3. CORN

.1 Introduction

Corn is used as a feedstock for fuel ethanol production in Canada by Commercial Alcohols Inc. of Tiverton, Ontario and has been used at various times by Mohawk Oil in Minnedosa, Manitoba. Nearly all of the fuel ethanol produced in the United States uses corn as a feedstock, although this represents only 5% of their total corn crop or 400 million bushels (Lee et al., 1994; Turhollow and Kanhouwa, 1993). Approximately nine and a half litres of ethanol are produced per bushel of corn (Wyman and Goodman, 1993a,b). Without government subsidies or tax credits, it is generally agreed that the fuel ethanol industry could not exist, unless byproducts much more valuable than animal feed, can be developed (Turhollow and Kanhouwa, 1993; Cemcorp, 1992).

Vaughn (1995) reported that an acre of land in the U.S. can produce, on average, 115 bushels of corn which in turn can be used to produce 228 gallons of ethanol, 1437 lbs. of 21% gluten feed, 345 lbs. of 60% protein gluten meal and 173 lbs. of corn oil. Ethanol yield from corn was estimated at 380 litres/tonne by St. Lawrence Reactors Ltd. in Ontario (Beaulieu and Goodyear, 1985). Byproduct output, on a 90% dry matter basis, was estimated at 287 kg/tonne.

In 1994 there were 43 fuel ethanol plants spread throughout 21 of the American states, with a total production of more than 1.4 billion gallons (Vaughn, 1995), up from approximately 1 billion in 1993 (Wyman and Goodman, 1993a,b). This is an increase in the number of production facilities from 1992, when 32 plants were operating (Lee et al., 1994).

Eric Vaughn, the president of the Renewable Fuels Association in the United States, emphasized the importance of creating high-value markets for the byproducts of fuel ethanol production from corn. The most important variable cost factor in fuel ethanol production is the net cost of corn, which is the cost of the corn entering the plant minus the profit that can be derived from the sale of byproducts (Kane and Reilly, 1989). The price of corn tends to be much more variable than the price of coproducts which have tended to rise in recent years. The sale of coproducts from the wet milling process of producing fuel ethanol accounts for approximately 30% of revenue and more than 50% of corn feedstock cost (Lee et al., 1994). Wet milling is the process of choice in 60% of ethanol plants in the U.S.

The existence of nearly 4000 discrete uses for refined corn products were noted in 1989 (Munro, 1994). While a few products are used directly by the consuming public, most act as inputs for further processing, building layers of value-added activity. *

Maize – general → uses

▲

.2 Composition of the Corn Kernel

Corn is composed of approximately 70-75% starch, 10% protein, 4.5% oil and 10-15% other materials such as fibre and ash (Wyman and Goodman, 1993a,b; Keim, 1983). More than 75% of the protein is located in the endosperm (Reiners et al., 1973). The nutritional quality of the protein in terms of amino acid content is poor. Additionally, protein can cause problems during the milling process. Endosperm proteins are, however, nearly completely insoluble and this characteristic aids their recovery during wet milling.

▲

.3 Ethanol Production from Corn

3.3.1 Introduction

The fractionation of corn into its component parts has been practised for many years. The two main processes by which fractionation is achieved are wet milling, which originated in the mid-1800's, and dry milling, that was developed in the early 1900's (Rankin, 1982). Both processes are subjects of continual refinement and modification. In addition, new processes are being developed to make corn fractionation more cost effective.

▲

3.3.2 Wet Milling

The products of corn wet milling for fuel ethanol production have been outlined by Hayman et al. (1995) and Köseolu et al. (1991). The corn kernel is presoaked and milled to produce three streams including starch, germ and fibre. The germ is extracted to produce corn oil, the most valuable coproduct of the process. The fibre portion consists of the seed pericarp and the bran, which has a composition of 70% xylose, 23% cellulose and 0.1% lignin. The starch fraction undergoes centrifugation and saccharification to produce gluten wet cake, which when dried is the second most valuable coproduct, and glucose that is fermented to produce ethanol. The ethanol is distilled leaving thin stillage, that when dewatered leaves corn condensed distillers' solubles containing 20% carbohydrate and 18% protein. The condensed distillers' solubles can be sprayed onto the corn fibre and fermented to produce corn gluten feed.

Lee and associates (1994) indicated that one of the key factors in the sustainability of the fuel ethanol industry is the development of new technology for corn wet milling. This includes, for example, techniques that would allow the cellulose in corn hulls to be converted to ethanol, resulting in an increase in ethanol yield. The coproduct stream would change significantly as a result. While less material would remain after fermentation, what was left would have a much higher protein concentration and therefore a higher value.

The need for fresh water in a corn wet milling plant is very high, reaching 1.5 m3 per ton of corn (Kollacks and Rekers, 1988). Water must be removed from the byproducts produced at various stages of the process. In order to provide an option to evaporative drying, Wu and Sexson (1985) and Wu et al. (1983) used reverse osmosis and ultrafiltration to concentrate stillage from corn grits, flour, degerminated meal and hominy feed remaining after ethanol fermentation and distillation. Most of the solids and nitrogen were recovered, leaving a final permeate that could be recycled back into the production process as water, could undergo further treatment or be discharged.

3.3.3 Dry Milling

Dry milling of corn involves breaking down the kernel to fine particles. The germ is removed by sieving and aspiration and/or by gravity methods (Köseolu et al., 1991). Generally, prepress-solvent extraction is used to remove the oil from the germ. Milling and air classification or alkali extraction-acid precipitation processes are used to obtain protein concentrate from the defatted germ meal. Enzymes are used to convert the starch fraction to glucose and yeast is added to perform the fermentation step. From this process, 9.5-9.8 litres of ethanol, 7.3-7.7 kg of carbon dioxide and 7.7-8.2 kg of DDGS with a protein content of approximately 27%, are produced (Wyman and Goodman, 1993a,b).

3.3.4 Sequential Extraction Process

The sequential extraction process (SEP) for corn milling was developed out of a need for new low-cost methods of corn milling that could produce higher value coproducts than are currently on the market (Chang et al., 1995; Hojilla-Evangelista et al., 1992a,b,c). The two innovative features of this method are the use of ethanol in upstream steps of the process and the simultaneous extraction of corn oil and dehydration of ethanol from approximately 95%-99%. Oil yield and quality are enhanced by the SEP process since the entire kernel is extracted. There is a yield increase from 72% for conventional repress hexane extraction to 90-94% for SEP, depending on whether dent or high lysine corn is used (Hojilla-Evangelista et al., 1992b,c).

The SEP process eliminates the need for steeping in sulphur dioxide, a treatment that has been found to have negative effects on the characteristics of the protein. The SEP process generates a high quality product that can be used for food and industrial purposes. Total protein extraction ranges from 70-

80%. Approximately 10% of the protein is removed in the oil extraction step. The protein, since it is soluble in ethanol, is believed to be zein. The extraction step, involving ethanol/alkali, results in recovery of about two thirds of the protein from the intact grain, depending on the type of corn used. Freeze-dried protein concentrates were produced that contained nearly 80% crude protein, compared to 60-62% in corn gluten meal. Amino acid quality was similar to that of the untreated corn and better than that of corn gluten meal. Because germ proteins are also extracted, the protein would be expected to have a higher nutritional value.

The protein produced by the SEP process was white, unlike corn germ meal which was bright yellow, and had a mild corn flavour (Hojilla-Evangelista et al., 1992b). The material had a high degree of solubility in aqueous mediums at a pH value of greater than 7. At dilute concentrations, it exhibited substantial foaming capability. It has been found to have excellent emulsifying capacity and emulsion stability, as well as good heat stability (Myers et al., 1994; Hojilla-Evangelista et al., 1992b). Because of all these characteristics, SEP protein could establish itself as a very effective material for both food and non-food uses.

After the two extraction steps, a fraction rich in fibre and starch remained. The starch was not as pure as that obtained from conventional wet milling in that it contained a higher protein concentration, but it was still a good substrate for ethanol fermentation. The fibre portion is being evaluated for use as an alternative to gum arabic (Anonymous, 1995). Chang et al (1995) concluded that before the SEP process can be commercialized, coproduct markets require development. They suggested that ethanol be considered the byproduct and that efforts should focus on the protein fraction.

[illegible] Potential Coproducts of Ethanol Production from Corn

3.4.1 Protein *

A great deal of research effort has gone into the development of corn protein concentrates (Shukla, 1981; Sternberg et al., 1980). A concentrate containing 90% protein has been isolated from corn gluten meal (Satterlee, 1981). The isolate was light coloured and only slightly soluble in water, but could absorb triple its weight in water and could bind its own weight in fat. For use in food, it complemented other protein sources that are rich in lysine and tryptophan, but low in methionine and cystine. For corn protein concentrates to be accepted by the food industry, they must have unique characteristics that recommend them for commercial exploitation. The ability of corn protein concentrates to complement oilseed proteins in terms of amino acid composition could be considered one of these characteristics.

At present, markets for corn protein concentrate use in food have not been developed. Chang and associates (1995) suggested that use as feed for infant animals or aquaculture may prove profitable. Zein is the only corn protein that has been developed for non-food industrial applications (Hojilla-Evangelista et al., 1992c). Between 1939 and 1967, up to 6 million pounds per year were produced (Reiners et al., 1973). The characteristics that make zein of interest for industrial application include the ability to provide a tough, glossy coating that is resistant to water, grease, scuffing and microbial attack (Reiners et al., 1973). Zein is soluble in 90% ethanol and will form a clear tough film when the solvent is evaporated. In the past, zein was utilized in the production of packaging films, linoleum tiles, coatings, ink and textile fibres, but usage diminished because of less costly petroleum based alternatives.

Currently, small quantities of zein are produced and marketed by Freeman Industries, Inc. of New York, for use as a coating on pills, nuts, candies and other foods where it forms a moisture resistant covering (Wilson, 1987; McCurdy, 1986). N[illegible]yan (1994) has been investigating the use of zein as a coating on paper or paperboard, to replace currently used polyethylene or wax coatings.

Researchers at the University of Nebraska, Lincoln, have developed techniques to co-ferment corn and whey using two different yeasts (Anonymous, 1994). Using continuous fermentation methods with columns for immobilization of yeast, they were able to combine increased ethanol yields with faster processing time, compared to conventional fermentation. A high protein byproduct was produced.

▲

3.4.2 Fibre *

B[illegible]ast (1994) suggested that value-added opportunities for use of corn fibre should be explored. Corn fibre is presently used in animal feed. However, with the growth of the fuel ethanol industry the feed market will rapidly become saturated and corn fibre, that is available at a relatively low cost, will be available for other, potentially more valuable uses. With hydrolyzation of the starch and hemicellulose fractions of corn fibre to fermentable sugars, it is possible that valuable chemicals could be produced by microbial fermentation. The unfermentable portion would be available for the feed market.

Because of the interest expressed in increasing dietary fibre, particularly in breakfast cereals and snack foods, corn bran flour was developed and test marketed in the 1980's (Alexander, 1987; Shukla, 1981). Substantial amounts of corn bran flour can be generated as a coproduct of dry milling. However, market development is a key factor and despite their advantages in terms of nutrition, colour and flavour, dry milled byproducts do not compete well with wet milled products. Corn bran has been used in non-food applications as an extender and a viscosifier for use in urea-formaldehyde plywood adhesives (Alexander, 1987).

▲

3.4.3 Germ *

Corn germ is a byproduct of both wet and dry milling, though its protein may be somewhat altered during wet milling by the steeping process (Nielsen et al., 1973). Shukla (1981) reported that wet milled corn germ meal has a higher protein content and lower caloric value than the dry milled product. Amino acid profiles were similar. Inglett and Blessin (1979) reviewed the composition of defatted corn germ flour originating from both processes. They suggested that corn germ protein products have one of the highest potentials for use in human food. It is not as pure, flavourless or as pale as casein or soy isolates and research to improve these characteristics is necessary (Nielsen et al., 1973).

Corn germ makes up 10-20% of the total product generated when corn is dry milled (Blessin et al., 1973). Defatted corn germ flour (DCGF), developed from commercial dry milled corn germ, has been suggested for use as a protein supplement in baked goods (Nielsen et al., 1979; Tsen, 1976; Blessin et al., 1973, 1974). DCGF is high in protein, oil, minerals and vitamins; has a pleasant flavour and texture; and good hydration and emulsifying properties (Blessin et al., 1979). Addition of corn germ to cookies, bread and cakes will affect baking characteristics (Tsen, 1980). However, as long as levels are within an acceptable range, satisfactory products can be produced.

Blessin and coworkers (1973,1974) ground and screened corn germ to remove the fibre. The resultant product contained approximately 25% protein, 24% starch, 2-4% fibre and less than 0.5% fat. Use in cookies to replace 25% of the wheat flour led to increases in iron, phosphorous, potassium, magnesium, lysine and tryptophan contents. Fibre and protein were slightly elevated as well. Blessin and associates concluded that DCGF could be used in a number of foods, such as cookies, muffins and beef patties, to enhance protein and mineral contents.

Tsen (1976) used DCGF in oatmeal cookies. Taste panel evaluation indicated that cookies supplemented with DCGF in amounts as high as 48% on a wheat flour basis, had acceptable texture and taste. Indeed, cookies containing amounts up to 36% actually rated higher than the controls. Because bread forms a staple part of the diet in many countries, it is an ideal candidate for fortification. Tsen et al. (1974), reported that DCGF could be used in wheat bread at levels up to 12%. Where loaf volume is not an important factor, levels could be increased to as much as 24%. Odour and flavour were deemed acceptable.

Nielsen and associates (1979) upgraded wet milled corn germ to produce a value-added flour product that contained 30% protein, 5.9% lysine, a good balance of the other essential amino acids and a significant amount of fibre. As part of the process, ethanol was used to extract some of the oil. Nielsen and coauthors suggested that this product should be further evaluated for use in human food.

3.4.4 Gluten Meal

Steeping of corn kernels in sulphur dioxide at the beginning of the wet milling process aids the separation of starch and insoluble protein. The corn gluten meal produced is a high protein product (43-65%) and is one of the most valuable coproducts of the process (Ott and Rask, 1982, 1983; Satterlee, 1981). It contains mostly zein, but also glutelin and a small quantity of globulin (Buck et al., 1987; Wright, 1987).

Two of the problems associated with corn gluten are its un[illegible]ractive flavour and odour, caused by its high unsaturated fatty acid content and its potentially harmful sulphite content (Hojilla-Evangelista et al., 1992b; Buck et al., 1987). Wu and coworkers (1994) found that treatment by either hexane-ethanol or supercritical CO2 (SC-CO2) extraction, significantly diminished the fermented flavour and made the product more acceptable for human consumption. SC-CO2 is particularly appealing as a solvent since it is non-explosive, non-toxic, easily removed from the extracted media and is not expensive. It is interesting to note that in a grain biorefinery, both ethanol and CO2 could be available for use in extraction procedures.

Buck and coworkers (1987) incorporated corn gluten meal into cookies, bread, pasta and extruded snack foods. They found that while protein efficiency was improved, flavour acceptability was diminished for all products except cookies. Texture was acceptable only for pasta. The functional characteristics of br[illegible]d doughs and extruded products were affected.

Corn gluten meal can also be combined with defatted soy flour for use in food (Neuman et al., 1984). Even though zein, the main protein, contains virtually no lysine or tryptophan (Wright, 1987), corn gluten has a high sulphur amino acid content that improves the nutritional value of soy flour.

3.4.5 Oil

More than 90% of the corn oil generated in the United States originates as a byproduct of the wet milling process (Orthoefer and Sinram, 1987). Orthoefer and Sinram discussed a number of coproducts generated from the processing of corn oil. Wet gum is derived from the degumming process. It can be used with refining soapstock in animal feed or further processed to form lecithin, a potentially valuable commodity for use as an emulsifier, antioxidant, nutrient or dispersant. Vegetable oil distillate, removed from the oil during deodorization, contains a number of chemicals including tocopherols, carotenoids, flavour and colour components that can be extracted for value-added use.

▲

3.4.6 Distillers' Dried Grains (DDG), Distillers' Dried Solubles (DDS) and Distillers' Dried Grains with Solubles (DDGS)

Walker (1980) reported that soy protein concentrates in the 1940's were in a similar position to what corn distillers' dried grains were in the 1980's, i.e. lots of potential but little application. Intensive research and marketing activity are required for DDG to become an accepted and important food commodity. Economic competitiveness, flavour, functionality and presentation to the consumer are all critical factors. Distillers' grains from different sources can vary considerably in colour, protein, fat, pH, fibre and taste and must be chosen selectively for use in human food (O'Palka, 1987).

Wu (1989) considered the effects of corn type on the residues from ethanol fermentation. In addition to dent corn that is used exclusively by the ethanol industry at present, he studied high-lysine, waxy and white corn strains. He concluded that high-lysine corn distillers' grains showed the most promise for incorporation into human food, because of their higher protein quality. White corn distillers' grains may have potential use in baking because of their light colour.

The neutral sugar contents of corn DDGS, DDG and DDS were reported by Wu (1994). He felt that determination of the carbohydrate composition of these coproducts would increase their potential for subsequent processing. DDS was found to have the highest concentration (39%) of neutral sugars. Chemical analysis showed that glucose was in the greatest abundance, followed by glycerol. DDGS had the next highest content of neutral sugars at 38%, with glucose and xylose being predominant. DDG had the lowest content of neutral sugars at 36%, with the most prevalent types being xylose followed by arabinose.

DDGS is traditionally used for animal feed. In the United States, DDGS from the dry milling and fermenting of corn generally returns 25-50% of the original feedstock cost (Keim and Venkatasubramanian, 1989; Sauer and Compton, 1982). However, numerous researchers have suggested that if this material could be diverted to the food industry, it would have a greater monetary value and could help sustain the viability of the fuel ethanol industry.

The Cemcorp study (1992) suggested that wet distillers' grains from the dry milling process could be chemically altered to produce ingredients for the food industry. The American Xylan process can convert this material into either a dietary food supplement or an environmentally friendly barbecue briquette, both of similar value (Cemcorp, 1992). The stillage and the corn fibre also can be used to manufacture insulation and construction materials.

In addition to the yeast cells from the fermentation, DDGS contains all of the material present in the intact grain, with the exception of the starch (Scheller, 1981). Protein and fibre are concentrated three-fold in corn DDGS compared to the original grain (Rasco et al., 1987a). Levels of protein ranging from 23-35% and fibre ranging from 27-55% have been reported for DDG and DDGS (Dong and Rasco, 1987; Rasco et al., 1987a; Dawson et al., 1984; Tsen et al., 1982, 1983; Ranhotra et al., 1982). Although the protein content is fairly high, the amino acid balance is poor (Ott and Rask, 1982). Dong and co-workers (1987) studied the quality of the protein found in DDG. They found that the amino acid profile of the whole grain was not affected by the fermentation process. Lysine was the most limiting amino acid.

Distillers' grains can be used in food without restriction in the U[illegible]. as long as the original grain used to produce ethanol is fit for human consumption and the processing plant approved for food manufacture (Anonymous, 1993). Rasco and coworkers (1987c) substituted 25% of the all-purpose flour in breading formulations with DDGS. The product had a darker colour than controls that did not contain DDGS, but was still deemed acceptable by the taste panelists.

DDGS were used in yeast and quick breads by O'Palka (1987) to replace 33 and 40% of the flour, respectively. In order for the products to be acceptable, light coloured DDGS with a pleasing smell had to be used. Sufficient quantities of baking soda were required to adjust the pH of the DDGS and additional liquid was necessary to offset the higher fibre content.

Researchers at the South Dakota State University have washed, freeze-dried, steam/pressure sterilized, oven toasted and ground DDG to produce a product suitable for use in baked goods (Anonymous, 1993). Because it contains approximately 40% fibre and 36% protein it is highly nutritious. One cup of DDG would supply the entire daily requirement (U.S.) of fibre, compared to 30 cups of corn flakes. Incorporated into human food, it would provide a significant source of dietary fibre (Dong and Rasco, 1987; San Buenventura et al., 1987).

DDG were used by Reddy and associates (1986) to supplement canned products such as stew, bean-less chili and hot dog sauce. Levels up to 2% did not significantly alter appearance, taste, mouthfeel or general acceptability. In stew, DDG acted as a thickening agent, while in bean-less chili and hot dog sauce, it replaced vegetable protein, soy or wheat flour.

DDG can be incorporated into puff-extruded products with rice, potato, wheat or corn flour doughs (Kim et al., 1989; Wampler and Gould, 1984). In terms of functionality, DDG can be used at levels ranging from 0-100% to produce extruded products (Kim et al., 1989). However, Wampler and Gould (1984) found that a mild astringent, grainy flavour could be detected at the 10% level and increased as the DDG content was augmented, becoming more unacceptable. They concluded that DDG could be used to a maximum of 20%.

Wu and coworkers (1987) considered the use of corn DDG in spaghetti. They tested this material both untreated and extracted with hexane-ethanol, at three concentrations: 5, 10 and 15%. Both products, used at the 10% level, resulted in an improvement in protein and fibre content in the spaghetti. Flavour, texture and cooking characteristics were acceptable.

The use of corn DDG in cookies and in bread was discussed by Tsen and coworkers in 1982 and 1983, respectively. DDG were found to be acceptable at levels up to 15% in bar, spice and chocolate chip cookies. Since these products normally have a darker colour than sugar cookies, the dark colour of the DDG was masked. No flavour differences were found between the supplemented and non-supplemented chocolate chip cookies. However, bar and spice cookies without the DDG were found to have significantly better flavour.

The use of distillers' dried grain flour in bread was found by Tsen and coworkers (1983) to be acceptable at a 10% level. Compared to whole wheat bread, the supplemented product had better volume, crumb grain, colour and storagability. Fibre content was lower than for whole wheat bread, but significantly higher than white bread.

One of the problems associated with utilizing corn DDG in food is poor flavour (Wu et al, 1990; Bookwalter et al., 1984). Wu and coworkers used supercritical carbon dioxide (SC-CO2) to remove the oil from distillers' grains. The resultant product received acceptable flavour scores from taste panels. Some fermentable flavour was still detectable, but even this may be masked when the product is incorporated into baked goods.

Wu and Stringfellow (1986) looked at the further processing of distillers' grains and distillers' grains with solubles in order to increase protein concentrations and reduce fibre. They found that this could be done with a simple screening process. The increase in protein content was more marked than what they had achieved previously using a more complicated dry milling procedure (Wu and Stringfellow, 1982). Selective use of screens could be used to develop a range of products with different fibre:protein ratios.

Wall and coworkers (1984) looked at the potential use of corn distillers' grains, corn distillers' grains with solubles and corn protein concentrates, produced by fermenting degermed, dehulled dry milled corn, for use as food sources in foreign aid projects. The corn products were considered as part of corn-soy-milk mixtures at levels up to 10%. The authors concluded that additional processing was needed before these products could be considered for use. Two other important factors for use of corn byproducts in food aid are taste and storagability (Bookwalter et al., 1984). Use of DDGS and protein concentrates were negated because of flavour and lysine deficiency, respectively. Distillers' grains could be used up to a concentration of 2.5% without deleterious effects. Further processing of distillers' grains by washing or defatting with a hexane-ethanol solution, led to an improvement in taste.

Wu et al. (1985) took the grits, degerminator meal, and hominy feed produced from corn dry milling and fermented each to form ethanol. The distillers' grains from the fermentation of corn grits and corn flour exhibited higher protein and lower fat and fibre concentrations than corn distillers' grains (Wu et al., 1981). Low fibre would be beneficial in the manufacture of products such as baby food where fibre is a limiting factor. Lower fat has the potential to increase storagability and may also improve flavour. The distillers' grains from the degerminator meal and hominy feed fractions were particularly rich in lysine, thus increasing their nutritional value. Wu and coworkers (1985) again emphasized the potential for developing a number of coproducts from corn fermentation to ethanol in order to fully exploit value-added opportunities.

3.4.7 Minor Components

3.4.7.1 Stillage Effluent

3.4.7.1.1 Introduction

Distillation of ethanol after the fermentation process leaves a primarily aqueous broth which contains organics, proteins and salts (Cheryan and Parekh, 1995; Dowd et al., 1993). In the United States, approximately 108 m3 of stillage are produced each year (Dowd et al., 1993), typically 10-15 litres of stillage per litre of ethanol produced (Maiorella et al., 1983). Most stillage enters the feed market in one form or another. However, it can also be used as a fermentation medium to produce other products, extracted to isolate minor components or recycled back into the fermentation process to provide a source of nutrients for yeast growth (Maisch, 1987).

Corn stillage from an ethanol distillery contains 7.5% solids, 2.3% protein, 1.5% ash, 0.5% sugar and a high content of vitamins on a weight basis (Maiorella et al., 1983). It has an extremely high biological oxygen demand (BOD) at 15-25,000 ppm. A 100 million litre/year plant would have a similar pollution load to a city of 1.4 million people. For this reason, treatment and byproduct recovery are very important and methodology to extract value-added material will become even more crucial as the fuel ethanol industry grows.

3.4.7.1.2 Extraction of minor components

Besides ethanol, a number of compounds are formed during the fermentation process. Dowd and coworkers (1993) used highly sensitive gas chromatography, mass spectrometry and high pressure liquid chromatography to characterize the composition of corn stillage in order to determine the potential for producing value-added products. They found that the broth contained ethanol, acetic acid, propionic acid, a mixture of higher boiling or non-volatile hydroxylated, dicarboxylic, amino and other nitrogenous acids, polyhydric alcohols and various sugars, sugar alcohols, glucosides, proteins, fats and salts. Four of the amino acids (alanine, valine, leucine and proline) were present in significant quantities. Membrane technology may provide an inexpensive and efficient means for isolation of minor components from stillage.

Some ethanol plants reuse the thin stillage in order to reduce fresh water consumption (Cheryan and Parekh, 1995). The result is that compounds in the thin stillage concentrate over succeeding cycles. Cheryan and Parekh (1995) suggested that if these components could be removed in relatively pure form they would have potential added value. They treated the thin stillage with microfiltration followed by electrodialysis and crystallization. They were able to separate a pure glycerol product as well as other organic acids. However, they stated that commercial development would depend on creation of markets and ability to compete with compounds currently in use.

Besides ethanol and carbon dioxide, glycerol is one of the major byproducts of corn fermentation (Busche et al., 1992; Julian et al., 1990; Oura, 1977). Glycerol has over 1000 uses in pharmaceuticals, cosmetics, foods, explosives, textiles and other industries, and the world market is greater than a billion pounds a year. Although glycerol from plant sources has not been competitive with petrochemically produced glycerol up until present, this may change with the continued depletion of fossil fuels (Vijaikishore and Karanth, 1986).

It has been proposed that the profitability of an ethanol plant struggling to survive, could be improved by slightly reducing ethanol production in order to generate a glycerol stream. Ethanol production necessarily diminishes because of the consumption of sugar in the glycerol producing process. In addition, further capital investment would be required.

Methodology to recover glycerol from stillage is under development (Keim and Venkatasubramanian, 1989). Julian and coworkers (1990) found that when corn thin stillage was recycled through 5 consecutive fermentations, ethanol yield did not increase but glycerol concentration grew from 0.8% in the original thin stillage to a maximum of 2.1%. Jian and Liu (1991) suggested that glycerin could be recovered from the fermentation media by filtering, vacuum evaporation, vacuum distillation with inorganic powder, decolouration and deodorization. They reported a recovery rate of industrial grade glycerin of 95%.

3.4.7.1.3 Use as a growth medium

Stillage or corn steep liquor has been proposed for use as a medium to produce a number of other products including riboflavin, enzymes such as amylase, invertase or glucose oxidase or antibiotics such as penicillin (Chan et al., 1991, 1992; Maiorella et al., 1983; Linko and Linko, 1981). Steepwater, which contains the soluble compounds, when dried is composed of approximately 50% crude protein (Reiners et al., 1973). It could be further processed to yield methane or ammonia. Amartey and Jeffries (1994) used corn steep liquor as a nutrient source when fermenting D-xylose (found in hemicellulose from corn fibre and hulls) to ethanol. They found that corn steep liquor provided a good and inexpensive source of nitrogen, vitamins and other nutritional factors essential to the activity of the fermenting yeast.

Paik and Glatz (1994) suggested that although propionic acid is generally produced from petroleum feedstocks, production from corn steep liquor merits consideration. Propionic acid is used in thermoplastics, antiarthritic medicines, perfumes, flavours, solvents and as an antifungal agent in foods and feeds. Corn steep liquor, as a byproduct of fuel ethanol production, represents a potentially abundant and inexpensive substrate for fermentation by propionibacteria. Paik and Glatz (1994) achieved concentrations of 45.6 g/litre of propionic acid using fed batch fermentation and immobilized cells. Production of acetic acid using corn steep liquor was also proposed.

3.4.7.2 Carotenoids

Hayman and coworkers (1995) indicated that selected coproducts from fuel ethanol plants have potential as microbial growth media for the production of value-added products. They tested six outputs of the commercial wet milling process as substrates for the growth and carotenoid production of Phaffia rhodozyma. Carotenoids are valuable pigments used in poultry and aquaculture feeds to achieve colours necessary for consumer acceptance. Biologically produced carotenoids, such as astaxanthin which is synthesized by P. rhodozyma, could provide an alternative to synthetic compounds currently in use, if they could be produced economically.

Hayman and associates (1995) found that use of thin stillage, condensed distillers' solubles and corn gluten feed resulted in the highest accumulation of biomass and carotenoids. Since thin stillage and condensed distillers' solubles have the least potential for economic recovery, they would be the media of choice.

3.4.7.3 Pullulan

Leathers and Gupta (1994) looked at the potential use of corn wet milling byproducts as media for the production of pullulan by Aureobasidium sp.. Pullulan is an industrial biopolymer that is used in food, pharmaceuticals and other industries and is useful as a film for coating and packaging food and as a low calorie ingredient (Yuen, 1974). At present, pullulan is produced from petroleum products. While Aureobasidium sp. was found to grow well on both corn fibre and condensed distillers' solubles, pullulan was not produced when corn fibre was used (Leathers and Gupta, 1994). Use of condensed distillers' solubles, that sell for as little as $0.01 U.S. per pound, did result in pullulan production. The biopolymer was separated from the culture supernatant using organic solvents. In theory, ethanol produced on-site at a biorefinery could be utilized as the organic solvent. The diluted ethanol from the pullulan precipitation could be recovered by distillation. The key to commercialization will be economic competitiveness with current sources of pullulan.