The Potential for Production of Bioethanol and Bioplastics from Potato Starch in Colombia

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ABSTRACT

Potato is an important product in Colombian agriculture. About 10% of total production is lost due to partial damages incurred during the processes of harvest, storage and transport, and to imperfections in form, color and size, which are undesirable for the food industry and fresh consumption in the market. On the other hand, the production costs of this crop have been increasing in recent years. The exploitation of remnants of potato crops for the production of bioethanol and bioplastics is therefore a viable solution to address these problems. In this review we assess the situation of potato crop in Colombia, the perspectives of bioethanol as a high-impact product for the economy of our country, and the advantages that potato starch offers in the production of alcohol and other materials, such as bioplastics.

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INTRODUCTION

Starch is the primary energy source of cereal grains and tubers. This polysaccharide has been used for a long time in the production of paper, corrugated board, adhesives, binders and in many processed foods. The use of starch as an ingredient requires that its functional properties match a particular application.

Nowadays, there is great interest in the utilization of starch as a renewable resource in the production of ethanol and plastics. It has been found that starch constitutes a rich resource of fermentable sugars to produce fuel ethanol (Sánchez and Cardona 2008). On the other hand, starch-based plastics have found uses in a variety of ways, such as packing materials, mulch films, and single use articles. The abundance, low cost, easy modification, and renewability of starch have made it an attractive industrial material.

Although corn and cassava are the predominant commercial sources of starch, the high content of this material in potatoes and the actual status of the potato industry in Colombia, have made this tuber a potential raw material of starch in the production of bioethanol and bioplastics in the country.

Bioethanol (ethanol used as fuel) is considered a real

Invited Review

solution to oil and environmental problems. Bioethanol production from potatoes is based on the use of waste potatoes. Waste potatoes are produced in different countries as by-products in potato cultivation. At present, waste potatoes are used as fuel ethanol feedstock in countries like Finland, Austria, USA and China (Vincent 1999; Gapes 2000; Liimatainen *et al.* 2004; Schwartz 2008).

Bioplastics are plastics manufactured from renewable vegetable resources. Among all vegetables, potato starch has several advantages for the production of bioplastics. Potato starch is grown all over the world. Bioplastics are not only a type of high value products from starch, but also constitute promising market for sustainable agriculture and urban waste reduction.

In addition, the spirits industry uses cereal grains as raw material for alcohol production from starch. Other types of starch are available from potatoes of all kinds. Johann Joachim Becher developed a method of producing spirits from potatoes in 1669, but it was not until 1798 that the first instructions for "*A practical new way of distilling vodka from potatoes*" were published (Pochlebkin 1992).

It is important to note that potato productivity is higher in tropical and subtropical countries due to the possibility of having more than one harvest per year. Additionally, the disposal and use of considerable quantity of potato residues are a problem to be solved. For this reason, in this work, the production of bioethanol and bioplastics from potato starch in Colombia is analyzed.

POTATO CROP IN COLOMBIA

Potato is a product that plays an important role in Colombian nutrition due to the historical and cultural features of the region. About 90,000 families are linked with direct exploitation of this crop. It is estimated that, in the entire country, potato crop provides about 84,200 direct jobs (Arias 2008), in addition to other jobs related to distribution, packing, equipments, seed production, processing and commercialization. Furthermore, the potato crop uses most of the services of terrestrial transport, given that more than two million tons are produced per year (Espinal *et al.* 2006).

Data from 2004 reveal that the potato crop in Colombia occupied the fifth position in the national agricultural production with 2.8 million tons. It was the ninth crop in extension with 161,873 ha and the sixth in production value. In constant terms, the production increased at a rate of 0.6% in 1992 and 2004. Colombia occupied position number 18 among the potato producers in the world, even though its participation was very low (0.9%) (Espinal *et al.* 2006).

In Colombia, potato production is well distributed into 14 states or regions (Herrera 2006; CIP 2007). The main producers are in the center and south of the country, which concentrate nearly 80% of production (**Fig. 1**) and 80% of cultivated surface (**Fig. 2**). Commercial production is carried out in zones between 2,000 and 3,000 meters above sea level (m.a.s.l). Ninety percent of production is realized in hillside territories, and 10% in mechanized plane grounds. The sowing time is determined by climatic conditions, especially by rains and temperature changes in the night in Colombia. In general, two harvests of potato are obtained in one year, but depending of the altitude and other microclimatic conditions, the production is continuous all the year in the country.

The guild of potato producers in Colombia is classified into three groups: small, medium and big producers. The categories differ only in cropping technology and farm size. As is shown in **Table 1**, the major production of potato is in small properties. The small producers have limited access to technology and limited financial resources, and as a result the yield per sowed hectare varies throughout the country. Production oscillates between 8.4 ton/ha (South) and 28.9 ton/ha (North east). However, Colombia is the second producer of potatoes in the Andean Community (**Fig. 3**).

It is calculated that in Colombia, 8% of national production is destined to industrial processing (**Fig. 4**). Of this per-
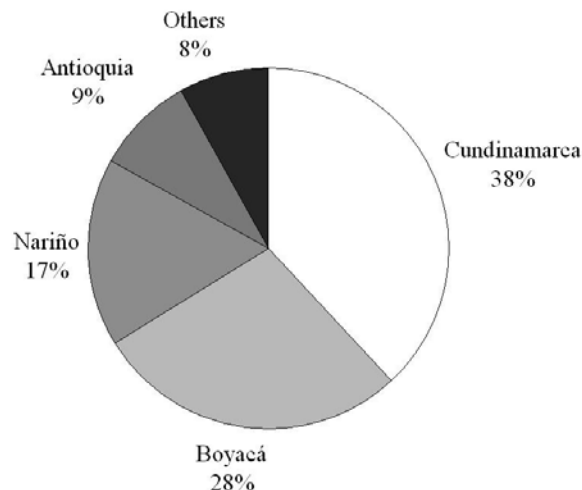

Fig. 1 Contributions of Colombian departments in the national potato production.
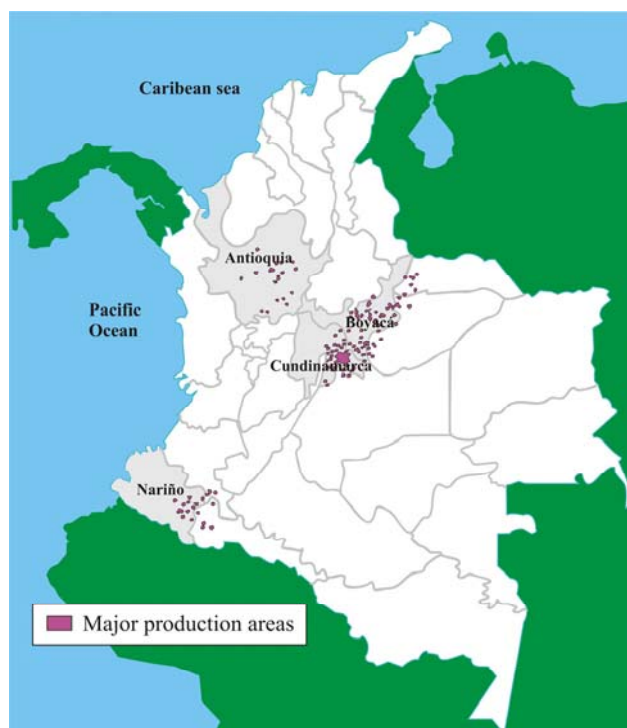

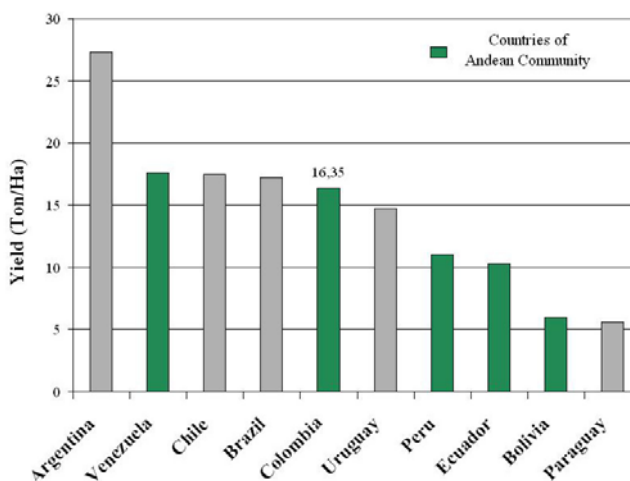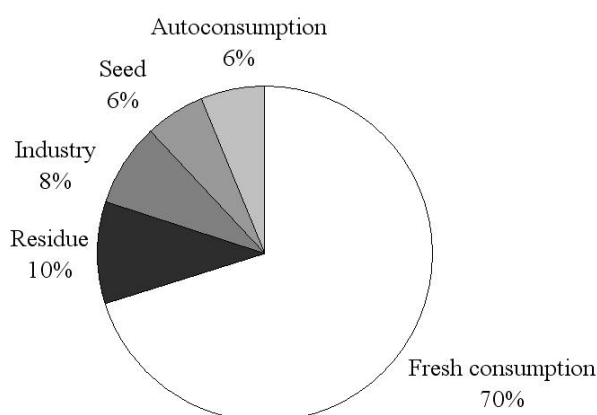**Fig. 2 Main areas of potato production in Colombia.**

Fig. 3 Production yield of potato in Colombia and others countries in Latin America.

Table 1 Classification of potato producers in Colombia.

Producers	Sow area (ha)	Crops features	National cultivators (%)	National production (%)
Small	Less than 3	Land is not suitable for mechanization. Simple technology	90	45
Medium	3 to 10	Semitechnified process	7	35
Big	More than 10	Technified process	3	20

Fig. 4 Destination of annual potato production in Colombia.

centage, 80% is used to produce fried potatoes snacks. The remaining 20% is used mainly in the manufacture of frozen precooked potatoes, while a minimum quantity is utilized in the generation of dehydrated potatoes, flour and starch. On the other hand, 10% of total potato production is rejected due to form and quality restrictions imposed by the food industry and fresh consumption (Espinal *et al.* 2005).

According to statistical analysis, an excess of production about 1% exists in Colombia. This guarantees the self-sufficiency of the country in the supply of potato that it consumes, and in the exportation of the small surplus. During the period between 1991 and 2004, the potato export was 1% of total production, while the incoming imports did not overcome 0.1%.

In absolute terms, the production and consumption of potato in Colombia have been increasing; however, the market for this product has lost dynamism in the last decade. This situation is attributed to the increasing consumption of substitute products, mainly of wheat derivates (pasta) and other market reasons.

BIOETHANOL PRODUCTION FROM POTATO STARCH

Bioethanol

Ethanol is a compound used as fuel for internal combustion engines, either alone or as an additive to gasoline. It can be blended with gasoline in varying quantities to reduce the consumption of petroleum fuels and to diminish air pollution. Ethanol has a higher oxygen content which implies that a small amount is required as an additive. The increased percentage of oxygen allows for better oxidation of gasoline hydrocarbons, with the consequent reduction in the emission of carbon monoxide and other toxic pollution from the tailpipes of vehicles, making the air cleaner. Its use as a fuel has been given much attention mostly because of its pos-

sible environmental and long-term economical advantages over fossil fuel. Ethanol can be obtained synthetically from petroleum feedstock. It can also be obtained via ethene or acetylene, from calcium carbide, coal, oil gas, and other sources. On the other hand, ethanol can be easily obtained from sugar or starch in crops and other agricultural products by fermentation. For this reason, it is considered a renewable resource, and is referred to, in this instance, as bioethanol. Bioethanol can be produced from different natural feedstocks. Scientists are working on cheaper ways of making ethanol by using all parts of plants and trees. Furthermore, wastes from food or beverage processes are used as the feedstock at some ethanol plants. These feedstocks include potato wastes, cheese whey, rice straw, sawdust, urban wastes (Wang *et al.* 2008), paper mill wastes, yard clippings, seaweed, surplus food crops, even bread residues (Ebrahimi *et al.* 2008) and other cellulose waste.

Feedstocks for ethanol production

In general, bioethanol can be obtained from three groups of feedstocks: raw materials containing fermentable sugars, polysaccharides that can be hydrolyzed to obtain sugars convertible into ethanol, and lignocellulosic biomass.

Feedstocks containing fermentable sugars. The materials containing fermentable sugars most frequently used to produce ethanol around the world are sugarcane and sugar beets, because they are rich in sucrose. The sugar cane to produce ethanol is used in form of cane juice or cane molasses (by-product of sugar mills). These materials are the most important feedstocks used in tropical and subtropical countries. The sugar beet is used in the form of beet molasses and is the most utilized in European countries (Cardona and Sánchez 2007). **Table 2** shows some countries where these materials are used as feedstock to produce ethanol. Additionally, sweet sorghum has become a prospective raw material in countries, such as Australia (Nguyen and Prince 1996) and China (Gnansounou *et al.* 2005) because juice with a high sucrose content can be extracted from its stalks. Additionally, its grains contain a high amount of starch and its bagasse can be an important source of lingocellulosic biomass (Winner Network 2002).

The conversion of sucrose into ethanol is easier compared to starchy materials and lignocellulosic biomass because previous hydrolysis of the feedstock is not required since this disaccharide can be broken down by the microorganisms. Moreover, the conditioning of the cane juice or molasses favors the hydrolysis of sucrose (Cardona and Sánchez 2007). The microorganisms more widely used in industrial ethanol production are the yeast *Saccharomyces cerevisiae*, the bacterias *Zymomonas mobilis* and *Scherichia coli*. In the **Table 3**, a resume of advantages and disadvantages of these microorganisms is presented.

Table 2 Utilization of feedstocks containing fermentable sugars in some countries.

Feedstock	Country	Production based on feedstock	Reference
Sugar cane juice	Brazil	79%	Wilkie *et al.* 2000
	Colombia	Main feedstock	Sánchez and Cardona 2008
Sugar cane molasses	Brazil	11%	Wilkie *et al.* 2000
	India	Main feedstock	Ghosh and Ghose 2003
	Thailand	Main feedstock	Thu Lan *et al.* 2008
Sugar beet	France	One of main feedstocks	Poitrat 1999

Table 3 Employed microorganisms in the production of ethanol by fermentation from sugars.

Mircoorganism	Advantages	Disadvantages
Yeast *Saccharomyces cerevisiae* Bacteria	Capability to hydrolyze cane sucrose into glucose and fructose.	Aeration is an important factor for growth and ethanol production.
Zymomonas mobilis	Low energy efficiency resulting in a higher ethanol yield (up to 97% of theoretical maximum) (Sánchez and Cardona 2008).	Range of fermentable substrates is narrow (glucose, fructose and sucrose) (Claassen *et al.* 1999). During the fermentation of sugar cane syrup and other sucrose based media, polysaccharides as levan increase the viscosity of fermentation broth. Sorbitol decreases the efficiency of the conversion of sucrose into ethanol (Lee and Huang 2000).
Escherichia coli	Ability to ferment many different types of sugars especilly pentoses. No requirements for complex growth factors (Lefebvre *et al.* 2008).	Narrow and neutral pH growth range, less hardy cultures compared to yeast, biotoxicity, negative public perceptions regarding the danger of *E. coli* strains (Lefebvre *et al.* 2008).

Starch as a polysaccharide that can be hydrolyzed to obtain sugars. Starch is a high yield feedstock for ethanol production. To produce ethanol from starch, it is necessary to break down the chains of this carbohydrate to obtain glucose syrup, which can be converted into ethanol by yeasts. Traditionally, the break down process, named hydrolysis, was done with acids. At present, enzymes are used, due to their specificity, inherent mild reaction conditions and the absence of secondary reactions. The amylases, such us α-amylase, are the enzymes generally used for this first step of hydrolysis of the starch suspensions. It is obtained from thermoresistant bacteria, like *Bacillus licheniformis* or from engineered strains of *Escherichia coli* or *Bacillus subtilis*. Corn and wheat starch are the feedstock most utilized for ethanol production in North America and Europe. In tropical countries, other starchy crops, such as tubers (e.g. cassava), are used for the commercial production of fuel ethanol (Cardona and Sánchez 2007).

Corn is milled to extract starch. This starch is enzymetically treated for obtaining glucose syrup which is then fermented into ethanol. The two types of corn milling used in the industry are wet and dry. During the wet-milling process, corn grain is separated into its components. The produced starch is converted into ethanol and the remaining components, such as corn oil, animal feed, and starch, are sold as co-products. At dry-milling plants, grains are not fractionated. All their nutrients are fed to the process and they are concentrated during the distillation as a co-product utilized for the animal feed. In general, the other steps of process are the same for both technologies. Fermentation is performed using *S. cerevisiae*. *Z. mobilis* also has been researched for ethanol production from dry-milled corn starch (Krishnan *et al.* 1999).

Wheat is used as feedstock to produce bioethanol in some countries, like France (Sánchez and Cardona 2008) and Australia (Moghtaderi *et al.* 2006). Studies carried out in England show that wheat could compete with conventional fermentation feedstocks, such as sugar and starch derivates, in terms of profitability to produce many chemical products, including bioethanol (Koutinas *et al.* 2004). The process with wheat is similar to that of corn, and some efforts have been directed to optimizing fermentation conditions (Wang *et al.* 1999; Soni *et al.* 2003).

Cassava represents another important alternative source of starch. Cassava has gained interest due to its availability in tropical countries. The tuber is one of the top ten important tropical crops. Ethanol production from cassava can be accomplished using either the whole cassava tuber or the starch extracted from the tuber. Starch extraction can be carried out through a high-yield, large-volume industrialized process or by a traditional process for small- and mid-scale plants (Sánchez and Cardona 2008). The production of cassava with high starch content (85–90% dry matter) is relatively simple. The hydrolysis of cassava flour has been proposed for the production of glucose (López-Ulibarri and Hall 1997), considering that cassava flour production is more simple and economic than cassava starch production.

However, it is considered that cassava ethanol could have better economic indicators if the whole tuber is used as feedstock, especially when small producers are involved. Fuel ethanol production from whole cassava is equivalent to ethanol production from corn using dry-milling technology.

Another crop for fuel ethanol production is the sweet sorghum, which produces grains with high starch content, stalks with high sucrose content and leaves and bagasse with high lignocellulosic content. This crop can be cultivated in both temperate and tropical countries and requires only one third of the water needed for cane cropping and half of the water required by corn (Winner Network 2002).

Bioethanol can be produced from rye, barley, triticale (Wang *et al.* 1997), and sorghum (Zhan *et al.* 2003). In addition, the production of ethanol from bananas and banana wastes (Hammond *et al.* 1996), and from sago palm (Abd-Aziz 2002) has been suggested.

Lignocellulosic materials. Lignocellulosic biomass is a complex comprised of several polysaccharides. This complex is the most abundant biopolymer in the Earth and comprises about 50% of world biomass. Its annual production was estimated between 10 and 50 billion tons (Claassen *et al.* 1999). Many lignocellulosic materials have been proposed and tested for bioethanol production. According to Sánchez and Cardona (2008), the lignocellulosic materials for fuel production can generally be divided in six main groups: crop residues, hardwood, softwood, cellulose wastes, herbaceous biomass and municipal solid wastes (MSW). The crop residues that have been tested include, cane bagasse, wheat straw, rice straw, rice hulls, barley straw, sweet sorghum bagasse, olive stones and pulp. Among the hardwoods are aspen and poplar, and among softwoods are pine and spruce. The cellulose wastes tested are newsprint, waste office paper and recycled paper sludge. Among herbaceous biomass used are alfalfa hay, switchgrass, reed canary grass, coastal Bermuda grass and Timothy grass.

Lignocellulosic biomass is regarded as the most promising feedstock because of its great availability, non food competition and low cost. However, the main limiting factor of this alternative is the pretreatment step of the feedstock. Due to the structure of the lignocellulosic complex, two of the main polymers of the biomass should be broken down into fermentable sugars to be converted into ethanol or other valuable products. Overall, fuel ethanol production from lignocellulosic biomass includes five main steps: biomass pretreatment, cellulose hydrolysis, fermentation of hexoses, separation and effluent treatment.

The solution obtained from the degraded cellulose and hemicellulose fractions consists mainly of hexoses and pentoses. *Saccharomyces cerevisiae* and *Zymomonas mobilis* do not metabolize pentoses, which may constitute 8-28% of the raw material. Strains of recombinant *Escherichia coli*, such as KO11, have been developed in order to ferment pentoses with high yield and productivity of ethanol (Von Sivers *et al.* 1994). Recently, one method was patented for producing fuel-grade ethanol from cellulosic biomass using
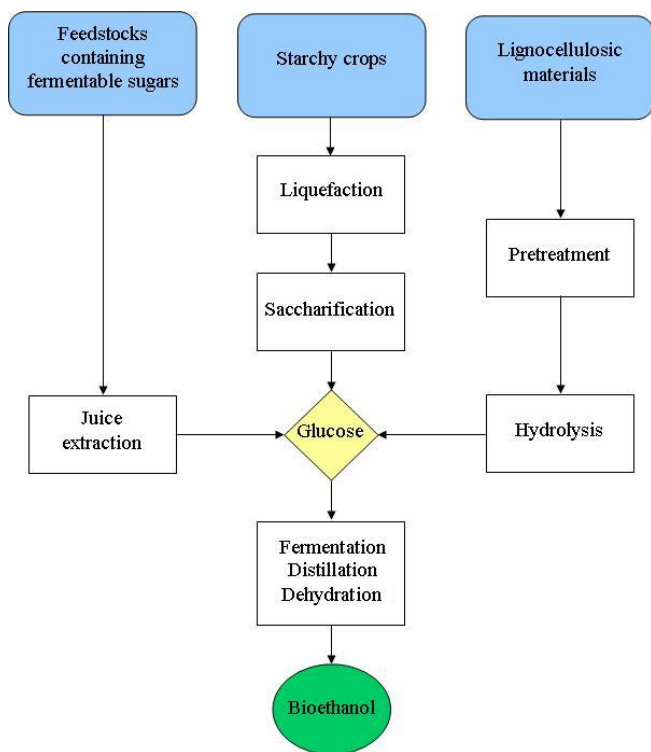
Fig. 5 Block diagram of ethanol production from sugars, starch and lignocellulosic materials.

E. coli FBR5. This strain can ferment and grow on both pentose and hexose sugars, and is resistant to ethanol and furfural. This last compound is one major inhibitory toxin produced during the dilute-acid pretreatment employed to release usable sugars from the hemicellulose (Lefebvre *et al.* 2008).

The process for obtaining ethanol from lignocellulosic materials is complex and costly and is still currently in the research and development stage. In recent years, pilot plants have proven the technical feasibility. Several North American companies have considered building factories that would convert cellulose from organic plant wastes into ethanol, but the large-scale commercial production has still not been implemented.

However, many lignocellulosic materials are by-products of agricultural activities, industrial residues or domestic wastes, and offer large possibilities for the production of bioethanol as renewable fuel. In countries where the cultivation of energy crops is difficult, lignocellulosic materials could be an attractive option for the production of bioethanol. **Fig. 5** summarizes the processes involved in ethanol production from the three different types of feedstocks.

Ethanol production from potato in the world

Due to high content of starch in potato and to the high production of this tuber in some countries, the use of this product as feedstock to produce bioethanol is an alternative that has been proposed in some places of the world. However, there is not much available information related to the process, and only in a few regions some investigations have been initiated, and the operation started.

To avoid a conflict between the demand of potato for food and for alcohol, the bioethanol production from this crop is based on the utilization of waste potatoes. For example, in Finland one plant uses 1.5 million kg of waste potatoes per year, produced from 5 to 20% of crops as by-products in potato cultivation, as feedstock to obtain ethanol (Liimatainen *et al.* 2004).

In bioethanol production, firstly the potato is ground into small particles and then is heated. The pH is adjusted between 4.2 and 4.5. This slurry is treated with enzymes for starch hydrolysis. Starch is initially reduced to dextrins (liquefaction) and the mash is cooled and treated with a second enzyme to reduce the dextrines to sugar (saccharification). After the sugars are obtained, they undergo fermentation to obtain the ethanol by means of microorganisms such as *Saccharomyces cerevisiae.* The alcohol is distilled and dehydrated (Liimatainen *et al.* 2004). In addition, the byproducts are further processed to reduce the water content and are sold as animal feed. **Fig. 6** is a general flowsheet of bioethanol process production from potato.

On the other hand, in some countries, like Canada, large volumes of starchy feedstock consisting of potato waste formed from processing plants offer an important renewable biomass resource to produce bioethanol. For example, 44.000 tons (dry weight) of processing waste per year from all the processors of the potato region of New Brunswick are potentially convertible by fermentation into 4–5 million liters of ethanol (Kettle 2008). The J. R. Simplot Company has fermented potato waste into fuel grade ethanol at two plants in Idaho for many years. These plants are small, and their design is similar to that of sweet potatoes ethanol plants. However, potato wastes contain less fiber, which would likely necessitate the use of less enzymes quantity (Warren 2008).

In general, the ethanol yield is a function of the starch content of the feedstock used in ethanol production. Depending on the potatoes varieties, starch contents can vary from 11.2% to over 19.3% (Liimatainen *et al.* 2004). For this reason, alcohol yields vary significantly between zones. For example, in Finland, among ten potato varieties analyzed, the highest alcohol yield was 0.095 kg/kg, and the lowest yield was 0.065 kg/kg. The average alcohol yield was 0.076 kg/kg (Liimatainen *et al.* 2004). On the other hand, the yield is greater for potatoes that are processed with peel. The varieties of potato having very high content of dry matter appear most desirable for ethanol fermentation, since less fresh sweet potato is needed for a fixed amount of ethanol production (Wu and Bagby 1987).

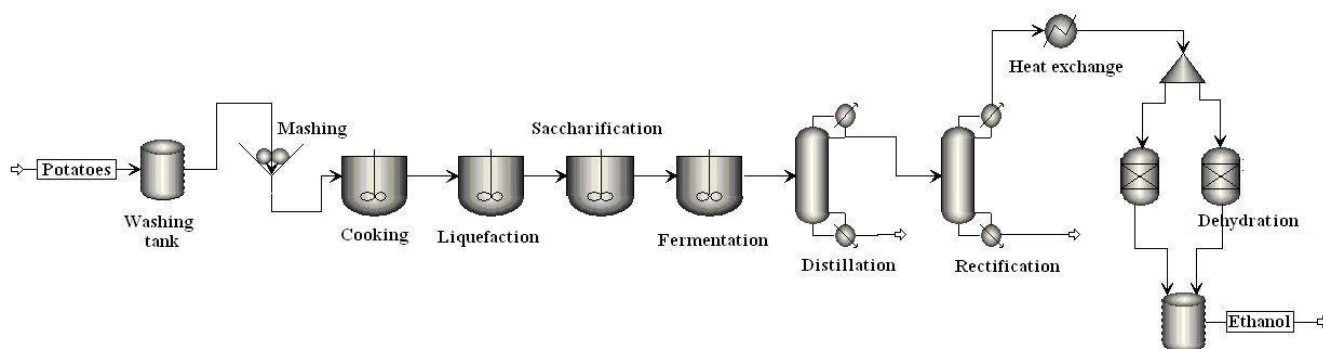If the yield of ethanol production from different crops is

Fig. 6 General flowsheet for bioethanol production from potato.

Table 4 Yield of ethanol from different starchy materials.

	Dry matter (%)	Ethanol yield (L/kg $_{dry\ mass}$)	Reference
Barley	88.7	0.41	Kim and Dale 2004
Barley straw	81.0	0.31	
Corn	86.2	0.46	
Corn storver	78.5	0.29	
Oat	89.1	0.41	
Oat straw	90.1	0.26	
Rice	88.6	0.48	
Rice straw	88.0	0.28	
Sorghum	89.0	0.44	
Sorghum straw	88.0	0.27	
Wheat	89.1	0.40	
Whear straw	90.1	0.29	
Sugarcane	26.0	0.50	
Baggase	71.0	0.28	
Potato	24.7	0.34 (0.083[♦])	Del Valle 2008;
Potato waste		(0.042[♦])	Warren 2008

[♦] wet base

compared, potato yields the less (**Table 4**). However, the potato commonly used for ethanol production comes from remnants of crops, which practically is considered a residue. Comparison of these yields with the ones obtained with other starchy residues show higher quantity of ethanol per kilogram of dry material. **Table 5** summarizes some data reported in literature for yield of ethanol production from the potato crop.

In the commercial processes, the starch is hydrolyzed to glucose by thermophilic enzymes. Commercial amylases (frequently produced by *Aspergillus* species) are used for liquefaction and saccharification of starch and represent a significant expense in the production of fuel alcohol from starchy materials. Some studies have been carried out to on the elimination of enzymatic liquefaction and saccharification steps by using symbiotic coculture of amylolytic and sugar fermenting organisms. For example, Abouzied and Reddy (1986, 1987) studied the elimination of enzyme hydrolysis step in order to reduce some operation cost of the ethanol production process. They proposed and analyzed a single-step process for enhanced fermentation of unhydrolyzed potato starch to ethanol using a coculture of *Saccharomycopsis fibuligera*, *Lipomyces kononenkoae*, or *Aspergillus niger*, which hydrolyze starch to glucose, and *Saccahromyces cerevisiae*, which ferments glucose to ethanol. The results of the investigation show that the efficiency of starch conversion to ethanol could be more than 90% of the theoretical maximum. Thus, the use of this combination of organisms allows elimination of the enzymatic starch hydrolysis step, which could improve the economy of starch fermentation to ethanol.

Likewise, ethanologenic strains of *Escherichia coli* have been developed which can express thermostable enzymes for starch saccharification. These enzymes can be harvested within cells at the end of fermentation and liberated by heating to the temperature at which they exhibit maximal activity (60-70°C). Organisms such as these could be used to supply enzymes for yeast-based fermentations while producing ethanol as a co-product (Guimaraes *et al.* 1992). Other studies have investigated genetic approaches to simplify the hydrolysis process by the addition of starch degrading genes to *Saccharomyces cerevisiae* (Ruohonen *et al.* 1991). Also, strains of recombinant *Zymomonas mobilis*, such as 8b and AX101, have been developed to converting effectively the sucrose, fructose and glucose contained in

pretreated sweet potato (Karim and Han 2007).

Ethanol production in Colombia

Although Colombia is a country with oil reserves, these are being depleted. For this reason, and due to environmental considerations, Colombia has decided to replace part of the fossil fuels with alternative energy resources. The production and use of liquid biofuels (bioethanol and biodiesel) is a strategy adopted by the Colombian goverment to decrease the oil dependence and reduce the polluting gases released by the transportation sector in the country's cities. Moreover, it is expected that the implementation of biofuels programs will allow for the development of the rural sector (Quintero *et al.* 2008).

Ethanol production and use as fuel recently started in Colombia. The Congress of Colombia issued the Law 693 of 2001 (named E10 Program), where it is established that gasoline used in urban centers with more than 500.000 habitants should be oxygenated with 10% of ethanol (gasohol). Thus, in November 2005, the gasohol use started in the capital of Colombia, Bogotá, and in the centre of country in February 2006. Eventually, the use of ethanol-gasoline blends will be extended to the whole nation.

The amount of fuel ethanol required for zones where the Law is being implemented is about 1,200.000 L/day. The expansion of the program to the rest of the country will require a total ethanol production of almost 2,500.000 L/day. If Colombia becomes an ethanol exporting country, it is estimated that 3,800.000 L/day of bioethanol should be produced to meet the national demand and export the surplus (Quintero *et al.* 2008).

The implementation of the E10 programs depends on technological limitation and availability of the feedstock. For this reason, in Colombia the bioethanol production started using sugar cane as feedstock (**Table 6**), and currently the viability to use other feedstocks is being investigated.

Investigations of Colombian Agricultural and Rural Development Department presented information about the annual yield of ethanol per hectare of crop and energetic efficiency for different analyzed feedstocks (Arias 2007). **Table 7** indicates that the crop most suitable for ethanol production, according to yield, is sugar cane, followed by

Table 6 Plants producing ethanol in Colombia.

Investors	Installed capacity (L/year)	Consumption of feedstock (ton/year)	Planted area (ha)
Incauca	97.200.000	97.690	10.781
Providencia	81.000.000	81.408	8.984
Manuelita	81.000.000	81.408	8.984
Mayagüez	48.600.000	48.845	5.390
Risarald a	32.400.000	32.563	3.593

Actually, plants operate at 86% of their installed capacity, and use sugar cane as feedstock.

Table 7 Profits in agricultural jobs.

Crop	Annual yield (L/ha)	Jobs $_{Agric + Ind}$/ ha year	Energetic efficiency (Energy $_{produced}$/ Energy $_{consumed}$)
Sugar cane	9.000	0.18	8.3
Cassava	4.500	0.60	1.2
Sugar beet	5.000	0.65	1.5
Sugar sorghum	4.400	0.20	2.9
Corn	3.200	0.41	1.7

Table 5 Process data for ethanol production from potato.

		Reference
Yield of crop	9350 L $_{ethanol}$/ha	Wu and Bagby 1987
Ethanol yield for the global process	0.0746 kg$_{ethanol}$/kg$_{potato\ with\ peel}$	González and Molina 2006
Max. ethanol concentration (industrial scale)	7-8% (v/v)	Araya 1998

Table 8 Producer plants of ethanol in feasibility.

Investors	Feedstock	Installed capacity (L/year)	Consumption of feedstock (ton/year)	Planted area (ha)
Petrotesting	Fresh cassava	6.800.000	36.757	1.470
Ingenio Sincarare	Fresh cassava	9.345.000	51.000	2.040
	Sugar cane	16.000.000	27.397	2.000
Finagro - MADR	Fresh cassava	34.000.000	209.877	8.395

sugar beet and cassava. Given the existence of abundant cassava crops in the country, and the location of new producer plants of ethanol, the installation of new plants that use as feedstock fresh cassava has been started (**Table 8**).

However, it is feared that demand of agricultural products for fuels may eventually be higher than the food demand, resulting in a shortage in alimentary sector. When the competition for both uses exists, the price of agricultural products can be unexpectedly increased. For this reason, other alternative feedstocks that allow the release of the agricultural products for food are searched.

Use of potato as feedstock to produce ethanol

In Colombia, the profitability of potato crop has diminished in recent years. The costs of this crop have increased due to many factors such as:
- Increase of the price for some inputs,
- Introduction of more demanding varieties to manage in the plagues and diseases,
- Insufficient technical assistance, which causes an excessive use of fertilizers, fungicides, pesticides, herbicides and other inputs,
- Lack of technology and infrastructure to implement irrigation systems,
- Deficiency of technology and infrastructure for storage,
- High dependency on an intermediary for commercialization of product,
- Deficiency in systems of marketing and merchandising, and
- Little added value of the product.

In an attempt to alleviate these problems, the state and private entities stepped in to improve the commercialization channels for supplying fertilizers, fungicides and adhesives and to minimize the number of intermediaries and lower inputs prices. Likewise, the technical training of farmers on the cultivation process, use of certified seeds, control of plagues and diseases, and harvest, was established. Some public and private entities, like Universidad Nacional de Colombia, Colombian Corporation of Agriculture Research (CORPOICA) and Colombian Agriculture Department advanced projects aimed at the production and multiplication of certified seeds, with which the actual yields could be doubled, from 16 or 20 ton/ha to about 35 or 40 ton/ha (Espinal *et al.* 2006).

On the other hand, except for some potato varieties produced in Colombia, most potato varieties contain high levels of reducer sugars, low percentage of dry material, and undesirable color of pulp and peel for the industrial processing of foods. However, the processing food companies reject potato for quality defects, in the order of form, use of second packing, deep holes, cuts, turn green and size, among others. It is estimated that on the average 10% of reaped potato is rejected for cuts produced by spade during the harvest. According to data of 1998, net exploitation level of potato in the food industry (chips and French fries) was between 36 and 45%, depending on the species used. For each kilogram of potato to be processed, the final product weighs at the most 450 grams, and the remainder constitutes wastes (water, solid residues, peel, etc.) (Espinal *et al.* 2005). For these reasons, the exploitation of this potential waste of potato varieties produced in the country has motivated its use in several industrial applications (Del Valle 2008). Then, among other options, the development of

technologies for the processing of potato was proposed to use it as feedstock in ethanol production. In Colombia, the process of obtaining ethanol from potato is established as an alternative in which inappropriate species for the food industry and production remnants are used to find solution to an environmental, economic and social problem.

Ethanol production from potato in Colombia

In Colombia, as other countries, part of potato crop production is not consumed in its totality by the food processor industry and customers of the fresh product. It is due to factors previously described, which in brief are: partial damage by plagues, poor harvest practices, damages incurred during processes of storage and transfer to storing centers or markets, and imperfections in form, color and size. It is estimated that these losses correspond to more than 10% of production. Such remnants are generally destined for self-consumption by most poor families of farmers, for animal food, and in the worst case, are rejected.

As an alternative to this economic and environmental problem, the exploitation of remnants of potato crops was established for the generation of an added value product, such as alcohol. Due to its starch content, this tuber is considered a potential source of polysaccharides, and as feedstock for obtaining ethanol in Colombia. **Table 9** gives the average composition of potatoes in Colombia reported by Del Valle (2008).

Potato production in Colombia is about 2.8 million of tons per year in a planted area approximately of 160.000 ha. More than 10% of this production is discriminated due to consumption specifications for food showing that, almost 280,000 ton of potato could be used as feedstock for ethanol production. According to data referenced above, 24.7% is dry material; then 69,160 tons of dry material could be obtained. Assuming a yield of 0.34 liters of ethanol per kilogram of dry material, 23,000,000 liters of ethanol could be obtained per year. This productivity is comparable to the one that is provided by new bioethanol plants being actually under construction in the country.

The location of a proposed plant could be fixed in Nariño, Cundinamarca or Boyacá Departments, due to higher productivity of the crop and to the actual absence of projects of ethanol production in these regions. The decision depends on many factors, which must be balanced in an optimal point:
- Region with major quantity of remnants.
- Region with easier accessibility from the rest of the country to economically collect and transport the raw materials.
- Region of major coverage for ethanol commercializa-

Table 9 Average composition of crude potato (Del Valle 2008).

Component	Content (%)
Moisture	75.3
Proteins	2.47
Fat	0.28
Fiber	0.53
Ash	1.37
From 100% of dry material:	
Starch	60 – 85
Sugars	0.5 – 1.8
Citric acid	0.5 – 0.7

tion.
- Region, where the installation of a plant for fuel ethanol production has priority due to social considerations.

Independent on the selected region, the installation of a plant to produce ethanol from potato crop remnants in Colombia, would promote the economic and social developments of all regions that produce the crop. When an added value is given to potato, it contributes to farmers revenues. In addition, an environmental problem could be solved when a correct disposition of "crops residues" is found. At long term, the potential crop areas could be exploited as reserve when the quantity of generated remnants varies notoriously.

BIOPLASTICS PRODUCTION FROM POTATO STARCH

There is an increased interest in the utilization of renewable resources for the preparation of alternative materials to conventional petroleum-based plastics that would combine renewability and biodegradability with the functionality of petroleum-based plastics. Biodegradable materials, including bioplastics may be grouped as follows: natural biodegradable polymers or biopolymers (starch, cellulose, chitin and chitosan, alginic acid, polypeptides of natural origin and bacterial polyesters), polymers with hydrolyzable backbones susceptible to biodegradation (e.g. polyesters and polycaprolactone) and polymers with carbon backbones (e.g., vinyl polymers) that require an oxidation process for biodegradation. In the category of biobased biodegradable materials suitable for production of biodegradable films can be include these main categories: cellulose-based films, starch-based polymers, polyhydroxybutyrate polymers, and polylactides (Briassoulis 2004).

Starch

The storage of carbohydrates in plants is starch. It occurs in most higher plant species in the form of roughly spherical granules consisting of about 77% of starch and 1% of other dry matter (lipids, proteins, minerals); the remainder of the mass being water. The moisture content of air-equilibrated starches ranges from about 10–12% (cereal) to about 14–18% (some roots and tubers). Most natural starches are composed of at least two types of alphaglucan, amylose and amylopectin, which represent approximately 98–99% of the dry weight. The 'waxy' starches contain less than 15% amylose, 'normal' 20–35% and 'high' (amylo-) amylose starches greater than about 40% (Tester *et al.* 2004; Thunwall *et al.* 2006). Amylose is a linear polymer with α-1,4 linkages between the anhydroglucose units, and its molecular mass is typically in the range of 10^5–10^6 g/mol. Amylopectin is an extensively branched polymer. It has a backbone structure of α-1,4 linkages between the anhydroglucose units with branching at the α-1,6 position. Some of these characteristics (Lui *et al.* 2002) are shown in the **Table 10**.

Starch properties depend on the physical and chemical characteristics, such as mean granule size, granule size distribution, amylose/amylopectin ratio and mineral content (Kaur *et al.* 2007). Average molecular weights of 2×10^6 g/mol and 20×10^6 g/mol, determined by light scattering, have been reported for amylose extracted from maize and potato, respectively and correspondingly. Values of $112 \times$

10^6 g/mol and 61×10^6 g/mol have been reported to amylopectin of maize and potato, respectively (Aberle *et al.* 1994). Starch granule size varies from source to source (e.g., average diameters, rice: 3 μm, potato: 35 μm, corn 10 μm) (Briassoulis 2004; Kaur *et al.* 2007).

Cereal starches produce an A-crystalline pattern (monoclinic lattice) with densely packed double helices in the unit cell. B-type polymorph appears mostly in potato and other tuber starches (hexagonal lattice), in which the double helices packed in parallel fashion are combined with structured water. C-type patterns occur in certain legume starches and is thought to be an intermediate structure between the A- and B-types (Thiré *et al.* 2003). The original structure can be disrupted by heating and shearing giving a thermoplastic material. This can be accomplished with a conventional extruder or by gel casting into films (Rindlav-Westling *et al.* 1998).

Biodegradable plastics in the world

The biodegradability of organic substances is the degree of the changes in physical and chemical characteristics and molecular structure of organic substances under degradation by natural microorganism over a period of time. Biodegradability is tied to a specific environment. For instance, the usual biodegradation time requirement for bioplastics to be composted is 1 to 6 months (Mohee and Unmar 2007). There are currently few international standards for compostability and biodegradability (ASTM-6400-99, EN13432, ISO14855, DIN V49000 and DIN V 54900).

The no degradable plastic waste fouling the environment is stimulating a rising demand for degradable plastics. Cellulose, starch, polylactic acid (PLA), microbial polyhydroxyalkanoates (PHAs) and polyamide 11 (PA11) are the most common types of bioplastics. From them, starch and PLA based materials can be found in potato and potato wastes. Baked starch foams have recently been intensely explored for use in disposable single-use packaging items. Increasing amylase content and starch concentration can be obtained denser, stronger but low flexible foams. Flexibility can be improved with the addition of softwood pulp fiber or $CaCO_3$ to the formulation. Baked starch foam properties were further improved with chemically modified starches and additives such as aspen fiber and monostearyl citrate. To overcome the effect of higher humidity on the foam products natural rubber latex could be used in the batter formulation (Shey *et al.* 2006). Polylactic acid (PLA) is aliphatic polyester made up of lactic acid (2-hydroxy propionic acid). This monomer and the biopolymer can be produced by fermentation of starch. PLA is a thermoplastic with high mechanical strength, thermal plasticity, biodegradability, and biocompatibility. Historically, the uses of PLA have been mainly limited to biomedical areas due to its friendly adsorption characteristics. Over the past decade, the discovery of new polymerization routes which allow the economical production of high molecular weight PLA, along with the elevated environmental public requirements, have resulted in an expanded use of PLA for use in service ware; grocery, waste, and composting bags, mulch films, and controlled release matrices for fertilizers and pesticides (Guan *et al.* 2005; Lim *et al.* 2008).

Microbial polyhydroxyalkanoates (PHAs) have attracted research and commercial interests worldwide because they can be used as biodegradable thermoplastics and also because they can be produced from renewable resources. Several types of PHAs have been identified to possess commercial value, i.e., poly(3-hydroxybutyrate) [P(3HB)], poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate [P(3HB-*co*-3HV)] PHBV, poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate [P(3HB-*co*-4HB)] and poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate [P(3HB-*co*-3HHx)] (Carole *et al.* 2004; Loo and Sudesh 2007).

The current production capacity for biodegradable materials globally is currently around 300,000 tons. The majority of plants entered in force since the year 2000. Cargill

Table 10 Some characteristics of amylose and amylopectin from potato and maize.

| | Amylose | | Amylopectin |
	Potato	Maize	Maize
Iodine binding capacity (g/100 g)	20.5	20.0	1.25
β-amylolysis (%)	80	84	60
DPW (Range)	840 - 21800	580 - 22400	--

DPW: Degree of polymerization by weight.

Dow LLC's polylactide (PLA) polymer, also known as NatureWorks, with a production of 140,000 tons per year, is the world's largest bioplastics producer. Other smaller producers come from countries such as Japan (10,000 tons per year) and China. The Italian company Novamont has been manufacturing materials based on complexing plant starch and biodegradable polyester (Mater-Bi®, 20,000 tons per year). Stanelco (UK) and its subsidiary, Biotec (Germany), also produce starch based bioplastics (Bioplast, 7500 tons per year). Germany. BASF's most important producer of biodegradable synthetic polymers – BSP – expanded its capacities in 2006 by a further 6,000 tons to 14,000 tons annual production. This company also produces thermoplastic starch, PLA and BDP blends (Ecoflex and Ecovio). BASF announced the construction of a new production facility in Ludwigshafen. Starting in 2010, this facility will take up the production of the biodegradable material 'Ecoflex' with an annual capacity of 60,000 tons. This step will increase the 'Ecoflex' production capacity from presently 14,000 to 74,000 tons per year. Various PHA type biobased polyester manufacturers are planning on establishing production capacity in the coming three to five years. In this time frame, DuPont and Tate & Lyle will also commence producing a polyester which consists of up to approx. 40% from 1,3-Propanediol (PDO), and is biotechnologically produced (50,000 tons capacity). Pyramid Bioplastics, a partnership of Pyramid Technologies Ltd., Switzerland, and German Bioplastics GmbH, is establishing a production facility in Guben (Brandenburg) for the production of PLA (polylactic acid) with a capacity of 60,000 tons annually (Japan Echo 2003; Novamont 2007; Bio-Polym Blog 2008; European Bioplastics 2008; Plantic 2008; Stanelco 2008).

## Plastification and gelatinization

The plastification process is the disruption of granular starch, which involves the transformation of the semicrystalline granule into a homogeneous, rather amorphous material by the destruction of hydrogen bonds between starch molecules. The process occurs synchronously with the formation of hydrogen bonds between the plasticizer and starch molecules (Yang *et al.* 2006). Disruption can be accomplished by the presence of an appropriate plasticizer and the application of thermomechanical energy in a continuous process. The combination of thermal and mechanical inputs is obtained by extrusion, injection-molding or casting techniques. Then, under temperature and shearing, starch is plasticized. After processing, a homogeneous molten phase is obtained. Swelling is accompanied by disruption of the native crystalline structure and solubilization of amylose. This phenomenon is known as gelatinization.

Several methods have been used to gain new insights into the physics of gelatinization. They include viscosity measurements, optical microscopy, electron microscopy, differential scanning calorimetry (DSC), X-ray diffraction, nuclear magnetic resonance spectroscopy (NMR) and Fourier transformed infrared spectroscopy (FTIR). The calorimetry technique is associated with both first order (melting) and second-order (glass) transitions. X-ray diffraction has been used to study starch crystallinity and to characterize the transition in starch gelatinization. The IR spectrum of starch has been shown to be sensitive to changes in molecular structure, such as starch chain conformation, helicity, crystallinity, retrogradation process and moisture content. FTIR is limited to study starch–water systems only at low starch contents (Lui *et al.* 2002). **Fig. 7** shows FTIR spectra of native and plasticized potato starch films.

Advantages and drawbacks of starch films

The starch films exhibit good mechanical properties and are excellent oxygen barriers. Their water vapour permeability has been reported to be high, and is explained by the hydrophilic nature of starch.

The attractive film properties are attributed mainly to
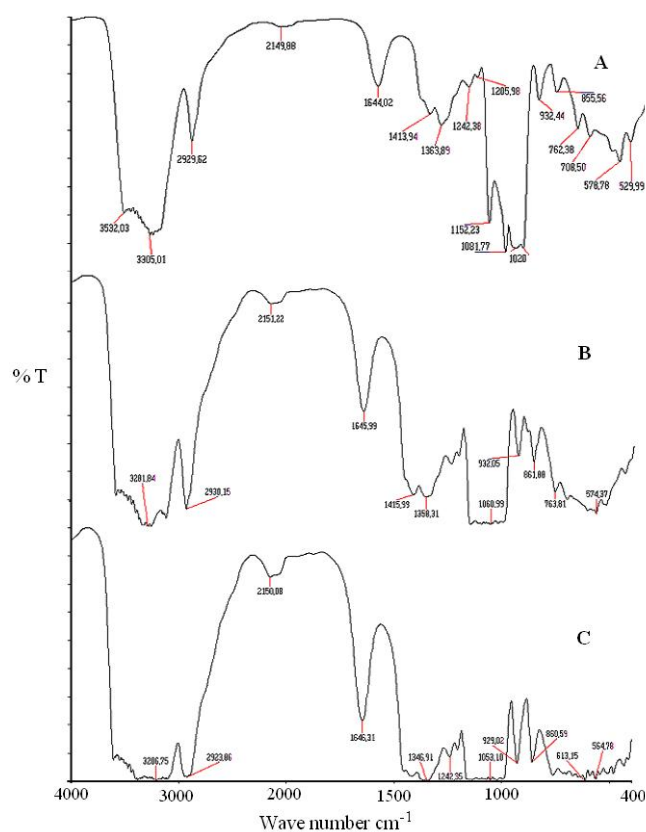
Fig. 7 FTIR spectra of starch films. (**A**) Potato starch. (**B**) Potato starch with sorbitol. (**C**) Potato starch with glycerol. The peak at 1020 cm^{-1} is assigned to the vibration of C–O–H deformation and is related to changes in the amorphous and crystalline parts of the granule (Lui *et al.* 2002). Another characteristic band was observed between 3305 and 3532 cm^{-1}. It was assigned to the hydroxyl group stretching vibrations. The characteristic peak 1082 and 1152 cm^{-1} (**Fig. 7A**) was ascribed to C–O bond stretching of C–O–H group. The intensity at 1640 cm^{-1} corresponds to the vibration of O–H stretching in starch and absorbed water. This is because H bonds and hydrophobic bonds may be affected at this temperature (Yang *et al.* 2006).

the amylase present in starch, rather than the amylopectin (Bengtsson *et al.* 2003). A major drawback of starch however is its high hygroscopicity and its sensitivity as a mechanical and barrier material to water or moisture. This hydrophilic nature of starch is a major constraint that seriously limits the development of starch-based materials. In fact, such products are highly water-sensitive, and their properties depend on the ambient humidity. Moreover, the ageing of hydrophilic polymers causes cracks at low and high partial water vapor pressures. Except for the lower water content, ageing can be explained by molecular motion enhanced with sorbed water. Induced macromolecular reorganization in a phenomena called crystallization or retrogradation at temperatures above glass transition and/or physical ageing by densification of microdomains below this temperature (Delville *et al.* 2002). The mechanical properties of starch in mean ambient humidity, particularly poor elongation (6%) and high maximal strength (40 MPa), are indicative of a vitreous material with glass transition temperature above ambient temperature (Lourdin *et al.* 1997).

Plasticizers

The glass transition temperature of amorphous starch can be controlled by adding a plasticizer (Lourdin *et al.* 1997). Traditional plasticizers are polyols, such as glycerol, glycol, xylitol, sorbitol, and sugars. Some small molecules containing –CO–NH– functional group, like urea, also proved to be a plasticizer for the native starch. Recently, formamide or formamide/urea and ethylene formamide could also plasticize starch (Yang *et al.* 2006). For plasticized (glycerol)

films, however, the tensile strength increases with amylose content, while elongation decreases. The mechanical properties stay unchanged above an amylose content of about 30–40%. The amylose/amylopectin ratio affects the morphology of the formed films: higher amylose content leads to a more homogeneous film, and a higher amylopectin content increases phase separation (Rindlav-Westling *et al.* 1998). Glycerol and sorbitol are the excipients most widely studied. At low plasticizer content, the plasticizer (glycerol or sorbitol) does not have the classical effect of elongating starch films. This phenomenon, well known from synthetic polymer science, is called the antiplasticization effect. The elongation starts to increase, with higher plasticizer contents that approximately reach 15% for glycerol and 27% for sorbitol. The tensile strength of starch films decreases continuously with the increase of plasticizer content (Lourdin *et al.* 1997).

Modified starches

Chemical derivatization has long been studied to produce waterproof materials. The main aim is to produce fully biodegradable thermoplastic materials. The control of the gel formation is a key factor in starch functionality, and is achieved mainly by chemical modification when starch is in a granular state. Crosslinking glucan chains within the granule restrict swelling, whereas the addition of charged groups to the chains stabilises gel formation. Starches that are modified in this way become tolerant of extremes of heat and cold and of high or low levels of pH, and thus, can be used in a wide variety of processing conditions.

The properties of some modified starches and their applications are noted as follows (Singh *et al.* 2007):

- *Partial pregelatinization by acid or enzymatic hydrolysis*: Cold water dispersibility, reduced molecular weight of polymers, increased retrogradation and setback.
- *Oxidation/bleaching:* Low viscosity, high clarity, and low temperature stability.
- *Pyroconversion (dextrinization)*: Low to high solubility depending on conversion, low viscosity, high reducing sugar content. Used as coating materials for various foods, good film forming ability and as fat replacers in bakery and dairy products.
- *Etherification*: Improved clarity of starch paste, greater viscosity, reduced syneresis and freeze-thaw stability. Used in wide range of food applications such as gravies, dips, sauces, fruit pie fillings and puddings.
- *Esterification*: Lower gelatinization temperature and retrogradation, lower tendency to form gels and higher paste clarity.
- *Cross-linking*: Higher stability of granules toward swelling, high-temperature, high shear and acidic conditions.
- *Dual modification*: Stability against acid, thermal and mechanical degradation and delayed retrogradation during storage.

In some chemical modification processes, it is common to use organic solvents, and mixtures thereof, to achieve firstly starch solubilization, and then modification. However, the utilization of an organic solvent is prohibited in industrial applications, especially in food sector. Among the various derivatives of starch, starch esters are suitable candidates for potentially replacing non-degradable thermoplastics in certain applications (Kapusniak and Siemion 2007).

Plastics and bioplastics in Colombia

The production of bulk plastics in Colombia reached US$ 2.160 millions in 2005. The employment jobs by plastic industry were 37.580 (Acoplásticos 2005). The total value of Colombia's plastic and packaging products exports raised to US$871 millions in 2006. This is an increase on about 132% compared to US$ 375 millions achieved in 2002. However there is no information about degradable plastics production, imports or exports. Canadian company EPI, represented by Biopack of Colombia, and the British Symphony Environmental Limited are commercializing special additives to reduce the degradation time of synthetic plastics. A local industry, Plastiaromas, is planning on establishing biodegradable plastic production in the coming year (Proexport 2007). Recently some Colombian researchers have been interested in bioplastics based on cassava and potato starch as a good alternative for using residues. Additionally, reduction of oil consumption (used for non renewable plastics) and environmental advantages of bioplastics are an attractive area of development for Government and Industry.

Properties of starch films

In general, granular starch may be used in two ways in biodegradable plastics. It may be compounded into plastics in the form of biodegradable filler or it may be plasticized with water (5–20%) and other compatible polymers to become part of the plastic matrix (Singh *et al.* 2007).

Films formed of starch are amorphous. The degree of crystallinity depends on the film forming conditions. For synthetic polymers, it is known that the process technique and conditions affect the mechanical properties of the material. This also applies to thermoplastic starch, but the situa-

Table 11 Mechanical properties of some kinds of starch films.

Polymer	% RH	Stress at break, σ_b (MPa)	Strain at break, e_b (%)	Maximum stress (Mpa)	Reference
Amylose	50	20	31	---	Rindlav-Westling
Amylopectin	50	6	29	---	*et al.* 1998
Amylose	65	20	46	---	
Amylose	RC	23	10	---	
Amylopectin	RC	5	25	---	
High-amylose corn starch ~50% amylose	50	50	2,5	---	
High-amylose corn starch ~55% amylose	60	38	9	---	
Low density polyethylene	---	7 - 16	100 - 800	---	
Normal potato starch 10:3:4.5 *	33	19 (4)	8.4 (0.3)	564 (82)	Thunwall *et al.*
Normal potato starch 10:3:4.5	53	56 (9)	4.5 (0.2)	117 (29)	2006
Normal potato starch 10:3:4.5	70	53 (14)	2.2 (0.4)	13 (3)	
High-amylose potato starch 10:3:4.5	33	44 (8)	14 (0.5)	797 (53)	
High-amylose potato starch 10:3:4.5	53	49 (4)	10 (0.6)	164 (30)	
High-amylose potato starch 10:3:4.5	70	73 (35)	3.0 (1.1)	11 (0.3)	
Normal potato starch 10:0:8	53	2.2 (2.4)	25 (2.4)	2530 (675)	
High-amylose potato starch 10:0:8	53	8.4 (7)	33 (6.9)	2180 (669)	

* 10 : 3 : 4.5 (starch: glycerol: ether).

RC: room conditions.

In parentheses: standard deviations

Table 12 Values of permeability of some synthetic and non synthetic films.

| Film/coating material	Test conditions	O_2 ($m^3 \cdot m / m^2 \cdot s \cdot Pa$)	CO_2 ($m^3 \cdot m / m^2 \cdot s \cdot Pa$)	H_2O vapor ($g \cdot m / m^2 \cdot s \cdot Pa$)	Reference
Edible coating material					
Chitosan	25°C, 50-70% RH	1.4×10^{-21}	---	4.9×10^{-10}	Lin and Zhao 2007
Soy protein	25°C, 50-70% RH	3.14×10^{-19}	---	3.49×10^{-10}	
Sucrose polyester	25°C, 50-70% RH	2.10×10^{-18}	---	4.2×10^{-13}	
Wheat gluten	25°C, 50-70% RH	2.89×10^{-17}	2.13×10^{-18}	9.18×10^{-11}	
Cellulose-based					
Cellulose acetate	30°C, 90% RH	$5,928 \times 10^{-8}$	$5,168 \times 10^{-7}$	0,00057	Brandrup *et al.* 1999
Cellulose hydrate	0°C, 43% RH	0.00536×10^{-17}	0.00974×10^{-17}	---	Jasse *et al.* 1994
Cellulose hydrate	0°C, 76% RH	0.00665×10^{-17}	0.0539×10^{-17}	---	
Hydroxypropyl cellulose (HPC)	25°C, 50-70% RH	3.1×10^{-6}	1.13×10^{-4}	5.55×10^{-7}	Lin and Zhao 2007
Hydroxypropyl methylcellulose (HPMC)	24°C, 50% RH	$3,1481552 \times 10^{-18}$	---	---	Miller and Krochta
Methylcellulose (MC)	24°C, 50% RH	$1,1226877 \times 10^{-18}$	---	---	1997
Methylcellulose (MC)	25°C, 50-70% RH	3.85×10^{-6}	6.9×10^{-5}	9.35×10^{-11}	Lin and Zhao 2007
Starch-based					
Amylomaize starch	25°C, <100% RH	$<7,523165 \times 10^{-19}$	---	---	Miller and Krochta 1997
Amylose	50-85% RH	$8,1018 \times 10^{-17}$	---	$1,1921 \times 10^{-6}$	Rindlav-Westling *et*
Amylose	1-53% RH	n.d	---	$5,44 \times 10^{-8}$	*al.* 1998
Amylose	29-81% RH	n.d	---	$2,662 \times 10^{-7}$	
Compression molded thermoplastic potato starch	---	---	---	$7,2916 \times 10^{-8}$	
Compression moulded thermoplastic potato starch	---	$7,407 \times 10^{-17}$	---	$1,495 \times 10^{-7}$	
Hydroxypropylated amylomaize starch	25°C, <78% RH	~ 0	---	---	Miller and Krochta 1997
Protein-based					
Collagen	RT, 63% RH	$2,6967653 \times 10^{-19}$	---	---	Miller and Krochta
Collagen	RT, 93% RH	$1,0300949 \times 10^{-17}$	---	---	1997
Gluten: glycerol (2.5:1)	25°C, 0% RH	$7,060201 \times 10^{-20}$	---	---	
Soy protein isolate: glycerol (2.4:1)	25°C, 0% RH	$7,060201 \times 10^{-20}$	---	---	
Zein	25°C, 50-70% RH	7.84×10^{-19}	2.67×10^{18}	1.17×10^{-10}	
Zein:PEG+glycerol (2.6:1)	25°C, 0% RH	$4,4791767 \times 10^{-19}$	---	---	
Whey protein isolate (WPI)	25°C, 50-70% RH	1.13×10^{-18}	---	1.1×10^{-9}	Lin and Zhao 2007
Whey protein isolate: glycerol (2.3:1)	23°C, 50% RH	$8,8078901 \times 10^{-19}$	---	---	Miller and Krochta
Whey protein isolate: sorbitol (2.3:1)	23°C, 50% RH	$4,976863 \times 10^{-20}$	---	---	1997
Synthetic polymer					
Ethylene vinyl alcohol copolymer (EVOH) 70% VOH	23°C, 95% RH	$1,388892 \times 10^{-19}$	---	---	Miller and Krochta 1997
High-density polyethylene (HDPE)	30°C, 90% RH	$8,056 \times 10^{-8}$	$2,66 \times 10^{-0,7}$	$9,88 \times 10^{-0,7}$	Brandrup *et al.* 1999
High-density polyethylene (HDPE)	25°C, 50-70% RH	5.02×10^{-18}	---	2.52×10^{-13}	Lin and Zhao 2007
Low-density polyethylene (LDPE)	30°C, 90% RH	$4,18 \times 10^{-7}$	$2,6752 \times 10^{-0,6}$	$6,08 \times 10^{-6}$	Brandrup *et al.* 1999
Low-density polyethylene (LDPE)	25°C, 50-70% RH	2.25×10^{-17}	---	8.1×10^{-13}	Lin and Zhao 2007
Nylon 6	30°C, 90% RH	$2,88 \times 10^{-9}$	$1,21 \times 10^{-8}$	$5,32 \times 10^{-4}$	Brandrup *et al.* 1999
Polyester	25°C, 50-70% RH	2.69×10^{-19}	2.61×10^{-17}	3.6×10^{-13}	Lin and Zhao 2007
Polyestyrene	30°C, 90% RH	$8,36 \times 10^{-8}$	$6,688 \times 10^{-7}$	$9,12 \times 10^{-5}$	Brandrup *et al.* 1999
Poly(vinylidene chloride) (PVDC)	30°C, 90% RH	$4,028 \times 10^{-10}$	$2,204 \times 10^{-9}$	$1,064 \times 10^{-7}$	
Polypropylene (PP)	25°C, 50-70% RH	5.5×10^{-17}	---	6.5×10^{-13}	Lin and Zhao 2007
Poly(vinyl alcohol)	0°C, 0% RH	$0,00005 \times 10^{-17}$	$0,00924 \times 10^{-17}$	$5,25 \times 10^{-17}$	Jasse *et al.* 1994
Polyvinyl chloride (PVC)	25°C, 50-70% RH	5.15×10^{-19}	$1.35 \times 10^{-18} - 2.7 \times 10^{-17}$	2.16×10^{-11}	Lin and Zhao 2007
Polyethylene terephthalate (PET)	25°C, 50-70% RH	2.15×10^{-19}	$6.7 \times 10^{-19} - 1.12 \times 10^{-18}$	---	

RH: Relative Humidity

tion is somewhat more complex, since the initial water content (i.e., before processing the material) also has some effect (Thunwall *et al.* 2006). The mechanical and barrier properties of starch films depend (among other things) on the environment and place limitations on the use of the films. The mechanical properties of pure amylose and pure amylopectin films are different. Usually amylopectin films have a more brittle character than amylose (Krogars 2003). Higher strength and toughness are expected from thermoplastic starch materials with a higher amylose content are possibly associated with a more entangled starch network (Thunwall *et al.* 2006). **Table 11** shows the mechanical properties of pure amylose and pure amylopectin films compared with film-formers currently used as coating materials in similar applications. **Table 12** shows the water vapor,

oxygen, and carbon dioxide permeability values of some film materials.

Surface morphology with AFM

Atomic force microscopy (AFM) is a technique that provides direct spatial mapping of surface topography and surface heterogeneity with nanometer resolution without any specific sample preparation conditions. AFM has been used to examine the surface and internal structure of starch granules, the surface of extruded films and starch films prepared by casting (Thiré *et al.* 2003). Micrographs of three types of potato starch films are shown in **Fig. 8**. As shown in the figure in plasticized films (B and C), the matrix microstructure is similar, independent of the preparation
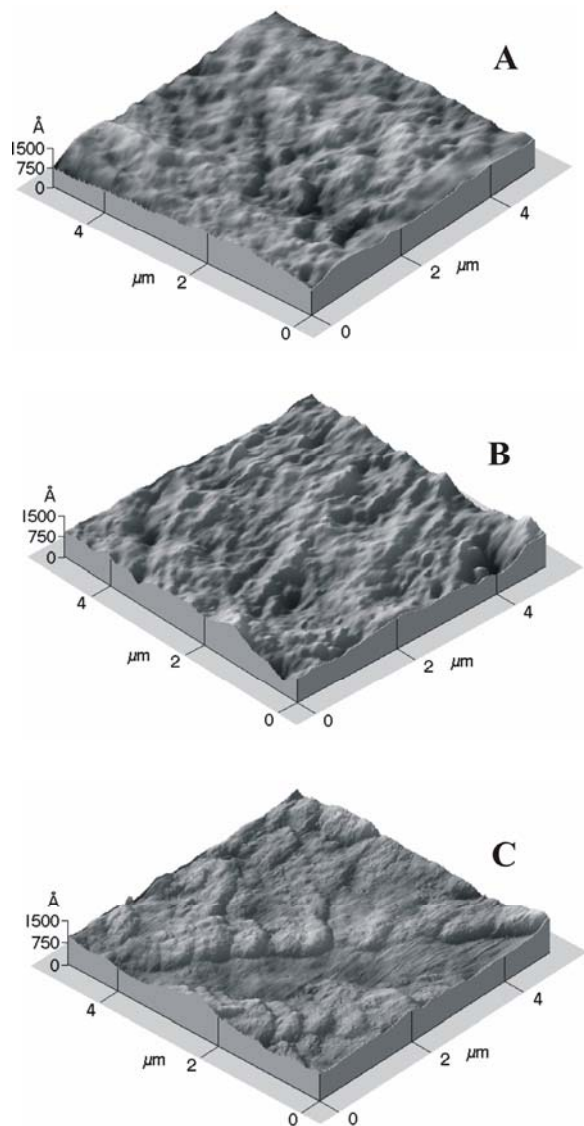
Fig. 8 AFM micrograph of starch films. (**A**) Potato starch. (**B**) Potato starch sorbitol. (**C**) Potato starch with glycerol. Test conditions: Starch: Plasticizer: water (10: 3: 4.5), 25°C, 60-80% RH.

conditions, and bright domains. This pecularity is attributed to the existence of glycerol-rich phases. This type of analysis can give very important information about the attributes of the potato starch films to be used in different industrial applications.

CONCLUDING REMARKS

Given the status of the potato industry in Colombia, manufacturers are looking towards the production of value added products from the tuber. Due to high content of starch in potato, it has been proposed as a feedstock for bioethanol and bioplastics production. The analysis realized reveals that the production of fuel ethanol from potato starch is technically viable and that it could provide solutions to many social, environmental and economical problems associated with the potato crop in the country. Previous analyses showed that bioethnol plants can produce up to 15.000 liters per day which invariably would be a sustainable alternative for rural communities located in the colombian mountains. Likewise, the production of bioplastics is a promising alternative since starch is considered an important biodegradable material suitable for the production of plastic films. The advantages of starch for plastic production include its renewability, good oxygen barrier in the dry state, abundance, low cost and biodegradability. Different mechanical properties can be obtained depending of the plasticizer content, bota-

nical origin of starch and film processing conditions. However, research is needed in this area to utilize the full potential of potato starch.

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