Opportunities for New Coproducts From Ethanol Production

by

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Abstract: New coproducts offer potential for improving the economics of ethanol production. However, technical challenges must be overcome before this potential can be realized. Chemicals coming from the production of ethanol, such as succinic acid and glycerine, could penetrate potentially large, new markets if prices were low enough. However, at lower prices, economic recovery of the coproducts is technically difficult. Research is underway to find new specialty chemical or foodgrade products that can be economically produced. These products will probably serve high-value niche markets, making them attractive candidates for ethanol producers.

Keywords: Ethanol production, coproducts, corn, biomass.

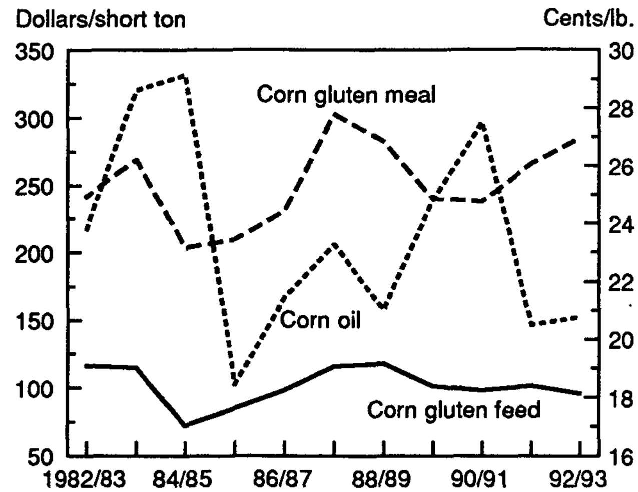
Coproducts are additional products that result from ethanol fermentation that can be recovered and sold to offset the cost of ethanol production. They are especially critical to the economics of ethanol production from corn, because corn comprises the largest portion of operating costs. The current coproduct from dry milling of corn is distillers' dried grains with solubles (DDGS), while the coproducts from wet milling are corn oil, corn gluten meal (CGM), and corn gluten feed (CGF). Dry milling yields 16.8 pounds of DDGS per bushel, while wet milling yields 1.5 pounds of corn oil, 2 pounds of CGM, and 14 pounds of CGF. Wet milling accounts for about 60 percent of ethanol production.

Why New Coproducts?

New coproducts are being sought for several reasons. The ethanol industry has increased its processing efficiency dramatically in the last several years. Although further technological innovations in processing, improvements in corn breeding and production, and the development of alternative feedstocks are expected, new profitable coproducts will make ethanol more competitive in fuel markets. The volatility in the prices of existing coproducts gives additional motivation to develop new coproducts (figure B-1).

Figure B-1

Prices of Corn Oil and Corn Gluten Feed and Meal[1/]



1/ Marketing year for corn gluten feed and meal, September 1 and corn oil, October 1. Dollars per short ton for corn gluten feed and meal; cents per pound for corn oil.

Two key issues for new coproduct development are selling price and market size. Obviously, it will not be economical to separate a component from a process stream or use current coproducts as building blocks for new products unless there is a clear economic incentive. There must also be a substantial market for the new products, given the large scale of the ethanol manufacturing industry.

For example, glycerine is produced during the fermentation of starch into ethanol and will typically comprise 3 percent of the stillage (the mash remaining after the alcohol is distilled). If glycerine were recovered from the four largest U.S. ethanol plants alone, it would place an additional 140,000 tons on the market. Since current world production is 600,000 tons, additional production of this magnitude could depress market prices, which currently range from 60 to 80 cents a pound. However, the glycerine market has been unexpectedly tight, with prices

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rising over 30 percent during the past year. It appears that both production capacity and new uses are growing simultaneously. As new biodiesel and sucrose polyester plants come on-line, the supply of glycerine, a byproduct of these processes, is forecast to increase 12 percent by 1997 (7).

Finally, new coproducts also should not overly disrupt the marketing of other agricultural commodities. For example, a new foodgrade coproduct made from corn protein could compete directly with protein concentrates made from soy, whey, or milk. The effects on commodity program payments are hard to predict and likely to be small. If a new corn product resulted in an increased use of corn, it could slightly lift the price of corn, and thus slightly lower corn program payments. To the extent new corn coproducts displace coproducts of other basic commodities, such as milk, new products could place slight downward pressure on those commodity prices. But since these coproducts constitute such a small fraction of the use of basic commodities, they are likely to have negligible or no effect on basic commodity prices, and thus should not alter federal commodity support payments.

Chemical Coproducts Show Promise

When ethanol is fermented from cornstarch, small amounts of other chemicals are produced, including glycerine, succinic acid, and lactic acid. In particular, succinic acid is a four-carbon dicarboxylic acid that is used to manufacture polymers and resins for lacquers, dyes, and perfumes. It is currently produced from petrochemical feedstocks, mostly in other countries (1). The market is small, 450 tons per year. However, market size could increase if succinic acid were used as an intermediate product to generate chemicals such as 1,4 butanediol (an industrial solvent), gamma-butyrolactone (a chemical intermediate and ingredient of paint removers and textile products), tetrahydrofuran (a solvent and ingredient of adhesives, printing inks, and magnetic tapes) and adipic acid (used in the manufacture of lubricants, foams, and food products). Succinic acid currently sells for $3.10 per pound.

The U.S. Department of Energy (DOE) recently presented an economic analysis of the cost to produce succinic acid from the fermentation of glucose (1). A schematic diagram of the process used to recover succinic acid is shown in figure B-2. Using this analysis, the costs of recovering succinic acid from ethanol fermentation stillage were estimated for a typical ethanol plant (table B-1). Approximately 12 pounds of succinic acid are produced from the fermentation of 100 bushels of corn. Assuming a 70-percent recovery rate, an ethanol plant that produces 58 million gallons of ethanol per year could produce over 2 million pounds of succinic acid. At the current selling price of $3.10 per pound, a profit of $3.17 million would be realized, lowering the cost of ethanol by 6 cents per gallon.

Obviously, the selling price is determined by supply and demand. Additional production of this magnitude cannot be absorbed by the market unless the price drops and demand increases. Recovery of the acid requires capital outlays to modify ethanol plants. To earn a 20-percent return on that investment, the selling price of the acid would have to be 74 cents per pound. At this price, the cost of ethanol would drop by only 0.4 cent per gallon. The real-world selling price may lie somewhere in between 74 cents and $3.10. However, this analysis demonstrates the potential benefits of recovering chemical coproducts from dilute fermentation streams.

The design presented by DOE incorporates only current technology. Some researchers believe that significant savings can be achieved if advances in membrane separation and ion-exchange chromatography are incorporated into the process.

Glycerine is present in larger amounts in the stillage than succinic acid, approximately 1 pound per bushel. Kampen has a patented process consisting of ultrafiltration, followed by ion-exchange chromatography that he claims will remove glycerine more economically (9). If supply increases and prices fall, glycerine would become more competitive with other polyols, such as propylene glycol and pentaerythritol. This should boost consumption and generate novel applications. However, a lower selling price will make it more difficult to recover glycerine from stillage economically. Still, production of glycerine would present an additional advantage to dry millers, since removing it before drying the stillage would decrease the drying time and make handling DDGS easier.

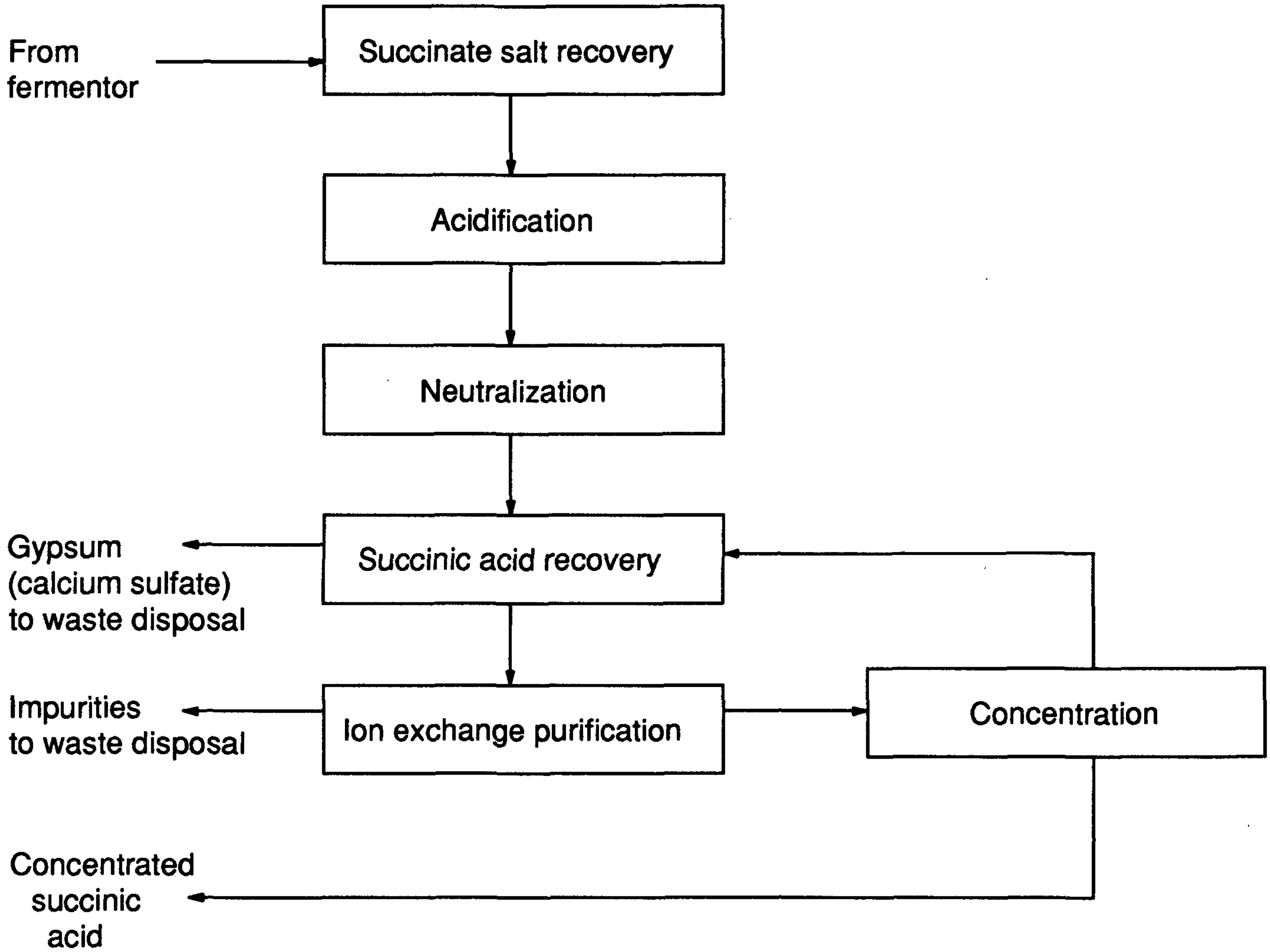
An acetic acid coproduct could be produced by an additional fermentation process, potentially using carbon dioxide as a feedstock. A process of this type is being developed by a group at the University of Arkansas (3). An anaerobic fermentation of syngas (a mixture of carbon monoxide, hydrogen, and carbon dioxide) can produce acetic acid and small amounts of ethanol with extremely high efficiencies. Capital costs are expected to be high, however, since a gaseous feedstock will require large-volume vessels. Acetic acid is used to produce plasticizers, pharmaceuticals, dyes, insecticides, photographic chemicals, and foods.

Corn Proteins Converted Into Biodegradable Films and Nutrition Supplements?

Interest is high in using the proteins from corn gluten meal as building blocks for biodegradable polymers. The major component of corn protein, zein, can be separated from

Figure B-2

Schematic Diagram of a Process To Recover Succinic Acid From Fermentation Broth



Source: (1).

Table B-1--Manufacturing cost estimate for the recovery of succinic acid from ethanol stillage 1/

Item	Unit	
Total capital investment	Dollars	1,876,000
Operating expenses:		
Raw materials	Dollars	140,000
Utilities	Dollars	132,000
Labor and labor-related expenses	Dollars	101,000
Maintenance, repair, and supplies 2/	Dollars	188,000
Waste disposal 2/	Dollars	52,000
Taxes, insurance, and overhead 2/	Dollars	169,000
Depreciation 2/	Dollars	188,000
Total	Dollars	1,198,000
Annual production	Pounds	2,009,522
Selling price	$/pound	3.10
Before-tax profit	Dollars	5,032,000
Profit	Dollars	3,170,000
Return-on-investment	Percent	179
Decrease in ethanol price	$/gallon	0.06

1/ Based on a 70,000-bushel-per-day ethanol plant and 70-percent recovery rate of succinic acid. 2/ Costs were estimated as a fraction of the total capital investment as follows: maintenance, repair, and supplies, 10 percent; waste disposal, 2.1 percent; taxes and insurance, 2 percent each; overhead, 5 percent; depreciation, 10-year, straight-line.

CGM using solvent extraction followed by crystallization. The remaining portions of CGM could be sold as low-protein animal feed.

Enzymes can be used to break down zein into polypeptides, which can be reacted with ethylene oxide, acrylamide, or methyl vinyl ketone to form durable biodegradable films. These films are professed to be superior to starch-based films, although they are more brittle and have lower tensile strength than films made from synthetic polymers.

Some scientists claim that adding plasticizers yields more flexible films (6). These films could potentially be used as wrappings for fruits, vegetables, and meats. Overall, the market for plastics is 50 billion pounds per year. It is expected that biodegradable polymers will attract an increasing, but small, portion of that market due to consumer and legislative concerns about solid-waste disposal (see the special article in the June 1993 issue of this report). Biodegradable polymers require composting to degrade, and widespread use is not expected until composting becomes more common.

Corn proteins can also be further broken down into amino acids. The amino acids could then be used as dietary supplements or fermentation nutrients. Amino acids that are known to be present in ethanol stillage include alanine, proline, valine, and leucine. The latter two are essential amino acids.

Some Coproducts Could Serve as Food Additives

The use of corn protein as a food ingredient is limited by its poor functional properties. Zein, for example, is not water soluble. Cheryan and Mannheim have developed a process that combines membrane separation with enzymatic treatment to modify zein's properties (12). The resulting product is water soluble and has improved clarity and foaming properties, making it better suited for food uses. The cost of producing these proteins has been estimated at 50 cents a pound. This compares favorably with the selling price of other purified protein concentrates, such as whey protein or casein that sell for $1 to $5 per pound. If a corn wet-milling plant converted some of its annual CGM production to zein hydrolysate, and sold the product for $1 per pound, the cost of ethanol could be reduced by 4.3 cents per gallon.

Other researchers (14) have demonstrated that levan, a polysaccharide, can be produced along with ethanol from the bacteria *Zymomonas mobilis*. Levan can be used by the food industry as a thickening agent, plasma expander, or fructose source.

Other possibilities include using CGM as a meat extender (15), or in combination with soybean meal as a textured protein product (13). Fujimoto, et al., have recently patented the use of defatted corn germ as a natural antioxidant additive for food and beverages (5).

Other potential high-value products include vitamins and colorants that could be recovered from the stillage in a membrane-separation step, followed by chromatographic separation. No economical product has been identified yet, although a commercial firm has expressed an interest in obtaining such products (16).

The yeast cell mass may also serve as a source of valuable coproducts. Examples of compounds that have been isolated from the yeast *Saccharomyces cerevisiae* include invertase (an enzyme used as a food additive), glucan (a polysaccharide with food and pharmaceutical applications), and other glycerides, phospholipids, and sterols (10). However, an economical method of recovering these compounds must be developed. The market size for these products is uncertain, but would probably be very small.

Making a foodgrade product in an ethanol plant will require some changes to meet U.S. Food and Drug Administration regulations. Additional investment would have to be made in sanitary vessels and cleaning devices, and operators would need training in foodgrade manufacturing practices.

Biomass-Based Coproducts Are Also a Possibility

The incentive to develop new coproducts for ethanol production from biomass is not as great because the feedstocks, such as paper sludge, grass clippings, and herbaceous crops, are low in cost. Biomass usually consists of cellulose, hemicellulose, and lignin. Lignin is a colorless-to-brown substance, which binds with cellulose to form the walls of plant cells. A byproduct of paper production, lignin has found some uses as adhesives and as an asphalt extender. It cannot be broken down and fermented, and in fact, it interferes with the breakdown of cellulose to sugars by impeding the action of the enzymes. In most proposed biomass-to-ethanol plants, however, lignin is more highly valued as a fuel to be burned in the ethanol-dehydration process.

Furfural, a common industrial solvent and chemical intermediate, is produced from the breakdown of pentoses during cellulose conversion. It is a potential coproduct when ethanol is made from biomass. The market for furfural is approximately 60,000 tons annually. It is obtained primarily from the hydrolysis and conversion of agricultural feedstocks, such as oat hulls. Prices range from 65 to 75 cents per pound. Furfural possesses excellent solvent and reactive properties and could prove to be an attractive chemical intermediate if the price were low enough. It is used to manufacture lubricating oils, weed killers, fungicides, and metals.

A biomass conversion plant could potentially produce acetic acid from hemicellulose and ethanol from cellulose. Acetic acid is now made from petrochemical feedstocks. Many organisms readily convert xylose (obtained from the breakdown of hemicellulose) to acetic acid. The acetic acid, in turn, could readily be converted to calcium magnesium acetate (CMA), which is a noncorrosive substitute for road salt (2). However, CMA is expensive and does not work as well as salt in extremely cold areas.

Some of the cellulose can be used to produce a noncaloric flour substitute. This product was developed and patented by researchers in USDA's Agricultural Research Service (8). An alkaline-hydrogen peroxide treatment for oat hulls was devised that yielded a cellulose product with good functionality as a food ingredient. It can replace up to 66 percent of the flour in many products without detrimental effects on quality. This cellulose product is now being marketed by Canadian Harvest USA, which is a joint venture of DuPont and ConAgra. Millions of pounds are being sold annually for use in bakery products, such as low-calorie, high-fiber breads, breakfast cereals, tortillas, no-fat muffins and cookies, and reduced-fat pie crusts and cakes. With the new food labeling regulations, use is expected to increase.

Dale (4) has proposed several alternatives for recovering the protein-fraction of biomass feedstocks for use as animal feed. High-protein crops, such as alfalfa, are promising candidates for this process. In this case, the biomass-to-ethanol plant would be operated similarly to corn-to-ethanol plants, where the high-protein stillage is dried and sold as DDGS.

Conclusions

New coproducts offer potential for improving the economics of ethanol production. However, technical challenges must be overcome before these gains can be realized.

Chemicals, such as succinic acid or glycerine, can command a large market size, but at a selling price that makes economical recovery difficult. Foodgrade products, which can be sold at premium prices, are promising candidates for new coproducts. However, making foodgrade products in an ethanol plant will require some processing changes. Specialty products, such as biodegradable films, have perhaps the greatest potential for improving the economics of ethanol manufacture. Research is underway to find novel, useful products that can be economically produced and recovered. Although the new products will serve high-value niche markets, which will require additional effort in market research and applications development, they likely will be an attractive opportunity for ethanol producers.

Acknowledgments

The authors wish to thank the following individuals who provided information for this manuscript: H. Bungay, Rensselaer Polytechnic Institute; M. Cheryan, University of Illinois; R. K. Conway, USDA, Office of Energy; W. L. Harris, R. Villet, D. J. O'Brien, and J. C. Craig, Jr., USDA, Agricultural Research Service; N. Hohmann, USDA, Economic Research Service; R. Katzen, Raphael Katzen Associates; W. H. Kampen, K-Engineering, Inc.; M. Ladisch, Purdue University; R. Landucci, DOE, National Renewable Energy Laboratory; R. Montgomery, University of Iowa; L. Russo, New Energy Company of Indiana; and R. M. Weinzierl, Illinois Corn Growers Association.

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