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Limitations and Challenges for Wheat-Based Bioethanol Production

Jessica Saunders¹, Marta Izydorczyk² and David B. Levin¹

¹*Department of Biosystems Engineering, University of Manitoba,*

²*Grain Research Laboratory - Canadian Grain Commission,
Canada*

1. Introduction

Bioethanol is currently the most widely used liquid biofuel in the world. Global ethanol production was ~19 billion L in 2000, and production has almost quadrupled over the past decade, with estimates for 2012 approaching 76 billion L [MRA, 2008]. In 2000, the total bioethanol produced in the U.S. represented 1.27% of the total gasoline pool by volume, and is expected to reach 7.5% of the gasoline pool by 2012 [EIA, 2007]. At present, bioethanol is produced exclusively via 1st generation technologies, utilizing sugar and starch-rich feedstocks, as no commercial size 2nd generation cellulosic ethanol facilities are presently in operation.

In countries like Canada, where wheat is locally available and abundant, the development of high yielding wheat-based bioenergy crops could contribute to reducing dependence on petroleum for transportation fuels and reduce green house gas (GHG) emissions. In order for wheat-based bioethanol to contribute maximally to the displacement of petroleum-based fuels, wheat varieties possessing characteristics optimized for end-use as bioethanol feedstocks are required. Wheat with characteristics tailored to the needs of the bioethanol industry would consist of high starch, low protein varieties, with the physicochemical parameters of the starch lending themselves to high conversion efficiencies under industrial conditions. However, no evaluative criteria of wheat starch quality, as it relates to maximized ethanol yield, is available. In this chapter, we review the rational for grain-based bioethanol production, the starch characteristics that would be optimal for a bioethanol feedstock, and propose selection criteria for development of dedicated, wheat-based, bioethanol feedstocks.

2. Background - the rational for 1st generation bioethanol

The largest ethanol producing industries, representing over 90% of the global 65.7 billion L produced in 2008 [CRFA, 2008], are located in Brazil and the United States of America (USA or US). Total production capacity in the U.S.A. is expected to reach about 90% of the 2015 goal of 56.2 billion L of corn ethanol production set in the 2007 Energy Independence and Security Act [Pryor, 2009]. In 2008, the USA produced 34 billion L (Table 1) of ethanol for use as fuel oxygenate. Most commercially made ethanol now comes from corn (~97.5% in

USA) [Zhao *et al.*, 2009] and the most commonly available blended gasoline contains 10% (E10) corn ethanol [Pryor, 2009; Tao & Aden, 2009]. Brazil produced approximately 24.5 billion L in 2008 but mandates 20-25% (E20-E25) blend ratios [Hahn, 2008]. According to Hahn [2008], the European Union (EU) has also set targets of 5.75% for blended gas, as has Argentina (at least 5%). China and India are also following this trend with nationa-wide fuel ethanol programs [Bai *et al.*, 2008], as is Canada, which will need to produce 2 billion L of ethanol by 2010 to meet the 5% federal renewable fuel standard recently mandated [CRFA, 2009].

Ethanol has been mandated for incorporation into many countries transportation economies largely in the hopes of addressing rising concern over anthropogenic greenhouse gas emissions, of which 80% is claimed accountable to fossil fuel combustion [Quadrelli & Peterson, 2007]. The role of ethanol as a blended gasoline product, in ratios of 5 – 20% (v/v) ethanol, referred to as gasohol, can be used without major modifications to pre-existing automobile engines and burns cleaner, due to the higher octane rating, reducing harmful emissions [Agarwal, 2007]. Most researchers agree that a net decrease in GHG emissions of 13 – 18% is likely to be observed with the incorporation of ethanol as E10-20 into the fuel supply [Farrel, 2006; Kim & Dale, 2004, Dale, 2008]. Fuel security, volatility in oil pricing and the development of local, rural economies, have all been cited as additional impetus for many nation’s inclusion of biofuels into the energy policy discourse.

Country	Billions of Litres
USA	34.1
Brazil	24.5
European Union	2.8
China	1.9
Canada	0.9

Table 1. Global ethanol production. Adapted from RFA [2008].

Most governments have helped their biofuel industries flourish with subsidies, suggesting these technologies are, at present, economically unviable. For example, subsidies per liter of ethanol total more than \$6 billion (USD) per year for US corn ethanol [Pimentel *et al.*, 2009; Koplow, 2006]. In Canada, between 2006 and 2008, total support to biofuels was between \$860 million and \$1.02 billion (CDN), averaging \$300 million (CDN) per year [Laan *et al.*, 2009]. However, at current energy prices, some agricultural feedstock have indeed already become competitive sources of energy, at least under certain production environments [Schmidhuber, 2006]. Sugarcane ethanol in Brazil is reported to offer higher energy return and greenhouse gas reductions per litre of ethanol than US-made corn ethanol [Rajagopal *et al.*, 2007], and is suggested to be cost competitive with petroleum at US\$25 per barrel (bbl) [Schmidhuber, 2006]. Regional variability in agricultural conditions, however, dictates the fuel crops that can feasibly be produced in an area. Sugarcane, for example, does not grow outside of tropical or sub-tropical climates. Starch-based bioethanol production, utilizing wheat and corn as feedstock, dominates the North American biofuels market, as these ubiquitous cereal grains are well suited to that environment.

Neither biofuels, nor any other petroleum alternative, are able to compete with fossil fuels if the price of oil is \leq US\$20/bbl, as it has been for most of the past three decades [Dale, 2008]. Dale [2008] claims that at \geq US\$50/bbl, many alternatives make economic sense, including

some biofuels and particularly cellulosic ethanol. Without subsidies, at corn prices of around \$3.25 per bushel, ethanol as a high-octane fuel is competitive with oil at about US\$60/bbl [Dale, 2008]. Schmidhuber [2006] puts the parity price closer to US\$58/bbl for maize-based ethanol in the US. In the past 4 years (April 2006 – April 2010) the average per barrel oil cost is cited as US\$72.55 [EIA, 2010], and in that time per barrel oil price has been less than US\$60 for only 6.5 months, where it averaged US\$54.84 [EIA, 2010]. In fact, the growth in ethanol production, according to an Iowa State University study, has caused retail gasoline prices to be \$0.29 to \$0.40 per gallon lower than would otherwise have been the case [Du & Hayes, 2008]. Wheat-based ethanol production, which represents a large fraction of production in the EU and Canada, has less favorable economics than corn-based production. In the EU, grain-based ethanol production cost was reported in 2006/2007 as ~ \$0.578/L [Tao & Aden, 2009], compared to ~ \$0.396/L for corn purchased at \$3.35 per bushel [Tao & Aden, 2009]. Although wheat represents a large fraction of production in the EU and Canada, only 1.6% of the total wheat harvest in Europe and 2.9% of the total wheat harvest in Canada was used for bioethanol production in 2007 [Harlander, 2008; Husky Energy, 2009].

Fossil fuels at present provide 85% of the commercial energy consumed worldwide [Lackner & Sachs, 2005] and 40% of the total energy consumption in the world is in the form of liquid fuels [Tan *et al.*, 2008]. Global coal, oil, and natural gas reserves have been estimated to last for 218 years (coal), 41 years (oil), and 63 years (natural gas), under a business as usual scenario [Agarwal, 2007]. The world's supply of low cost, "sweet" crude oil, however, is dwindling, with 'peak oil' having occurred or likely to occur before 2010 [Lackner & Sachs, 2005]. As the population swells towards 9 billion, it is estimated that oil demand will double in the rapidly developing economies of China and India, resulting in an estimated 52% increase in global oil demand by 2025 [IEA, 2005]. Projections for the 30-year period from 1990-2020 indicate that vehicle travel, and consequently fossil-fuel demand, will almost triple [Agarwal, 2007].

The development of an energy supply that is local, renewable and sustainable is highly desirable for nations with growing transportation fuel demands and who already import large fractions of their supply. For example, of the roughly 20 million barrels of crude oil the USA consumes daily [EIA, 2009a], almost 60% is imported [EIA, 2009b], making the US highly vulnerable to oil market fluctuations. China's oil consumption has seen a purported 7.5% annual growth over the last several years, 7 times faster than the US [Luft, 2004]. In 2008, China consumed an estimated 7.8 million bbl/d and imported approximately 3.9 million bbl/d, roughly 50% of demand [EIA, 2010]. If the burgeoning economies of India and China place the predicted stress on oil availability and market price, this "would be the single most important aid and rationale for biofuels as a commercial reality" [Mousdale, 2008].

Despite the limitations of starch-based biofuels (see Section 4.0, below), the ease of ethanol's adaptation to present oil infrastructure suggests that as gasoline prices increase and emission regulations become more stringent, ethanol is likely to assume a role of escalating significance in a market that no longer has access to cheap and abundant petroleum products. First generation bioethanol technologies offer an imperfect solution to the world's long-term energy needs, whose utility must be viewed in context to locations that can feasibly support the diversion of food to energy crops. Adopting present processing technologies to utilize a feedstock, however, without the necessity of heavy cultivation and diversion of agricultural lands and foodstuffs, could represent a long-term solution to bioenergy generation and sustainable supply. Farrell [2006] claimed "large-scale use of ethanol for fuel will almost certainly require cellulosic (2nd generation) technology."

Transportation biofuels such as cellulosic ethanol, if produced from low-cost biomass grown on agriculturally marginal land or from waste biomass, could provide much greater supplies and environmental benefits than food-based biofuels [Hill *et al.*, 2006]. The US government, under the Energy Independence and Security Act of 2007, has mandated 16 billion gallons (~60 billion L) of “cellulosic ethanol” be included into the renewable fuel supply [Tao & Aden, 2009] by 2022. The cellulosic ethanol industry, however, remains nascent and has failed to emerge from the current demonstration phase to produce commercial-scale quantities. The US Environmental Protection Agency (EPA) recently acknowledged that, despite generous levels of taxpayer funding, cellulosic ethanol was not scaling up as quickly as had been hoped [Rapier, 2010] and previous targets outlined in 2007 have been significantly revised.

Starch-based ethanol production, although problematic, remains a mature technology capable of immediate contribution to the pressing global environmental and energy security needs. First-generation technologies are seen as an intermediate step to reduce GHG emissions and to diversify transport energy security [Antizar-Ladislao & Turrion-Gomez, 2008] whose production, however, is an undeniable aid in development of an ethanol infrastructure. Until cellulosic ethanol becomes a commercial reality, starch-based production will likely be of growing significance in many countries liquid fuel supply, especially for nations possessing large surplus quantities of grain, such as the EU, Canada and the USA.

3. Limitations to 1st generation bioethanol technologies

Arguments in favor of starch-based ethanol production are countered by myriad of concerns related to land-use patterns and diversion of food supply, which generates significant uncertainty in the long-term utility of starch-based ethanol production. According to Rajagopal *et al.* [2007], production of biofuels takes land away from its two other primary uses – food production and environmental preservation. Some even argue that biofuels will cause dramatic changes in land-use patterns which could offset any CO₂ savings derived from the utilization of biomass. Searchinger *et al.* [2008] contends that land-use changes will cause a net increase in GHG emissions with a doubling of GHG emissions over 30 years and increasing atmospheric CO₂ concentrations for 167 years.

A number of sweeping condemnations of corn-based bioethanol production in the USA have been published in the past several years. The criticisms are centered around resource consumption, such as water, and agricultural practices: it has been estimated that a 50 million gallon per year ethanol factory consumes 500 gallons of water per minute, and that intensive corn production uses more nitrogen fertilizer [NAS, 2004], has significant phosphorus requirements [USDA, 2007], and uses more insecticides [McLaughlin & Walsh, 1998] and herbicides [Patzek, 2004] than any other crop grown. Compounding these environmental issues is the reality of ethanol’s lower energy density. Ethanol delivers only two-thirds the energy that petroleum does and therefore more is required [Srinivasan, 2009]. Diverting food crops for use as substrate in biofuel production has caused unceasing controversy since the inception of the biofuels movement. In 2004, 13% of the US corn crop was diverted to produce ethanol [Patzek, 2004], in 2006 that number increased to 20%. In 2009/2010, 4.2 billion bushels of corn were used to produce ethanol, an increase from 3.6 billion bushels in 2008/2009 [USDA, 2009]. Overall, ethanol consumed 33% of the corn crop in 2009/2010, compared to 30% in 2008/2009. Some authorities have claimed that bioethanol

production contributed to rising food prices, but these claims are controversial, and much uncertainty exists in the extent of the food price increases that may be attributed to bioethanol production [Sims, 2008]. For example, the use of corn for ethanol production was reported to have increased the prices of US beef, chicken, pork, eggs, breads, cereals, and milk by 10% to 20% [Brown, 2009]. However, in 2007 the UK, food prices increased even though no grain-based bioethanol was produced [Karl, 2010].

The switch to fuel crops, from other non-energy food crops, could cause additional food security issues. Projected corn ethanol production in 2016 would use 43% of the US corn land harvested for grain in 2004 [Searchinger *et al.*, 2009]. According to Searchinger *et al.* [2009], U.S. agricultural exports will decline sharply causing a myriad of problems for importing nations, who will be forced to become increasingly self-reliant, likely appropriating previously unused land for domestic agricultural production. In June 2007, due to concern over rising food prices, China's central government to ban the use of grain-based feedstocks for biofuel production and reoriented the country's bioenergy plans toward perennial crops grown on marginal land [Weyerhaeuser *et al.*, 2007]. In addition, Jacques Diouf, Director General of the UN Food and Agriculture Organization reported that using food grains to produce biofuels already is causing food shortages for the poor of the world [Diouf, 2007].

The most salient of arguments against 1st generation technologies are, however, (environmental and food diversion concerns aside), that grain-based bioethanol is "supply-limited" and cannot meet the expected US transportation fuel demand. Even if all current US soybean and corn production were dedicated to biofuels, only 12% of the gasoline demand and 6% of the diesel demand would be met [Srinivasan, 2009]. Globally seven crops (wheat, rice, corn, sorghum, sugarcane, cassava and sugar beet) account for 42% of cropland. If all land currently used to grow these crops were dedicated to biofuels, just over half of the global gasoline demand would be met.

4. The case for wheat-based bioethanol

As detailed above, feedstock sources for ethanol production vary around the world. Brazil, the largest ethanol producer, uses sugarcane as a primary feedstock source. Corn acts as the primary feedstock source in the United States. In Canada, corn is used as a feedstock for ethanol production in areas where grain corn can be produced. However, climatic conditions limit grain corn production in many areas. In western Canada, wheat is the most readily available, high quality feedstock. Therefore, the majority of proposals for expansion of ethanol production in western Canada include the construction of wheat-based ethanol plants.

Traditionally, Canadian wheat cultivars were developed to express high protein concentrations for functionality in the production of bread and pasta, extracting price premiums in the marketplace. High protein concentrations were accompanied, however, by low concentrations of starch, which make most small grain cereals less desirable for industrial ethanol production. Breeding efforts in the past 20 years have resulted in high-yielding wheat cultivars, such as those of the Canada Prairie Spring and the Canada Western Soft White Spring classes. Very high yielding triticale, hullless barley, and improved winter wheat cultivars have also been developed. All of these classes of small grains tend have protein concentrations between 10% and 14%, but their starch concentrations are mostly unknown [NRCan, 2003]. Starch concentrations are not generally determined, but

reported as “total carbohydrates”, which are estimated as the difference between 100% and the sum of moisture, protein, crude fiber, fat and ash [Wolff, 1982]. In addition to starch and fermentable sugars, the “total carbohydrates” also contain water-soluble hemicellulose, β -glucans and pentosans, depending on the grain. Not all total carbohydrates are fermentable, and ethanol yields are overestimated when calculated from this parameter in cereal grains.

There is limited information regarding the potential ethanol yields of small grain cereals in western Canada. Wang *et al.* [1997] reported the spring triticale cultivar AC Copia yielded 362 to 367 L t⁻¹ grain (14% moisture basis). Ethanol yields of 443 L t⁻¹ of hulless barley (dry weight basis) have been reported [Thomas *et al.* 1995]. Thomas & Ingledew [1995] obtained 317 +/- 1.3 L t⁻¹ on a dry weight basis from a hulled oat (cultivar unknown). Research in the USA reported that barley produced the greatest ethanol yield per hectare, slightly more than soft white spring wheat, while hard red and hard white spring classes produced the least [Lacerenza *et al.*, 2008].

More recently, however, McLeod *et al.* [2010] evaluated the potential of small grains in western Canada to supply feedstock to the ethanol industry. Thirty-one lines and cultivars of Canadian small grains were evaluated: eleven cultivars comprising five classes spring wheat, six cultivars of barley (feed, malting, and hulless varieties), eight cultivars of spring triticale, and six cultivars of oat were grown at seven locations in western Canada and evaluated as feedstock for ethanol production. Starch concentrations and, for certain grains, β -glucan and pentosans were determined and used to estimate ethanol yields in L t⁻¹ and L ha⁻¹. On average, the ethanol yield in L t⁻¹ was wheat > triticale > barley > oat.

Biologically, winter wheat has the highest yield potential of the *Triticum aestivum* wheat cultivars grown in western Canada. From 1993 to 2003 mean winter wheat yields were 107% of spring wheat yields in Alberta, 116% in Saskatchewan, and 127% in Manitoba [Canada Grains Council Statistical Handbook, 2003]. In the province of Manitoba, the mean yield of winter wheat was 140% of the Canada Western Red Spring wheat yield and 124% of the Canada Prairie Spring wheat yield from 1998 to 2004 (Yield Manitoba – Manitoba Crop Insurance Corporation). Therefore, commercially grown cultivars of winter wheat have a significant yield advantage over Canada Western Red Spring and Canada Prairie Spring wheat. The efficiency of ethanol production from grains, however, depends on process conditions, as well as the starch and fermentable sugar contents.

5. Cereal starch characteristics optimal for bioethanol feedstock

Starch is the predominant component of wheat grain, constituting 60-65% of the kernel. The functional properties of starch vary widely across botanical origin [Swinkels, 1985] and unique characteristics are desirable for different final product application [Franco *et al.*, 2002]. Lacerenza *et al.* [2008] recently pointed out that the traditional selection criteria for wheat-breeding, based on milling and baking quality, is not consistent with maximal ethanol yield per hectare. The lack of breeding programs for varieties designed specifically for ethanol production, suggests Swanston *et al.* [2007], is due to a lack of appropriate selection procedures due to limited understanding of the factors contributing to alcohol yield.

Recent research into optimized bioethanol production has focused on the development of new and improved cereal and maize hybrids with higher starch contents to increase ethanol yields [Wu *et al.*, 2006]. Grain preprocessing strategies are also being investigated and have the potential to ‘increase throughput rate and capacity of ethanol plants’ [Sosulski &

Sosulski, 1994; Kindred *et al.*, 2008] by decreasing non-starch carry-through. The outcome of present biofuel development is the inevitable processing of higher starch feed streams, achieved through adoption of new process technology or higher starch grains.

Starch content, although inarguably the most critical feature in determining ethanol conversion efficiency, is not necessarily the only influential parameter in understanding fermentation performance. Starch with high intrinsic resistance to enzymatic hydrolysis can yield a low sugar load to yeast, making it an erroneous selection as feedstock, especially when considering the industries move towards ever higher starch feed streams. Of particular interest to the bioethanol industry are the functional properties of starch that lend themselves to ease of amylolytic hydrolysis and high conversion efficiency of starch to fermentable sugars. The bioavailability of starch may differ among grain cultivars and may affect the conversion rate and final yield of ethanol [Moorthy, 2002]. A more thorough understanding of the influence starch structural and physicochemical properties have on the efficiency of gelatinization and liquefaction, the two most relevant industrial processes in the preparation of bioethanol feedstock, is therefore required.

5.1 The effect of physicochemical properties of wheat starch on enzymatic hydrolysis and fermentative alcohol yield

Presently no evaluative criteria of grain starch quality, as it relates to maximized ethanol yield, are available to bioethanol producers. The following five parameters have been shown to influence the functional properties of starch and are used as evaluative criteria in this study: amylose/amylopectin content [Zhao *et al.*, 2009; Wu *et al.*, 2006, Wu *et al.*, 2007; Lee *et al.*, 2001]; starch granule morphology [Liu *et al.*, 2007]; amylopectin fine structure [Zhang *et al.*, 2008a; Ao *et al.*, 2007; Sasaki *et al.*, 2002; Zhang *et al.*, 2008b]; thermal properties [Zhao *et al.*, 2009; Wu *et al.*, 2007]; pasting properties [Zhao *et al.*, 2009].

5.2 Amylose and amylopectin

Starch granules are composed of two types of alpha (α -)glucans, amylose (Figure 1) and amylopectin, which represent approximately 98-99% of the dry weight [Tester *et al.*, 2008]. The ratio of the two polysaccharides varies according to the botanical origin of the starch, but within wheat varieties maintains ranges of 25-28% amylose and 72-75% amylopectin [Hung *et al.*, 2006]. Starches with less than 5% amylose are found in “waxy” wheats, where as wheat varieties containing starches with greater than 35% amylose are considered “high-amylose” wheats [Wu *et al.*, 2006]. Amylose is an essentially linear molecule, consisting of α -(1,4)-linked D-glucopyranosol units with a degree of polymerization (DP) in the range of 50-6000 glucose residues. It is now well recognized that a fraction of the amylose molecules is slightly branched by α -(1,6)-linkages. In contrast, amylopectin is a very large, highly branched chain molecule with a DP ranging from 30,000 to 300,000 glucose units and consists of α -(1,6)-linked D-glucopyranosol units attached to glucose residues in the amylose chains [Zobel *et al.*, 1988]. Amylose and amylopectin strands are reported to have molecular weights in the range of 10^4 - 10^6 and 10^7 - 10^8 Daltons, respectively.

Wu *et al.* [2006] studied high-amylose starches and demonstrated that amylose content, more than protein or fiber content, had significant effect on ethanol fermentation efficiency. The study revealed that conversion efficiency decreased as amylose content increased. Starch in its native form is resistant to enzymatic digestion and must be gelatinized,

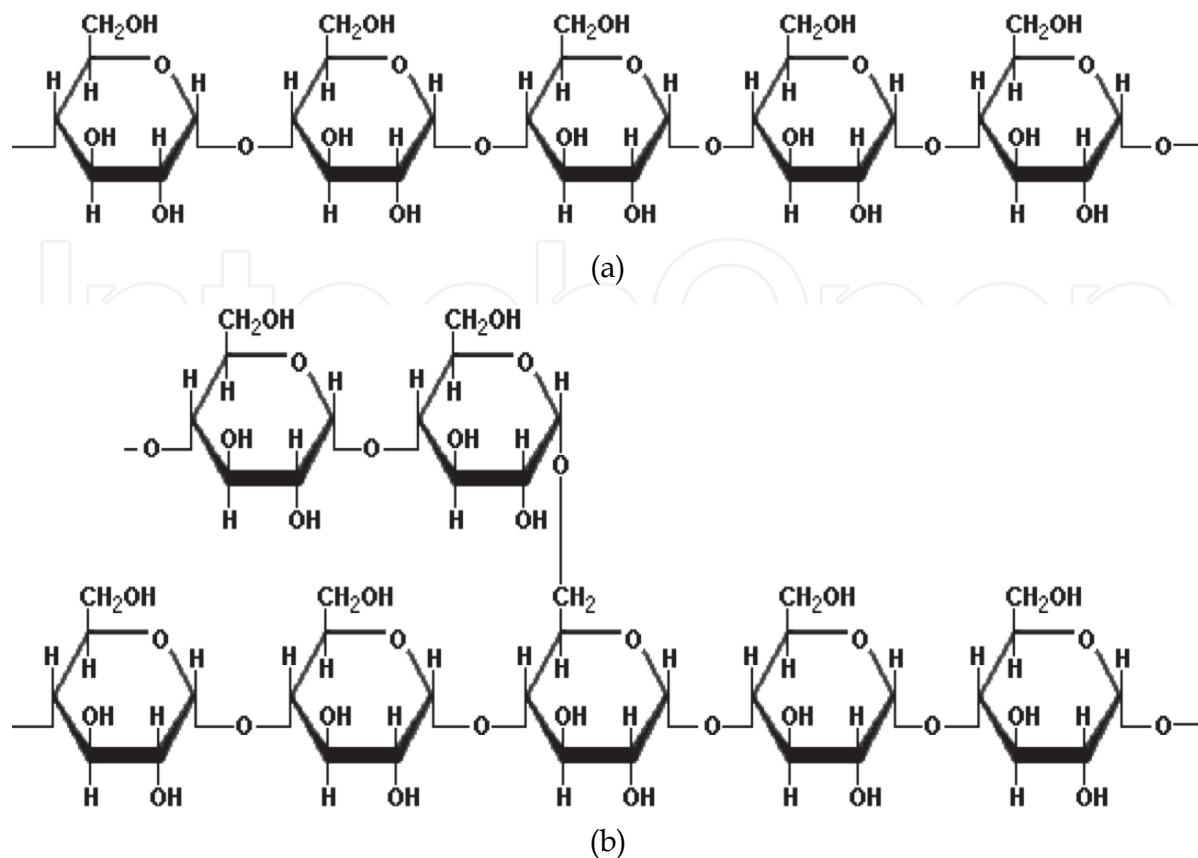


Fig. 1. Amylose molecules composed of glucose monomers connected as in **a**) via α -(1,4)-glycosidic bonds or as in **b**) with infrequent branch chains via α -(1,6)-glycosidic bonds. Adapted from Saunders [2010].

changing it into an amorphous mass, before it becomes susceptible to glucosidic enzymes. Because of the existence of starch granules with high gelatinizing temperatures, and the formation of amylose-lipid complexes (AML) and reassociation of amylose molecules during gelatinization and enzymatic hydrolysis, there is always some starch that escapes hydrolysis by amylolytic enzymes [Boltz & Thompson, 1999]. As much as 2% of the starch in industrial dextrose production remained undigested as insoluble particles in the hydrolysate [Hebeda & Leach, 1974]. Amylose is likely to form amylose-lipid complexes in the caryopsis or during mashing that are resistant to enzymatic hydrolysis [Wu *et al.*, 2007]. Wu *et al.* [2006] states that, in most instances, resistant starch content increases as the amylose content in starch increases. High amylose containing starches also inhibit fermentative ethanol production by yielding high viscosity mashes. Greater enzyme dosing, according to Wu *et al.* [2006], was not an effective strategy for increasing maltose and dextrin formation. It appears that high mash viscosity creates a bottleneck to enzymatic activity that can only be overcome with greater reaction time; greater reaction time, however, provides increased opportunity for deleterious retrogradation and amylose-lipid complexing, increasing the degree of insoluble sugars.

A reduction in amylose content has been positively correlated with enzymatic digestibility and represents the current accepted paradigm for the pattern of α -amylolysis on native starches. Fermentation studies consistently report higher ethanol yields on waxy (high amylopectin) substrates than non-waxy counterparts. A high percentage of amylopectin

seems to be more susceptible to α -amylase during fermentation, with higher gas production of waxy wheat flour as compared with the non-waxy wheat flour [Lee *et al.*, 2001]. Wu *et al.* [2007] reported that waxy and hetero-waxy sorghum hybrids generally have higher conversion efficiencies than non-waxy hybrids. Zhao *et al.* [2009] studied the effects of waxy vs. non-waxy soft and hard wheats for fuel ethanol production and found results consistent with Lee *et al.* [2001] and Wu *et al.* [2007]. High ethanol conversion efficiencies of waxy-wheats were reported as compared to non-waxy wheats, (95.4 to 96.2% versus 92.6%, respectively) [Zhao *et al.*, 2009]. Wu *et al.* [2006] observed that conversion efficiencies increased as the amylose content decreased, especially when the amylose content was >35%. Employing waxy wheat as feedstock for fuel ethanol production has been recommended [Lacerenza *et al.*, 2008]. However, waxy-wheats have lower starch yields [Zhao *et al.* 2009] and no waxy wheat varieties have yet reached the commercial stage of development.

5.3 Granule size distribution

Present research suggests wheat starch has a trimodal distribution of granule sizes [41-43]. However, the existence of the smallest C-type granule remains somewhat putative with many authors reporting only the A and B-type granule populations [Ao & Jane, 2007; Morrison & Gadan, 1987; Peng *et al.*, 1999]. A-type granules make up the bulk of starch (~75% by weight), but are fewer in number than the smaller sized B- and C-type granules (~25% by weight) [Ao & Jane, 2007]. A-type granules have been reported as 10-35 μm in average spherical diameter and account for less than 10% of the granules by number, small B and C-type particles therefore constitute over 90% of the granules by number [Lindeboom *et al.*, 2004].

The large lenticular A-granules and the small, spherical B-granules have different physical, chemical and functional properties [Raeker *et al.*, 2007; Morrison & Gadan, 1987; Dronzek *et al.*, 1972; Kulp, 1973; Meredith, 1981; Soulaka & Morrison, 1985; Park *et al.*, 2004]. The two types of granules (A- and B-) differ in their ratio of amylopectin to amylose [Morrison & Gadan, 1987; Soulaka & Morrison, 1985; Tester & Morrison, 1990], and have differing ratios of amylose to bound lipids [Raeker *et al.*, 1998; Ao & Jane, 2007]. In cereal starches there are small quantities of naturally occurring lipids which are capable of forming complexes with amylose [Kwasniewska-Karolak *et al.*, 2008]. The presence of amylose-lipid complexes negatively influence production of glucose syrups because it reduces water binding and swelling of starch granules, thus impairing the access of amylolytic enzymes [Matser & Steeneken, 1998]. Liu *et al.* [2007] studied the *in vitro* digestibility of A- and B-type granules from soft and hard wheat flours and found higher resistant starch content in the A-type wheat granule as compared to the B-type granule. Several studies have reported higher amylose content in the A-type granule, explaining, in part, their increased resistance to enzymatic hydrolysis [Liu *et al.*, 2007; Peng *et al.*, 1999]. For example, absolute amylose content of wheat for the A-type granule was measured as 30.9% and that of the B-granules 25.5% [Peng *et al.*, 1999]. Liu *et al.* [2007] also reported apparent amylose content as 25.4-25.8% for A-type (soft and hard wheat, respectively) and 16.5-19.3% for B-type.

Based on the findings of Liu *et al.* [2007], it appears that B-type granules may contain less resistant starch, due to lower concentrations of amylose, and may therefore yield higher conversion efficiency of starch to fermentable sugars during industrial feedstock preparation. The ratio of A- to B-type granules appears to vary significantly across cultivar type. However, a comparison of reported values across cultivars is challenging given genotype, environment, and method of analysis [Stoddard, 1999], which all appear to be influential in assessing the proportions of starch type in the granule. Various studies have

reported B-granule distribution in wheat starch as ranging from 25-40% [Dengate & Meredith, 1984], others report the range as 13-34% [Soulaka & Morrison, 1985]. Recent studies, however, have yielded more detailed information regarding variation between wheat cultivars. For example, hard red winter (HRW) wheat was found to have 48.4% by volume classified as B-type ($<10\ \mu\text{m}$ diameter) [Bechtel *et al.*, 1990]. In another study, B-granules occupied volumes in the range 28.5 – 49.1% (mean 39.9%) for HRW wheat, while hard red spring (HRS) wheat B-granules occupied volumes in the range 37.1 – 56.2% (mean 47.3%) [Park *et al.*, 2009]. In a study by Raeker *et al.* [1998], thirty-four starch samples from soft wheat cultivars were investigated for differences in particle size distribution. It was found that contributions from the large granule population ($>9.9\ \mu\text{m}$) to the total volume were 57.9 – 76.9%; B-type particles ($<9.9\ \mu\text{m}$) therefore represent a range of 23.1 – 42.1% of total volume. However, Raeker *et al.* [1998] also reported a negative correlation between total starch and volume % of small granules ($<10\ \mu\text{m}$) [Raeker *et al.*, 1998]. In general, according to these findings, as starch content increases, a trait highly amenable to bioethanol production, the volumetric quantity of A-type granules present in the endosperm appears to increase, as small B and C-type granules decrease, a trait not necessarily desirable for end-use as ethanol feedstock.

5.4 Amylopectin fine structure

The two key features of amylopectin fine structure are chain length distribution and branching pattern. According to Jenkins & Donald [1995], the currently accepted model for amylopectin structure involves short amylopectin chains forming double helices and associating into clusters. These clusters pack together to produce a structure of alternating crystalline (double helices) and amorphous lamellar composition (amylopectin branch points) [Jenkins & Donald, 1995]. The branched chains of amylopectin, according to the cluster model of amylopectin proposed by Hizukuri [1986], can be fractionated into B3, B2, B1 and A chains that are described as follows: A-chains, DP 6-12; B1-chains, DP 13-24; B2-chains, DP 25-36; and B3-chains, DP >37 . A and B1 chains dominate the distribution, forming double helices, with the longer B2 and B3 chains traversing two, three and four clusters (Figure 2) [Hizukuri, 1986].

The dominance of certain fractions of side chain length dictates the type of crystallinity displayed during X-ray diffraction studies, referred to as A-type, B-type and C-type [Jenkins & Donald, 1995]. Most cereal starches possess A-type crystallinity and have higher weights and number percents of short A chains [Chung *et al.*, 2008]. Amylose is thought to exist mainly in the non-crystalline state [Hizukuri *et al.*, 1996], but the exact location of amylose within the granule interior and the extent of its interaction with amylopectin is unclear [Gupta *et al.*, 2009]. It is likely that a large portion is found within the amorphous (lamellae), with only small amounts associated with the semi-crystalline (lamellae) [Jenkins & Donald, 1995].

During starch gelatinization, starch granular or supramolecular structure is disrupted, resulting in the pattern of enzymatic hydrolysis being predominantly related to the inherent molecular structure of amylopectin [Zhang *et al.*, 2008a]. The relationship between the molecular structure of starch (amylopectin fine structure) and its digestion rate after starch gelatinization is not well understood [Zhang *et al.*, 2008b]. Little variation in the branching pattern of amylopectin has been reported in normal wheat starches. Hanashiro *et al.* [1996] reported the following distribution of amylopectin side chains after debranching: DP 6-12, 27%; DP 13-24, 49%; DP 25-36, 14%; and DP >37 , 10%. These findings were

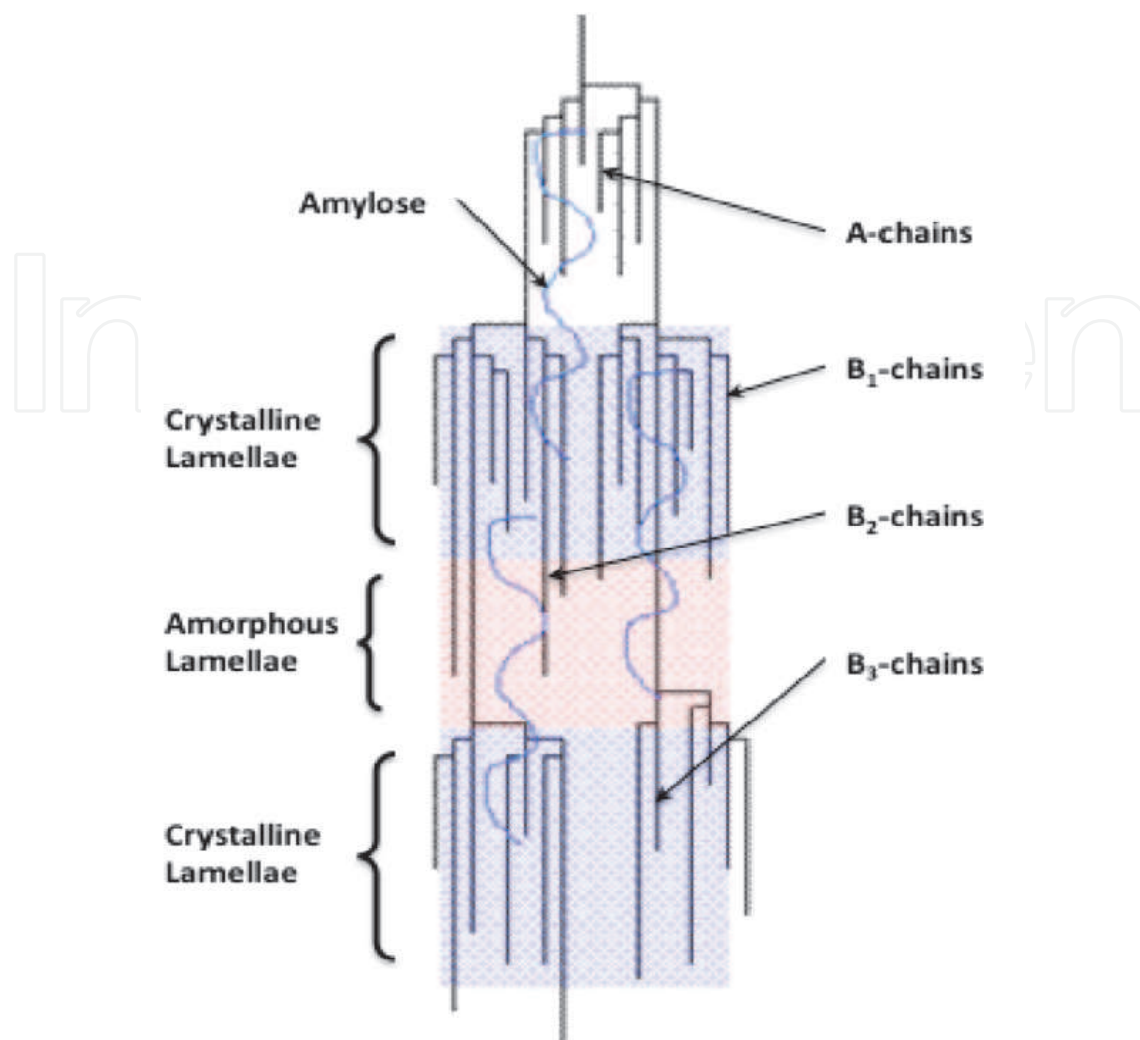


Fig. 2. Structure of amylopectin depicted as 'cluster model' proposed by Hizukuri (1986). A and B₁ chains dominate the distribution and occur as parallel strands, believed to wind into left-handed double helices. Larger B chains are thought to transverse two, three and four clusters. Short A-chains posses DP 6-12, B₁ chains range from DP 13-24, next B₂ chains occur at DP 25-36, and finally B₃ and longer chains at DP>36. Adapted from Hizukuri [1986].

supported in a study of 126 starch samples selected from the *Triticum-Aegilops* group, of which samples were derived from *Triticum aestivum*, or common bread wheat [Yasui *et al.*, 2005]. Additionally, in a study of 192 club and soft white winter wheat varieties, no measured difference in amylopectin side chain fractions was found between study samples [Lin & Czuchajowska, 1997]. These results were consistent with the findings reported by Hanashiro *et al.* [1996], and indicate that crystalline properties of starches considered should be indistinguishable.

Several studies have reported the effects of increasing branch density of amylopectin on decreased digestion rate of gelatinized starches through partial shortening of amylopectin exterior chains [Zhang *et al.*, 2008a; Zhang *et al.*, 2008b; Ao *et al.*, 2007]. Ao *et al.* [2007] reported that starch products exhibiting high branch densities, with shorter average chain lengths, showed reductions in rapidly digested starch of up to 30% and concomitant increases in slowly digested starch of up to 20%. Zhang *et al.* [2008b] found that amylopectin

of maize starch with high proportions of short chain fraction (SF, DP < 13) to long chain fraction (LF, DP > 13) showed increased quantities of slowly digested starch. The inherent molecular structure of amylopectin with a higher density of branches and shorter chains (high SF/LF ratio) is not favorable for rapid enzyme digestion [Zhang *et al.*, 2008a]. In general, the findings of Ao *et al.* [2007] and Zhang *et al.* [2008a] suggest longer branch chain lengths of amylopectin may be ideal for a rapidly digestible starch. In fact, waxy starches (>95% amylopectin), indicated as having favorable ethanol conversion performance, tend to have lower proportions of DP 6-12 side chains and higher proportions of DP >35 compared with non-waxy starches [Sasaki *et al.*, 2002]. Future work is needed, however, to quantify the average amylopectin chain length optimal for rapid enzymatic digestion during liquefaction.

5.5 Thermal properties

Gelatinization precedes liquefaction in the fermentation process and describes the physical break down of granular starch into solubilized, amorphous polymers readily hydrolyzed by α -amylase and amyloglucosidase (AMG), the two enzymes responsible for the conversion of starch to sugar. This irreversible loss of native structure occurs when sufficient energy is applied to break intermolecular hydrogen bonds in the crystalline areas [Rooney & Pflugfelder, 1986]. Two endothermic peaks are seen when thermal properties are determined using differential scanning calorimetry (DSC) (Figure 3). The first peak represents the melting of amylopectin and the second peak corresponds to the melting of amylose-lipid complexes [Hung *et al.*, 2006]. Gelatinization temperatures and enthalpies associated with gelatinization endotherms vary between starches. In a study by Gupta *et al.* [2009] native wheat and corn starch, measured at 70% moisture content, were reported to have onset temperatures (T_o) of 60.19 °C and 70.12 °C, respectively, peak temperatures (T_p) of 64.06 °C and 73.85 °C, respectively, and conclusion temperatures (T_c) of 68.42 °C and 78.20 °C, respectively.

Starch transition temperatures and gelatinization enthalpies by DSC may be related to characteristics of the starch granule, such as the amount of double helical domains (amylopectin) and single helical structures (amylose-lipid complexes) that unravel and melt during heating of aqueous starch dispersion. Van Hung *et al.* [2007] reported that waxy wheat starch with a predominant amylopectin content requires higher energy for gelatinization caused by its higher crystallinity as compared to non-waxy and high-amylose wheat starches. The presence of amylose, conversely, lowers the melting (gelatinization) temperature by decreasing crystallinity [Gupta *et al.*, 2009].

Limited research has been performed to elucidate the relationship between gelatinization temperature and industrial fermentation efficiency. From an energy standpoint, low gelatinization temperature starch may be favorable as feedstock to produce fermentation-based products due to lower temperatures required to efficiently process the grain. Low gelatinization temperatures, however, are associated with high amylose content starch [Hung *et al.*, 2006; Noda *et al.*, 2002], previously demonstrated to be unfavorable to maximizing ethanol yield. Zhao *et al.* [2009] found waxy wheat starch to have complete disruption/dissolution of the granule at 70-80 °C, compared to non-waxy cultivars which showed evidence of intact granular structure under hot-stage microscopic visualization for temperatures as high as 90 °C. Wu *et al.* [2006] also reports that waxy starches easily gelatinize and have concomitantly high conversion efficiency. In regards to bioethanol production, the most salient thermal property is likely the point of complete

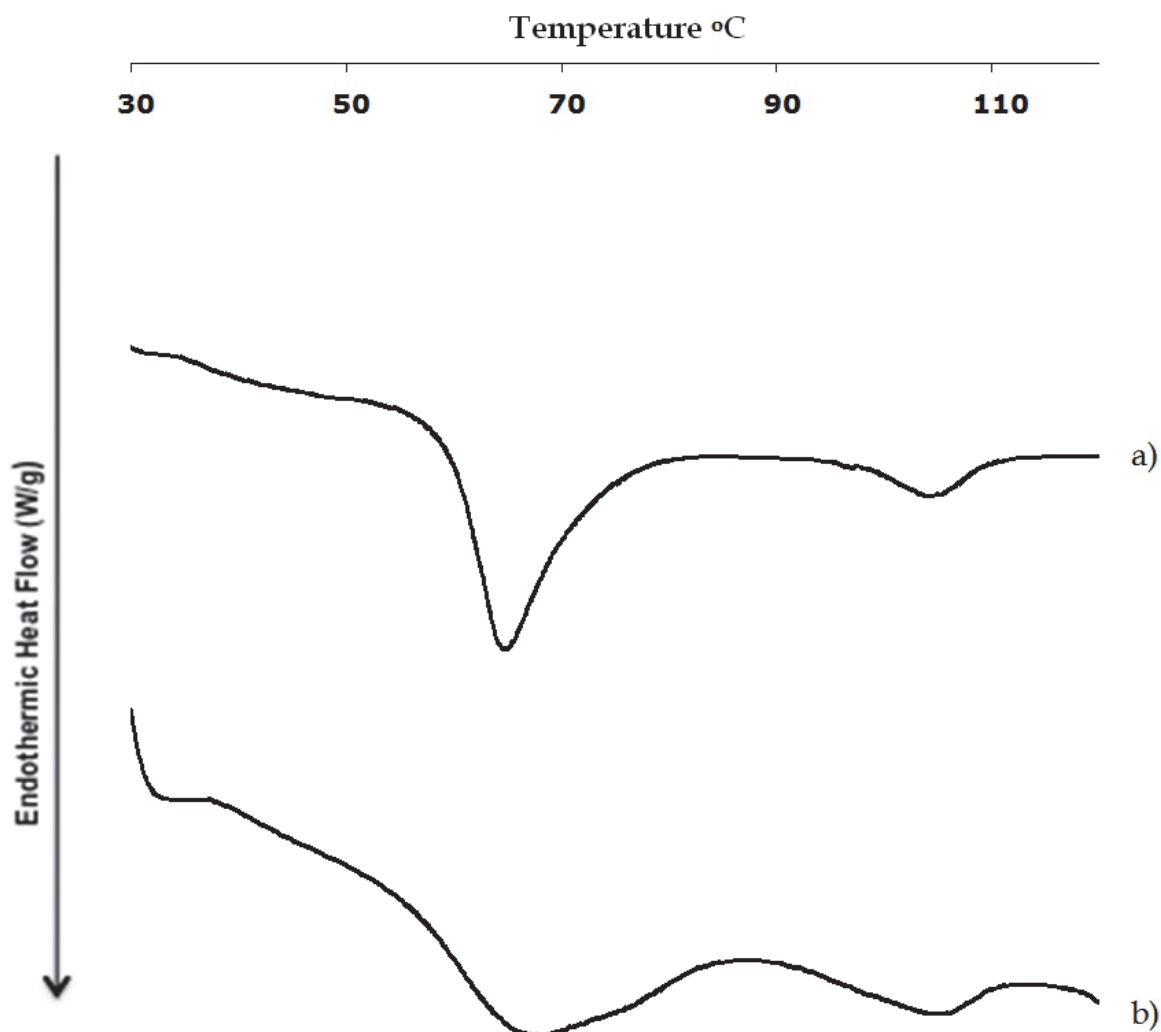


Fig. 3. Thermal properties of starch. Endotherm of A) wheat and B) maize starch, showing the first and second endothermic peaks, related to amylopectin gelatinization and amylose-lipid dissolution, respectively. Adapted from Saunders [2010].

disruption/dissolution, as pointed out by Zhao *et al.* [2009], and not necessarily traditional transition temperature ranges, as is generally reported. Amylopectin content appears to be the most influential feature dictating total granular disruption and is perhaps, in this regard, the best predictive metric for ethanol conversion.

The relationship between amylopectin fine structure and the thermal properties of starch has been well established [Franco *et al.*, 2002]. Starch that consists of amylopectin with a high proportion of long branch-chains purportedly displays higher gelatinization temperatures and enthalpy changes [Franco *et al.*, 2002; Jane *et al.*, 1999]. Several studies have reported the manipulation of branch chain length to modify thermal properties of starch. Amylopectin with increased quantities of longer branch chains produce more ordered double-helical crystallites, which require higher temperatures to uncoil and dissociate [Franco *et al.*, 2002; Song & Jane, 2000; Huang *et al.*, 2007]. Conversely, higher contents of extremely short chains within the amylopectin, DP 6 and 7, appear to lower T_o , T_p , and ΔH (gelatinization enthalpy) [Noda *et al.*, 2002]. In regards to bioethanol production, driving down the gelatinization temperature by manipulating amylopectin branch chain length may lead to a substrate with lower energy requirements to achieve high conversion

efficiency. However, the impact of amylopectin branch chain length on numerous other physicochemical properties [Franco *et al.*, 2002; Noda *et al.*, 2002], as well as enzymatic digestion rate [Zhang *et al.*, 2008; Ao *et al.*, 2007], suggest future work is needed to establish the amylopectin chain length distribution best suited for bio-ethanol end-use.

5.6 Pasting properties

Pasting viscosity profiles are analyzed using a Rapid Visco Analyzer (RVA). A typical profile is presented in Figure 4. The RVA curve describes pasting, a phenomenon following gelatinization, involving granular swelling, exudation of amylose and amylopectin, and total disruption of the starch granule. Pasting temperature is the point when the temperature rises above the gelatinization temperature, inducing starch granule swelling and resulting in increased viscosity. The peak viscosity indicates the maximum viscosity reached during the heating and holding cycle and is indicative of the water holding capacity of starch [Gupta *et al.*, 2009], and peak temperature occurs at peak viscosity. The breakdown viscosity is normally regarded as a measure of the disintegration of the starch granules as they are heated [Agu *et al.*, 2006] due to the rupture of granules and the release of soluble amylose. The degree of RVA breakdown is related to the solubility of the starch, and the more soluble the starch, the more it will thin on shearing [Hoseney, 1998]. As the mixture is cooled, re-association between starch molecules, especially amylose, results in the formation of a gel and the subsequent increase in viscosity. Total setback involves retrogradation, or re-ordering, of the starch molecule.

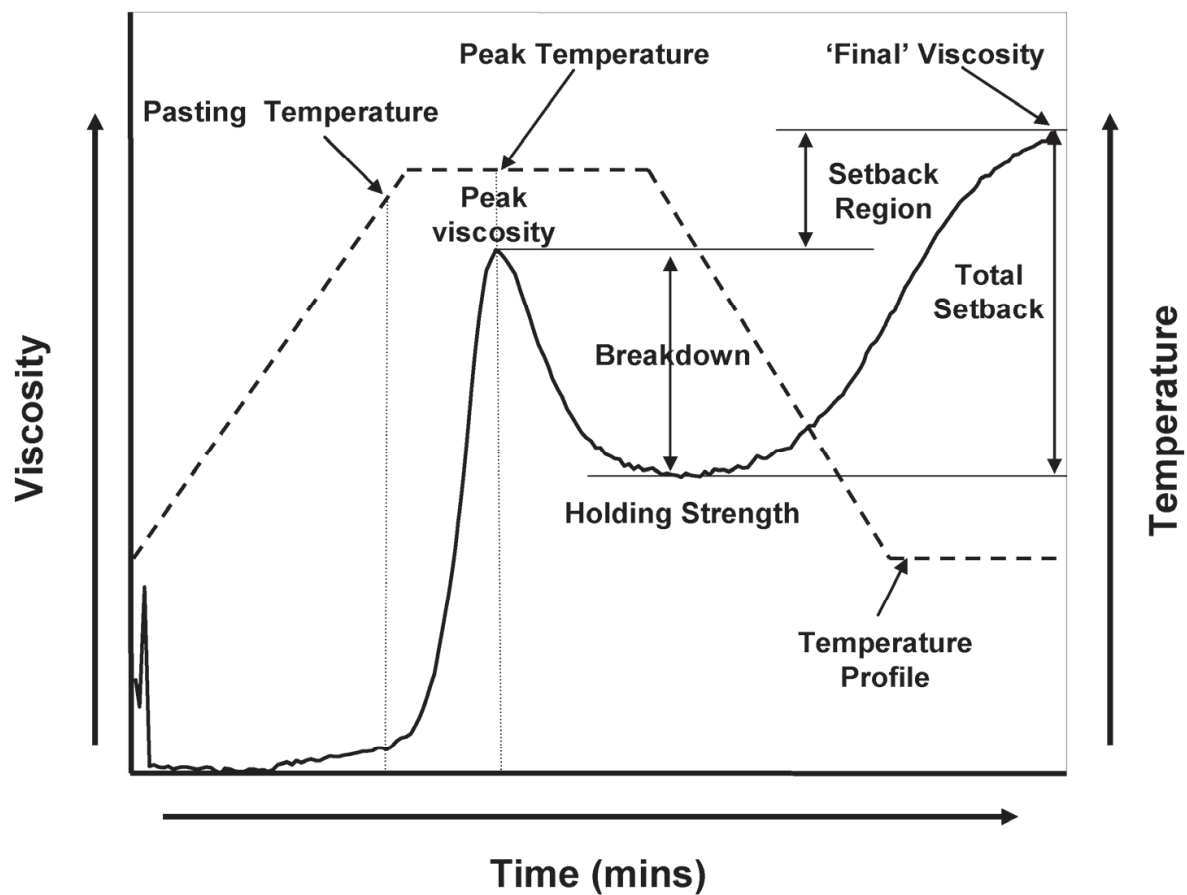


Fig. 4. A typical RVA pasting profile showing the commonly measured parameters. Adapted from Saunders [2010].

Pasting properties of starch are affected by amylose and lipid contents and by branch chain-length distribution of amylopectin [Gupta *et al.*, 2009]. Starches with larger amylose, lipid and phospholipid content have higher pasting temperatures, lower peak viscosity and shear-thinning (breakdown viscosity), and higher setback viscosity [Jane *et al.*, 1999; Zeng *et al.*, 1997]. Waxy wheat flour, conversely, has been shown to have significantly lower peak and pasting temperature, higher peak viscosity and lower setback viscosity than non-waxy or normal wheat flour [Gupta *et al.*, 2009; Zeng *et al.*, 1997; Abdel-Aal *et al.*, 2002]. Waxy starch swells rapidly and swollen granules degrade at lower temperature, indicating that waxy starch rapidly develops viscosity but cannot maintain the stability of paste viscosity [Gupta *et al.*, 2009]. Zhao *et al.* [2009] examined waxy starch granules using hot-stage microscopy and demonstrated that these starches rupture more extensively, even without mechanical shearing, and disperse more readily than non-waxy counterparts. Waxy wheat starch has been described as having lower final viscosity [Zeng *et al.*, 1997; Abdel-Aal *et al.*, 2002; Graybosch, 1998], an indication that it has less ability to retrograde and form strong gels.

Pasting properties, like thermal properties, are affected by the branch chain length distribution of amylopectin [Jane *et al.*, 1999]. According to Franco *et al.* [2002], amylopectin with longer branch chains display larger peak viscosity and lower pasting temperatures than shorter chain counterparts. Jane *et al.* [1999] also reported that long chains with DP > 50 accelerated retrogradation of amylopectin, whereas the short chains (DP 6-9) retarded it. It is plausible that very long chains of amylopectin mimic amylose to form helical complexes with lipids and intertwine with other branch chains to hold the integrity of starch granules during heating and shearing [Gupta *et al.*, 2009].

Wu *et al.* [2006, 2007] has described ideal feedstock for ethanol production as having rapid liquefaction characteristics and low viscosity during liquefaction. A high viscosity in the mash may impair the accessibility of starch to the enzyme and, thus, delay the liquefaction process [Wu *et al.*, 2007]. The ideal pasting properties, as depicted by RVA analysis, of a starch destined for use as bioethanol substrate include high solubility, demonstrated by a low viscosity after breakdown, and limited ability to retrograde upon cooling, demonstrated by a low final viscosity. Modified RVA analysis was performed by Zhao *et al.* [2009] to assess the viscosity of waxy versus non-waxy wheat during gelatinization and liquefaction. In this case, conventional RVA analysis was modified to include dosing with α -amylase, providing a metric for the balance between gelatinization and liquefaction. Zhao *et al.* [2009] states that “for waxy wheat cultivars, gelatinized starch granules were more susceptible to breakdown under liquefaction conditions; thus, starch molecules were more extensively exposed and more accessible to heat-stable α -amylase, so lower peak viscosities were obtained. Due to the low peak viscosity for waxy wheat during liquefaction, the dry-grind industry could thus increase the solids content in the mash, lower α -amylase dosages, or decrease energy requirements for stirring systems when waxy wheat is used as a feedstock.” The inherent pasting characteristics of starches, such as peak viscosity, are not distinctly observed in modern fuel ethanol production processes because of the addition of α -amylase to the cooking/liquefaction step, to aid pasting and reduce viscosity. Hence, the pasting properties of any particular starch may not have as much influence on cooking/liquefaction as one might anticipate, although accessibility of starch molecules to α -amylase would be a factor. The key is to have as much of the starch as possible (100%) converted to maltose and glucose in the saccharification step, which tends to be combined with fermentation in most modern processes.

6. Selection criteria for wheat as bioethanol feedstock

Ethanol yield, perhaps the most important fermentation performance criteria for the fuel ethanol industry, has been shown to be a starch related property of wheat [Zhao *et al.*, 2009; Lacerenza *et al.*, 2008; Kindred *et al.*, 2008]. Obviously a cultivar with higher starch content in its grain is desirable because it will provide more ethanol per ton of grain and produce smaller amounts of DDGS, resulting in less residual material left over and a greater energy saving during DDGS drying [Zhao *et al.*, 2009]. Elite genotypes for ethanol production have been described as having rapid liquefaction characteristics, low viscosity during liquefaction, high fermentation speed and high fermentation efficiencies [Wu *et al.*, 2007].

Starch properties conferring high conversion efficiencies to fermentable sugars, based on the available literature, are indicated in Table 2. Of particular note is the relationship of amylopectin to the majority of indicated parameters, and the marked benefit to each, in regards to bioethanol application, of an increase in amylopectin and concomitant decrease in amylose content. The encompassing recommendation of the present review is the selection of wheat with the highest amylopectin content achievable, theoretically delivering starch optimized for both rapid and complete degradation by industrial enzymes.

Parameter	Ideal Condition for Bioethanol Production	Reference
Amylose/ Amylose Content	> 75% amylopectin	Wu <i>et al.</i> [2006, 2007] Zhao <i>et al.</i> [2009]
Particle Size Distribution	High ratio of B-type granule	Liu <i>et al.</i> [2007]
Amylopectin Fine Structure	Increased long chain to short chain fraction	Ao <i>et al.</i> [2007], Zhang <i>et al.</i> [2008]
Thermal Properties	Total disruption/dissolution of starch granule	Wu <i>et al.</i> [2006], Zhao <i>et al.</i> [2009]
Pasting Properties	Low break-down, final & liquefaction viscosity	Zhao <i>et al.</i> [2009]

Table 2. Ideal Physicochemical Parameters of Starch Recommended for Use as Bioethanol Feedstock.

Identification of genetic factors within wheat cultivars contributing to these parameters is a topic that has received, to date, little attention. Wheat cultivars producing ‘feed class’ grain with high starch content, and thus relatively low protein content, have been highlighted as the preferred ideotype for ethanol production [Sosulski & Sosulski, 1994; Kindred *et al.*, 2008]. High starch, low protein content and high yield are reported as the most critical features of high ethanol producing wheat varieties. However, critical to starch conversion efficiency to fermentable sugars is the solubility of starch during gelatinization and the availability of solubilized material to liquefying enzymes. Therefore, a salient feature in the generation of varieties tailored to the needs of the bioethanol industry includes physicochemical parameters of starch lending themselves to high conversion efficiency under the conditions of liquefaction. High conversion efficiencies of starch to fermentable sugars will result in the greatest quantity of ethanol produced per unit of raw substrate when displayed in grains that exhibit both high yield and high starch content.

7. Future perspectives

Considering the probable economic parity of starch-based ethanol with petroleum, it is still unlikely that starch-based ethanol production has the potential to singularly address long-term, global transportation fuel demand. However, despite the great potential of cellulosic technologies to offset petroleum consumption in the future, cellulosic bioethanol production is not yet competitive with either sugar-cane or starch-based bioethanol production, and it is likely that starch-based bioethanol will continue to be a major source of fuel ethanol. As nations move toward increasing incorporation of bioethanol into their transportation fuel supplies, it is likely that starch-based technologies will play a growing role, at least in the near future, in fulfilling that demand. In countries where wheat is a major agricultural crop, wheat-based bioethanol would benefit from the development of high starch, low protein varieties of wheat with characteristics that are ideally suited for bioethanol production (high amylopectin and low protein content). This would ensure access to stable supply, increase ethanol yields, and thus increase the economic viability of wheat-based bioethanol production.

8. Executive summary

- Biofuels are of growing interest to many governments around the world as there is growing need to develop an energy supply that is local, renewable and independent of a financially volatile and potentially unreliable oil market.
- Cellulose-based (2nd generation) conversion technologies, although possessing tremendous potential to displace the demand for petroleum-derived transportation fuels, remains a nascent industry.
- Starch-based (1st generation) conversion technologies, although contentious in regards to diversion of food crops and land use patterns, are based on a mature industry capable of immediate contribution to pressing global, environmental and energy security needs.
- Recent developments in 1st generation technologies suggest that starch feedstocks are being processed increasingly with no clear understanding of the role starch structure plays on conversion efficiency to ethanol.
- Starch characteristics lending themselves to ease of amylolytic hydrolysis and high conversion efficiencies of starch to fermentable sugars would be desirable as bioethanol feedstock.
- Properties of starch that appear to influence susceptibility to amylolytic attack include: amylose to amylopectin ratio, particle size distribution, amylopectin fine structure, gelatinization and pasting properties.
- High amylopectin content appears to be the most meaningful predictive metric in assessing high conversion efficiency of starch to fermentable sugar.
- Starch with a high proportion of the B-type granule may contain starch that is less resistant to enzymatic hydrolysis.
- Amylopectin side-chain length fractions appear to vary little between wheat cultivars included in this review, making amylopectin fine structure an inappropriate metric for starch assessed as potential bioethanol feedstock.
- Gelatinization temperatures indicating a high quantity of amylopectin, i.e. exhibiting high pasting temperatures (Tp), are likely well suited to bioethanol application as they degrade more completely than high amylose counterparts.

- Pasting properties indicative of high amylopectin content suggest high solubility and low viscosity under the conditions of liquefaction.
- Cereal grain cultivars previously identified as preferred bioethanol feedstock include high starch and low protein content, but should also include, based on the findings of this review, high amylopectin content starch.

9. References

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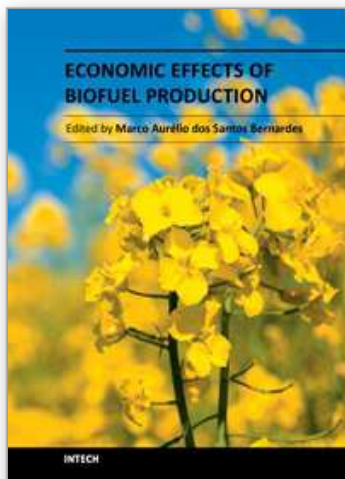
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This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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