibilities were selected as

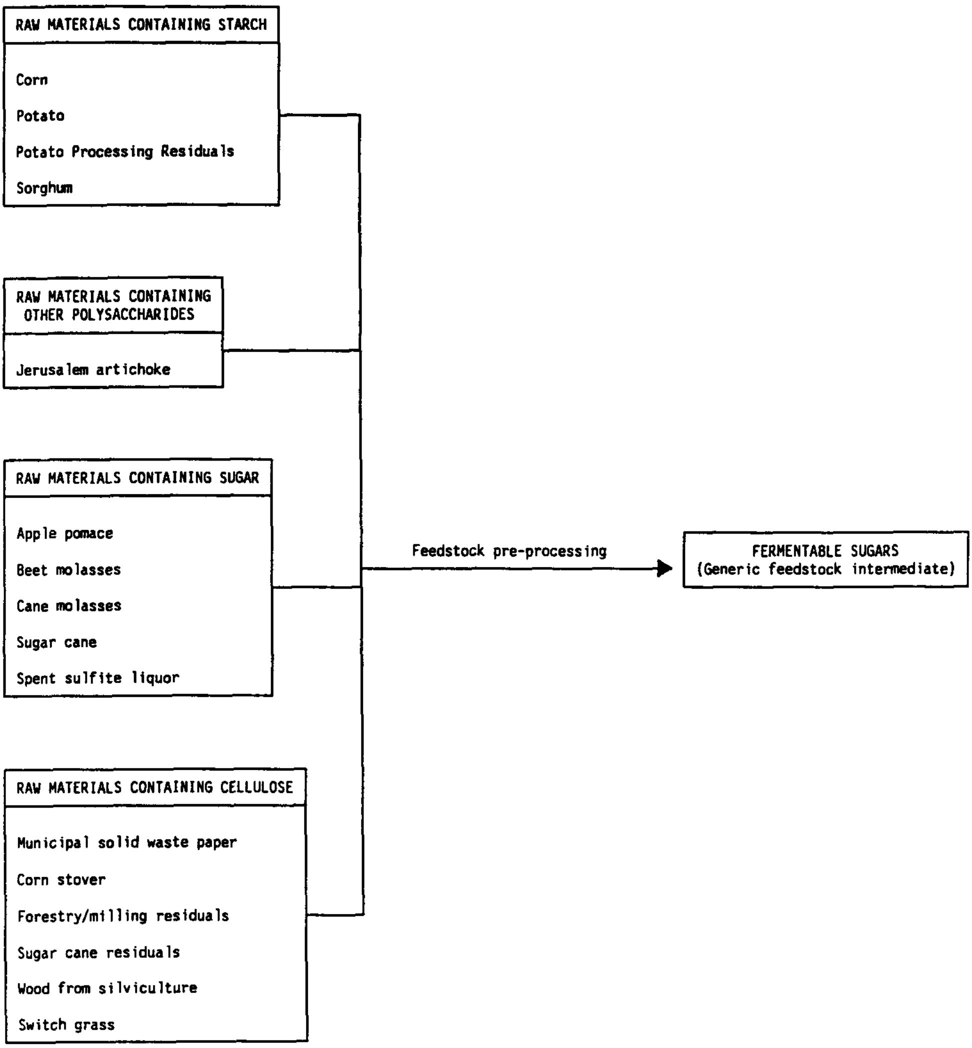

Fig. 1. Production of a generic feedstock intermediate from representative biomass-based raw materials.

sample representatives of biomass-based feedstocks that could support chemical production (Table 1). These 16 feedstocks represent cellulose, starch, free sugar, and inulin (another polysaccharide similar to cellulose and starch) type feedstocks. They also represent feedstock materials that are diversified according to their current usage, including materials that are food crops, sources of animal feed, waste materials, and materials that currently have no significant usage. Thus, the feedstocks listed in Table 1 are a good representation of biomass sources that have been proposed for chemicals production.

Table 1
Representative Alternative Feedstocks: Primary Feedstock Constituents and Current Usage (United States)

Feedstock	Primary feedstock constituent[1]	Current uses
Corn	Starch	Food, animal feed, ethanol production
Potato	Starch	Food, animal feed, ethanol production (low level)
Potato processing residuals	Starch	Animal feed, waste stream, ethanol production (low level)
Sorghum	Starch	Animal feed
Municipal solid waste paper	Cellulose	Waste stream
Corn stover	Cellulose	Waste stream
Forestry/milling residuals	Cellulose	Waste stream
Sugar-cane residuals	Cellulose	Waste stream
Silviculture	Cellulose	Proposed for chemicals production
Switch grass	Cellulose	Proposed for chemicals production
Apple pomace	Sugars	Waste stream
Beet molasses	Sugars	Animal feed, fermentation feedstock
Cane molasses	Sugars	Animal feed, fermentation feedstock
Sugar cane	Sugars	Food
Spent sulfite liquor	Sugars	Waste stream
Jerusalem artichoke	Inulin	Minor usage as food

[1] Primary feedstock constituent = chemical component of raw material that will be used to derive fermentable sugars for chemicals production.

Prices of representative raw feedstock materials range from 16¢/kg (7¢/lb) for potatoes down to 0¢/kg for feedstocks (such as waste paper and spent sulfite liquor) that make up waste streams and are currently liabilities for the industries that produce them (Table 2). All prices shown are low when compared to the market prices of products that are under consideration, i.e., commodity and specialty chemicals; product prices range from $0.90/kg ($0.41/lb) for a commodity neutral solvent, such as *n*-butanol, up to $9.57/kg ($4.35/lb) for a specialty organic acid, such as succinic acid (*13*).

Production levels that are shown in Table 2 are illustrative of the vast amount of renewables that are produced in the United States; this amount increases each year (*9–11*). Also shown in Table 2 are levels of biomass supply that could be dedicated to the production of chemicals. This is referred to as "dedicated production" of feedstocks. For waste materials, dedicated levels usually equal all of the current supply. For crops, dedicated production is the level that could potentially be reached using idle US cropland (*see* discussion *below*). Dedicated production levels for crops were calculated based on (1) current yields for those crops and (2) idle cropland available in regions that are suitable for their growth (*9,10,14,15*). Potential dedicated levels of production range from 0.8 million metric t/yr (1.8 billion lb/yr) of potato-processing residuals up to 742 million metric t/yr (1633 billion lb/yr) of potatoes (Table 2). Apparently, renewables are a large and potentially expanding source of raw materials in the US.

Dedicated production levels of crops shown in Table 2 are based on region-specific availability of some or all of the 27 million ha (68 million acres) of idle cropland in the US in 1989 (*10*). The amount of US idle cropland fluctuates on a yearly basis. In 1992, there were approx 22 million ha (54 million acres) of idle cropland in the US; this amount could decrease or increase in 1993 based on the prevailing circumstances (*16*). At the present time, this land is part of the Conservation Reserve Program (CRP) and the Acreage Reduction Program (ARP), both sponsored by the USDA. These programs serve to control the usage of designated cropland, for the purpose of reducing crop surpluses and protecting the environment by regulation of soil erosion. Land that is designated as CRP- or ARP-committed is not available for extensive cultivation and harvest of food, feed, and forage crops. However, there may be potential for this land for other uses, such as production of biomass feedstock; this biomass could be used for the production of biofuels and chemicals. If CRP- and ARP-committed land were utilized for biomass crops (or other crops), then appropriate measures would have to be taken in order to maintain sound soil conservation and environmental policy.

Dedicated production levels for raw materials were used to derive maximum theoretical sugar yields (Table 2). Values range from 0.09 million metric t sugar/yr (0.2 billion lb/yr) for apple pomace up to 154 million metric t glucose/yr (338 billion lb/yr) for silviculture. The amount of fermentable sugar that is potentially derived from a particular feedstock is directly proportional to the potential energy displacement (i.e., displacement of petroleum feedstocks) for that feedstock in terms of chemicals production.

A moderate production level of 13 million metric t sugar/yr (29 billion lb/yr), which is approximately a tenth of that potentially generated from dedicated corn crops, could theoretically supply 12 million metric t (26 billion lb) of a single organic acid (based on a theoretical yield of 0.98 lb of acid/lb of glucose for a representative organic acid, succinic acid; ref. *17*) or 5 million metric t (11 billion lb) of a neutral solvent (based on a theoretical yield of 0.41 lb of solvent/lb of glucose for a representative neutral solvent, butanol; ref. *17*). These quantities are much greater than current and projected demands for these types of chemicals. The total potential sugar produced from switch grass could yield 73 million metric t (161 billion lb) of an organic acid, e.g., succinic acid, or 31 million metric t (68 billion lb) of a neutral solvent, e.g., butanol. Based on current production in the US of 4.5 million metric t (10 billion lb) of total organic acids/yr and 9 million metric t (20 billion lb) of total neutral solvents/yr (*9*), the US has enough raw feedstock material to support the production of many commodity chemicals completely.

It should be noted that certain feedstocks may be particularly suitable for specific chemical products based on projected production levels. For example, if 45 million kg (100 million lb) is the desired single plant production level for a chemical, then a feedstock should be selected that will produce enough fermentable sugar to meet this demand. Regional differences in feedstock availability will also affect feedstock selection. For example, if the proposed chemical production plant is located in the northeastern US, then a feedstock whose production is concentrated in that area should be selected (*18*). In any given chemical plant scenario, most of the 16 representative feedstocks could meet the needs of a plant (because of feedstock flexibility described above), but there would be one or more "best choices" based on required production level, regional considerations, and preprocessing costs. Feedstock selection should be analyzed for individual scenarios; the top selections would be the primary (but not necessarily exclusive) feedstocks utilized.

Table 3 summarizes advantages and disadvantages for usage of representative feedstocks. All of the criteria listed are important when considering the suitability of a particular feedstock for industrial-level production of chemicals. Using the criteria shown in Table 3, an "ideal" feedstock material would have the following characteristics: minimal dependency on crop hardiness, low price, minimal preprocessing (to a fermentable sugar) requirements, minimal storage requirements, high sugar yield, chemicals production as a high value option compared to current usage

Table 2
Prices, Production, Potential Fermentable Sugar Yields, and Productivities of Feedstocks (United States)[1]

Feedstock	Price[2]	Production[3]	Yield[4]	Idle Land[5]	Dedication[6]	Sugar yields[7]	Productivity[8]
Corn	9 (4)	191 (421)	7294 (6513)	27 (68)	201 (442)	135 (297)	4.9 (4374)
Potato	16 (7)	17 (37)	32368 (28900)	23 (56)	742 (1633)	121 (267)	5.3 (4724)
Potato processing residuals	LTP	0.8 (1.8)	—	—	0.8 (1.8)	0.14 (0.3)	—
Sorghum	9 (4)	16 (34)	3474 (3102)	16 (41)	58 (127)	45 (99)	2.7 (2409)
Municipal solid waste paper	LTP	95 (209)	—	—	95 (209)	74 (164)	—
Corn stover	None	105 (232)	—	—	52 (116)	19 (42)	—
Forestry/milling residuals	LTP	100 (220)	—	—	50 (110)	29 (58)	—
Sugar-cane residuals	LTP	3.6 (8)	—	—	3.6 (8)	1.9 (4.1)	—
Silviculture	None	—	9993 (8922)	27 (68)	276 (608)	154 (338)	5.6 (4956)
Switch grass	None	—	7392 (6600)	27 (68)	204 (450)	75 (165)	2.7 (2421)

Apple pomace	LTP	1.3 (2.8)	—	—	1.3 (2.8)	0.09 (0.2)	—
Beet molasses	9 (4)	1 (2.3)	—	—	1 (2.3)	0.54 (1.2)	—
Cane molasses	9 (4)	1 (2.3)	—	—	1 (2.3)	0.54 (1.2)	—
Sugar cane	3 (2)	25 (56)	78176 (69800)	(3.5) 8.6	272 (599)	114 (252)	32.9 (29371)
Spent sulfite liquor	LTP	28 (62)	—	—	28 (62)	0.4 (0.8)	—
Jerusalem artichoke	None	—	29120 (26000)	23 (56)	668 (1470)	111 (245)	4.8 (4328)

[1] Sources of information include ref. *9–11,14,15,18,19,23–25.*

[2] Price of raw material, ¢/kg (¢/lb); "LTP" indicates that the material is a "liability to the producer," and has negligible or no price; "None" indicates that the material is not currently a US commodity.

[3] Total annual US production of raw material, metric t × 10^6/yr (billion lb/year); (–) indicates not currently produced as a commodity product.

[4] For crops, kg/ha/yr (lb/acre/yr); (–) is used for waste products, even those that are agricultural byproducts (since their supply is not dependent on land dedicated to chemicals production).

[5] Idle cropland available within the US, ha × 10^6 (acres × 10^6); acreage for each crop was determined by totaling available cropland in those states in which that crop is currently grown (or has potential for growth).

[6] Projected level of raw material production dedicated to chemicals production; based on availability of US idle cropland for that particular crop, metric t × 10^6/yr (billion lb/yr); complete dedication is assumed for waste materials; 50% dedication is assumed for corn stover and forestry/milling residuals, since some of this material must be returned to fields as part of sound soil conservation practice.

[7] Maximum potential yields of fermentable sugar based on dedicated production values of raw materials, metric t × 10^6/yr (billion lb/yr).

[8] Metric t of sugar/ha/yr (lb of sugar/acre/yr); these are projected values derived from sugar yields.

Table 3
Positive and Negative Characteristics of Representative Feedstocks

Feedstock	Hardiness[1]	Price[2]	Pre-processing[3]	Storage[4]	Sugar yield[5]	Waste minimization[6]	Technology base[7]	Land usage[8]
Corn	−	+/−	+/−	+	+	−	+	−
Potato	−	−	+/−	+/−	+	−	+	−
Potato processing residuals	+	+	+/−	−	−	+	+/−	+
Sorghum	−	+/−	+/−	+	+	−	+	−
Municipal solid waste paper	+	+	−	+	+	+	−	+
Corn stover	+	+	−	+	+	+	−	+
Forestry/milling residuals	+	+	−	+	+	+	−	+
Sugar-cane residuals	+	+	−	+	+	+	−	+
Silviculture	−	+/−	−	+	+	+/−	−	−
Switch grass	−	+/−	−	+	+	+/−	−	−
Apple pomace	+	+	+/−	−	−	+	+/−	+
Beet molasses	+	+/−	+	+	+	+	+	+
Cane molasses	+	+/−	+	+	+	+	+	+
Sugar cane	−	+/−	+/−	+	+	−	+	+/−
Spent sulfite liquor	+	+	+	−	−	+	−	+
Jerusalem artichoke	−	+/−	+/−	+/−	+	+/−	−	−

[1] Crop hardiness; (+) indicates that supply of the raw material is not directly influenced by the success of a crop dedicated to chemicals production; (−) indicates the raw material is derived from a crop that is dedicated to chemicals production; for example, the corn crop that is referred to above would be one that was grown expressly for providing feedstock material for the production of chemicals; however, the corn stover supply listed above would be derived from currently existing corn production (not dedicated to chemicals production); thus, corn stover is not directly dependent on the success of a dedicated crop—it is a waste material that will always be available in large quantities; even if existing corn production has a bad year, corn stover will be available in large quantities, since current corn production is very high (*see* Table 2).

[2] Price of raw materials; (+) indicates that the price is <1 ¢/kg; (+/−) indicates a current price (or probable price) of 1–10 ¢/kg; (−) indicates a price of >10 ¢/kg (refer to Table 2 for specific values).

[3] Level of preprocessing of feedstock necessary prior to utilization as a fermentation substrate; (+) indicates little or no preprocessing necessary; (+/−) indicates moderate level of preprocessing necessary; (−) indicates extensive preprocessing necessary.

[4] Storage properties; (+) indicates long-term storage possible; (+/−) indicates medium-term storage possible; (−) indicates long-term storage only possible if costly storage quality criteria are met.

[5] Maximum potential fermentable sugar yield from dedicated production values of raw material; (+) indicates ≥0.54 million metric t of sugar/yr; (−) indicates <0.54 million metric t of sugar/yr; cutoff value is based on 0.54 million metric t of sugar required to produce 0.27 million metric t of a commodity chemical (at a yield of 0.5) at six chemical production plants (based on six agricultural regions in US [ref. *26*]; 0.045 million metric t (100 million lb) of chemical/plant/yr); refer to Table 2 for specific values.

[6] (+) Indicates usage of feedstock constitutes a potential solution to a waste liability, or is a high-value option for the material; (−) indicates that the material is already a commodity product; (+/−) indicates that the material is neither waste nor a commodity product.

[7] Level and success of research and development associated with production and preprocessing of feedstock; (+) indicates high level and success; (+/−) indicates medium level and success; (−) indicates low level or high level, but low success.

[8] Utilization of land for growth of feedstock; emphasis is on reduction of environmental stress by using as little land as possible; (+) indicates that the material is not derived from land dedicated to producing feedstocks for chemicals production; (+/−) indicates a productivity ≥ to 10 metric t sugar/ha/yr; (−) indicates a productivity of <10 metric t sugar/ha/yr (refer to Table 2 for specific values).

(e.g., food, feed, fiber, or waste), high degree of technological advancement in production and processing of raw material, and high efficiency in terms of environmentally acceptable land usage.

The decision analysis of "best" feedstocks for production of chemicals might be considered in the context of short-term vs long-term goals. With respect to short-term adoption (0–5 yr from now) of alternative feedstocks technology, the raw materials that currently have the greatest number of positive aspects in our 16 samples are beet molasses and cane molasses (Table 3). These feedstocks share several advantageous properties. Processing costs are low, since they are already in a fermentable form. The technology base for utilization of molasses as a fermentation feedstock is large. Beet and cane molasses are waste materials (which means that they are not directly dependent on degree of crop hardiness and do not directly affect land usage). They have minimal storage requirements. In addition, chemicals production represents a potential high-value option for these feedstocks, and the conversion technology will directly transfer to dedicated crops with similar fermentable sugars, such as sugar beets and sugar cane. For short-term considerations, the feedstocks that have the greatest number of negative attributes in relation to the other feedstocks are silviculture, switch grass, and Jerusalem artichoke. These are potentially disadvantaged from a chemical processor's view by lack of a significant technology base for feedstock preprocessing and/or production.

With respect to long-term adoption (10–15 yr from now) of alternative feedstocks technology, the raw materials that have the greatest number of positive aspects are corn stover, forestry/milling residuals, municipal solid waste paper, and sugar-cane residuals (Table 3). For long-term scenarios, feedstocks were rated without considering preprocessing and technology base factors, since problems in these areas would probably have been worked out in 10–15 yr time. These feedstocks are good choices for chemicals production for many reasons. Chemicals production represents a high-value option. Supply does not have to be from land dedicated to chemical production. Raw material prices are low, and storage requirements are minimal. The technology used for developing these feedstocks would also be directly applicable to the usage of dedicated crops, such as silviculture and switch grass. For long-term considerations, the feedstock that has the greatest number of negative attributes (in relation to the other 16 representative feedstocks) is the potato. Potatoes are primarily disadvantaged by the high cost of raw feedstock material in relation to other feedstocks listed.

Recent technological advancements in sustainable farming/forestry practices and feedstocks preprocessing (to fermentable sugars) improve the clarity of an already bright picture. Such advancements include genetic engineering of crops, such as potatoes, to bring about an increase in dry matter production (*19*). Genetic engineering can also bring about increased crop hardiness (*19*). By May 1991, the USDA and EPA had approved 236 field tests for reviewing genetically modified plants and microorganisms

(*20*). The Biofuels Feedstock Development Program at Oak Ridge National Laboratory includes (among other projects) major efforts in genetic improvement research for woody and herbaceous crops (*21*). One of the results of this research program has been the development of hybrid poplar trees that have greatly increased yield and, thus, exhibit greater potential as energy crops (*18*). This development occurred through the implementation of hybridization and clonal selection, innovative physiology studies, and crop management studies.

Recent research concerning the pretreatment of cellulosic materials has positively affected the potential use of cellulose feedstocks (*4,22,23*). In addition, the US Department of Agriculture has historically sponsored much research concerning the advancement of crop generation. Because these research efforts directly address problems (e.g., fermentable sugar yield and raw material pretreatment) that affect process cost sensitivity, taking advantage of the opportunities that these types of recent technological advances present is a key component in the development of a bio-based chemicals industry.

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