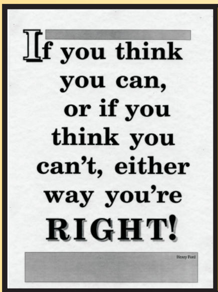
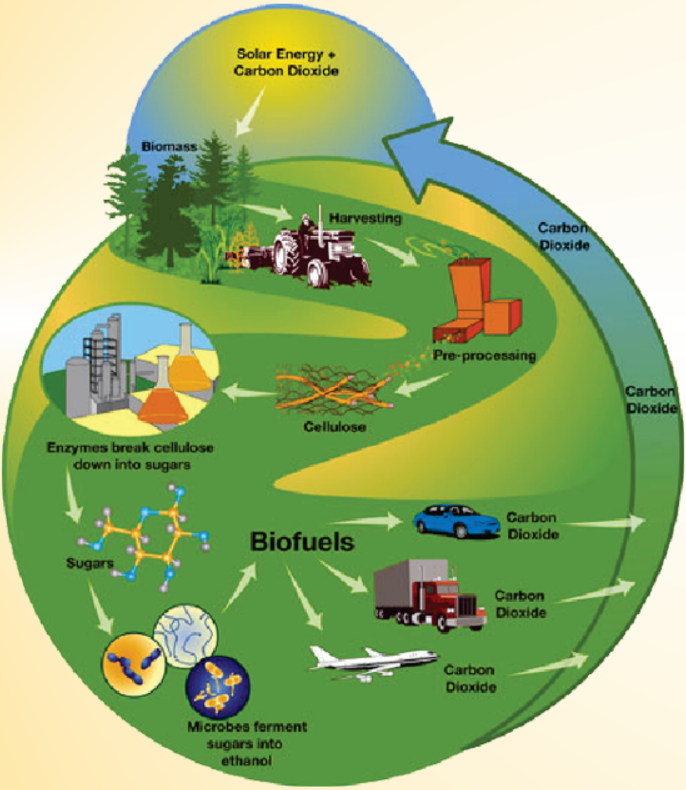


Corn to Ethanol : Retrospect's and Prospects

Maize: Leading to a new Paradigm



DIRECTORATE OF MAIZE RESEARCH
(Indian Council of Agricultural Research)
Pusa Campus, New Delhi -110 012

भा.कृ.अनु.प.
ICAR

Corn to Ethanol: Retrospect's and Prospects

Maize: Leading to a new Paradigm

**Sapna, D.P. Chaudhary,
S. Mandhania and R. S. Kumar**

भा.कृ.अनु.प.
ICAR

DIRECTORATE OF MAIZE RESEARCH
(Indian Council of Agricultural Research)
Pusa Campus, New Delhi -110 012 (India)
Website: www.maizeindia.org
Email: pdmaize@gmail.com
Phone: 011-25841805, 25842372, 25849725
Fax: 011-25848195

Citation:
Sapna, D.P. Chaudhary, S. Mandhania and R. S. Kumar. Corn to Ethanol: Retrospect's and Prospects, Maize: Leading to a new Paradigm. Directorate of Maize Research, Pusa Campus, New Delhi - 110 012,Technical Bulletin No.2011/2, pp.20.

Published by:
Directorate of Maize Research
(Indian Council of Agricultural Research)
Pusa Campus, New Delhi -110 012 (India)
Website: www.maizeindia.org
Email: pdmaize@gmail.com
Phone: 011-25841805, 25842372, 25849725
Fax: 011-25848195

Published in 2011

Cover page:
Henry Ford (Photograph), Bio-fuel process

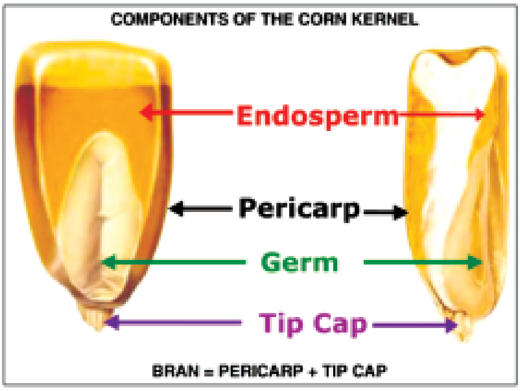
Back page cover:
Ethanol Plants and Corn Cob

Printed by:
Alpha Printographics (India)

CONTENTS

Background

Energy is the vital need of mankind and it is the priceless gift offered by the nature. Apart from food, we need lots of energy in various forms in our day-to-day life. At present, most of our energy requirements are fulfilled by non-renewable sources. The most extensively used non-renewable energy sources are the fossil fuels. Due to the unsustainable use of world's energy stores we had been encountered with numerous issues in the past and are fast approaching towards a similar crisis. The gasoline shortage of 1970's or the panic of fuel-price after Hurricane Katrina should be taken as wakeup calls so that we could remind ourselves from time to time regarding our ever depleting energy reserves. As we all know that energy can neither be created nor it can be destroyed, it can only be converted from one form to the other. So how long it will take us to realize the importance of energy and the difficulty in tapping the energy from geological reserves? Man need to think of "renewable" as replenishing only in the right circumstances and within the laws of balance of nature so as to allow the natural ecological cycles to remain natural, and not mess with Mother Nature.



As need is the mother of discovery, the foreseeing energy crisis has induced interest in the synthesis of bio-fuel. The global consumption of the liquid petroleum will increase tremendously in coming years. It is estimated that if the present trend continues, the energy demand is projected to grow by more than 50% by 2025 (Ragauskas, 2006). Most importantly, unlimited demand for limited petroleum resources can not be a satisfactory option for a long time. Therefore, before the things slip out of our hands, we must start working towards bringing transition from the non-renewable carbon source to renewable bio-resources. Corn to ethanol concept can be a road-map in this regard.

Use of ethanol as a fuel is not a novel concept. Henry Ford Model T was run by ethanol because his vision was to introduce such a vehicle that could be affordable by rural masses (Kovarik et al., 1998). During 1930's people used to use ethanol as a fuel source in cars, but the practice was brought to an end post world war-II due to the availability of petroleum and natural gas as cheap source of energy (Bothast and Schlicher, 2005). It burns more cleanly and also increases the octane level of gasoline. Only half the volume is required to produce the same oxygen level in gasoline by ethanol due to higher oxygen content as compared to Methyl tert-Butyl Ether (MTBE) (Dipardo, 2000).

Presently, USA is the major exporter of maize and shifted 30% of its maize grains towards bio-fuel production to meet society's prospective hidden requirements (Ragauskas, 2006). Corn is the most important and economical source of starch, comprising about 68-72% of kernel weight, which is easily converted into glucose and fermented into ethanol.

Maize is the major crop of India after rice and wheat that provides food, feed and fodder to the livestock (Fig.1) and serves as a source of basic raw materials for a number of industrial products mainly starch, corn oil, corn syrup, alcoholic beverages, cosmetics, bio-fuel and many more. Earlier the research emphasis was laid on the development of composite maize varieties, double cross and three way cross hybrids. However, with the realization of the advantages of single cross hybrid over double cross, three way cross and composites, the research was focused towards the development of single cross hybrids. The Directorate of Maize Research, India played a pivotal role in this direction. As a result of single cross hybrid (SCH) technology, maize achieved the highest growth rate (6.7%) amongst cereals as against the required growth rate of 4.7% set by the XI planning commission of India (Fig.2 & 3). As a result India became importer to exporter of maize.

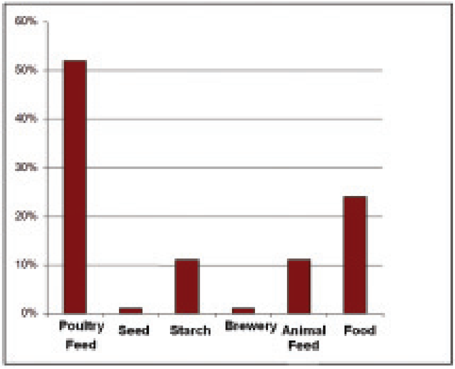


Fig. 1: Maize Utilization Pattern in India

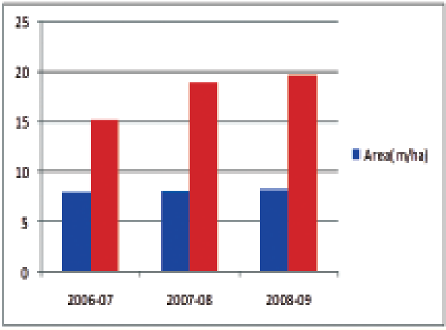


Fig. 2: Maize Growth Rate in India

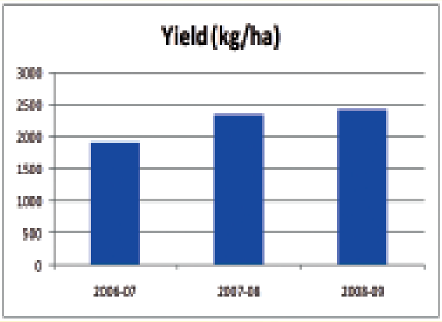


Fig. 3: Productivity pattern of India

Crop yields kept pace with rapidly expanding production demand of global population and the available biomass can be much more innovative with superior and improved cellulosic technologies. Technological improvements in plant breeding hold promise to improve grain quality as well as quantity in India. Due to increase in area, production and productivity, India is producing surplus maize and this trend is likely to go on and the excess from the food basket can be used to secure us at the platform of energy and increasing future fuel demand of the country as an individual and world as a whole. Today, maize has set the stage to roll the dice and definitely ethanol will hit the right note.

Unloading of maize grains

Corn Starch **Corn Syrup** **Corn Gluten Meal**

Co- Products

Ethanol Production Processes

New technologies are under experiment at various international research centers so as to provide more and better products to maintain the economics of the fuel ethanol. Further research in bio-fuel metrics is needed and the major thrust areas are: Production of hybrids with higher starch content, Conversion of corn-kernel fiber fraction to ethanol and identification and development of new and higher value co-products. Many processes are employed like quick fiber (Singh *et al.*, 1999), quick germ (Singh and Eckhoff, 1996), COPE process (Cheryan, 2002), enzymatic milling (Johnston *et al.*, 2003), dry grind and wet milling. Both dry grind and wet milling processes are popular now-a-days but most of the ethanol is produced by dry grind method only because it is less capital and energy-intensive (Butzen and Haefele, 2008).

Dry-Grind Ethanol Process

Ethanol is commercially produced by either of two ways, the wet mill or dry grind process. Wet milling involves separating the grain kernel into its constituents (germ, fiber, protein, and starch) prior to fermentation ((Butzen and Haefele, 2008). Whereas in dry grind process, the entire grain kernel is ground into flour. The starch in the flour is converted to ethanol during the fermentation process, creating carbon dioxide and distillers' grain. Fermentation is one of the oldest process known to man (Bothast and Schlicher, 2005). In USA, ethanol is mainly produced by dry-grinding process (approximately 67%) and its percentage is increasing rapidly (Butzen and Haefele, 2008). The various steps involved in this process are discussed below.

Mash Formation

The entire grains mass is screened to remove debris. The screened kernels are ground and then mixed with water to form slurry called "mash".

Cooking

In this process the starch in the flour is physically and chemically prepared for fermentation. The mash is further cooked and enzyme is added to convert the starch into sugar followed by the addition of yeast so as to accomplish the fermentation of sugar, leaving behind a mixture of ethanol and solids. The ethanol is extracted through distillation and dehydration and the solid remained are dried to produce distiller's dried grain solubles (DDGS).

Conversion of Starch

(Primary Liquefaction, and Secondary Liquefaction)

Corn Starch is composed of glucose units joined through a linkage in chains by α 1-4 and in branches by α 1-6 glycosidic bonds. The linear starch molecules are called amylase, whereas the branched one is called amylopectin. Starch usually comprises of 25-30% amylose and rest is amylopectin. Yeast can not metabolize this starch directly, but, it must be broken down into simple sugar i.e. glucose, prior to fermentation. The pH of the mash is adjusted at 6.0 so as to carry out this conversion. A thermo stable enzyme α-amylase is added to mash which breakdown the starch polymer (hydrolyze α 1-4 bond) and produce soluble dextrin.

Primary Liquefaction

The slurry is then pumped through a pressurized jet cooker at 221°F and held for 5 minutes. The mixture is then cooled by an atmospheric or vacuum flash condenser.

Ethanol plant

Secondary Liquefaction

After the flash condensation cooling, the mixture is held for 1–2 hours at 180–190°F to give the alpha-amylase enzyme time to break down the starch into short chain dextrins. The slurry is heated to 180–190°F for 30–45 minutes to reduce viscosity and to provide mechanical shearing to rupture starch molecule especially of high molecular weight. The mash is further liquefied for at least 30 minuntes to reduce the size of starch polymer. In overall, this step requires the addition of α-amylase and steam i.e. gelatinization and liquefaction. This dextrinized mash is further cooked and adjusted to pH 4.5 to facilitate the addition of gluco-amylase to convert liquefied starch into glucose. To accomplish the sacchrification of starch to glucose, gluco-amylase is added in enough quantity. Simultaneous Sacchrification and Fermentation (SSF) is again a better option to reduce the microbial interference and more yield per bushel of the corn.

Simultaneous Saccharification and Fermentation

Once inside the fermentation tank, the mixture is referred to as mash. The gluco-amylase enzyme breaks down the dextrins to form simple sugars. Yeast is then added to convert the sugar to ethanol and carbon dioxide. The mash is afterwards allowed to ferment for 48–72 hours, resulting in a mixture that contains about 10% ethanol as well as the solids from the grain and added yeast.

Fermentation

After sacchrification, cooling is done and mash is transferred to fermenter and yeast is added. *Saccharomyces cerevisiae* is commonly used species due to its quick and efficient production of alcohol. Consequently, addition of protease is of immense importance as it breaks down the corn-protein to free amino acids to serve as an additional source of nitrogen for the yeast. The whole process requires 48-72 hours and can concentrate up to 10-12% of ethanol. CO_2 formed during this process lowers down the pH below 4.0 in order to enhance the activity of gluco-amylase and to check the surrounding infection. The Batch and Continuous fermentation systems can be used and out of both batch process is more popular. CO_2 released can be captured and sold for the use in carbonating soft drinks, dry ice and some beverages industries.

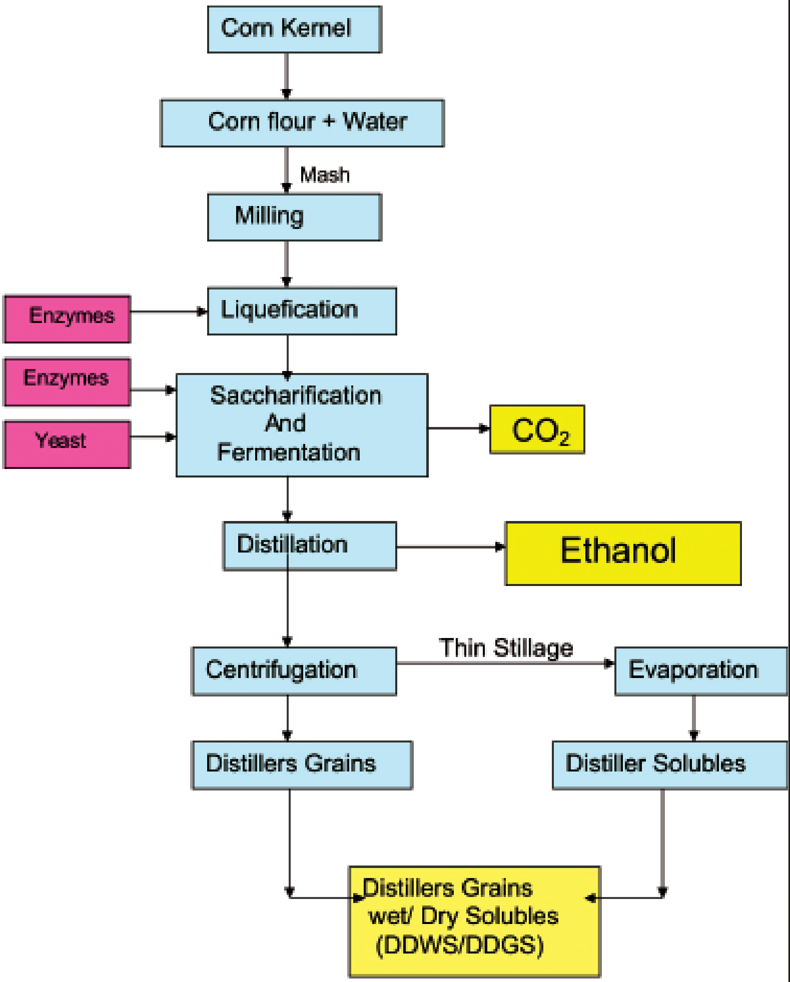
Distillation and Dehydration

Distillation

Distillation is the process of separating ethanol from the solids and water in the mash. The fermented mash is pumped into a multi-column distillation system where additional heat is added. The columns utilize the differences in the boiling points of ethanol (78^{o}C) and water (100^{o}C) as a milestone to boil off and separate the ethanol. By the time the product stream is ready to leave the distillation columns, it contains about 95% ethanol by volume (190-proof).

Dehydration

The 190-proof ethanol still contains about 5% water. Alcohol and water form an azeotrope at this point and can not be separated further. Rest of 5% water must be removed in order to blend it with gasoline. To carry out this operation It is passed through a molecular sieve to physically separate the remaining water from the ethanol based on the different sizes of the molecules. This step produces 100% pure (200-proof) anhydrous (waterless) ethanol.



Dry-Grind Ethanol Process

Ethanol Storage

Before the ethanol is sent to storage tanks, a small amount of denaturant (5% gasoline) is added to render it undrinkable (unfit for human consumption) and save the beverage alcohol tax.

Most ethanol plants' storage tanks are sized to allow storage of 7–10 days' production capacity.

Co-Product Processing

The residue from this process, called "whole-stillage" contains non-fermentable starch, fiber, oil, and protein component of the grain and water. It is pumped out from the bottom of the columns into the centrifuges. During the ethanol production process, two valuable co-products are created: carbon dioxide and distillers grains.

As yeast ferment the sugar, they release large amounts of carbon dioxide gas. This CO_2 can be released into the atmosphere, but it's generally captured and sold to food processing industries as discussed earlier. The stillage from the bottom of the distillation tanks contains solids from the grain and added yeast as well as liquid from the water added during the whole process. This is a valuable feed ingredient and can fed as such but it is usually sent to centrifuges for separation into thin stillage (a liquid with 5–10% solids) and wet distillers grain. Some of the thin stillage (15-30%) is routed back to the cook/slurry tanks as makeup water, reducing the amount of fresh water required by the cooking process. The rest is concentrated further into syrup containing 25–50% solids. After drying (evaporation), the thick syrup, which is high in protein and fat content, is then mixed back to create feed product known as wet distillers grain (WDG).

With the added syrup, the WDG (65% moisture) still contains most of the nutritive value of the original feedstock plus the added yeast. It is preferred as an excellent cattle ration for local feedlots and dairies due to high moisture content. After the addition of the syrup, it's conveyed to a wet cake pad having a self-life of 1-2 weeks. So, it is loaded for transport as soon as possible. Unless the target destination is within the vicinity of plant, it becomes hard to handle the same. Many ethanol facilities do not have enough nearby cattle to utilize all of the WDG. To reduce this burden WDGS is often dried to 10-13% moisture to give rise to Dried Distiller's Grain Solubles (DDGS). This facilitates the removal of moisture and extends its shelf life. This dried distillers grain (DDG) is commonly used as a high-protein ingredient in cattle, swine, poultry, and fish diets.

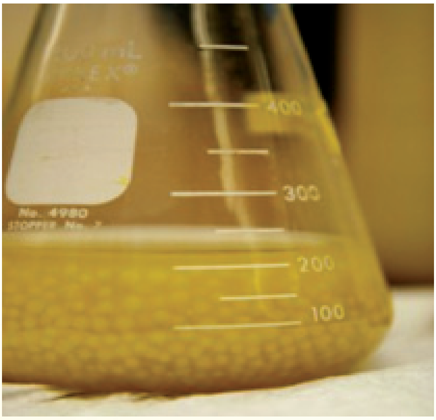
Wet Distiller Grains (WDG)

Dried Distillers Grain Solubles (DDGS)

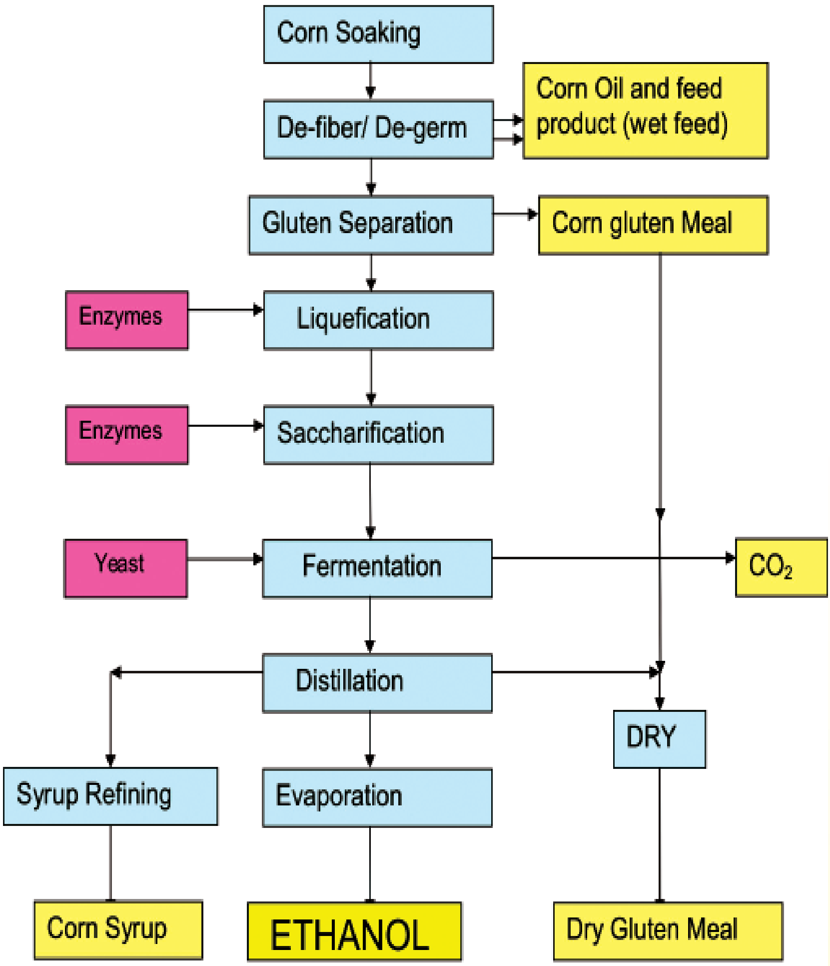
Wet-Milling Process

The major difference between the wet-mill and dry grind is the initial treatment of the grain. In wet-mill the grain is steeped or soaked into water and dilute sulfurous acid for 24-48 hours to facilitate the separation of component parts of the grain including starch, germ, fiber and gluten. The germ is removed from the kernel by processing the corn slurry through a series of grinders. The germ is used either to extract the corn oil on the site or sold to crushers who extract the corn oil. Other remaining components like starch, fiber and gluten are segregated further as by-products by centrifuge, screen and hydroclonic separators. The germ meal is then added to fiber to form corn gluten feed and sold to livestock industry. Corn gluten meal is a very high-protein animal feed and sought after as a feed ingredient in poultry broiler operations. Moreover, heavy steep water can also be sold as either feed ingredients or as a part of Ice-Ban (an environmental friendly alternative to salt) for removing ice from the roads in various countries. In this process, fermentable sugars are produced from the starch and fermented into ethanol. Fate of this starch and remaining water can be either fermented into ethanol or dried and sold as dried or modified corn starch or processed into corn-syrup. Wet-mill facilities are considered as true "Bio-refineries" as this process is followed by various high-value co-products.

Corn to Ethanol: Economics



The bio-fuel concept is gaining momentum slowly. Bio-fuel is garnering larger and larger shares of the fuel markets. In the USA, ethanol production tripled in last few years from 2.8 billion gallons in 2003 to over 9 billion gallons in 2008 (Ling Tao and Andy Aden, 2009). Under the Energy Independence and Security Act of 2007 (EISA, 2007), 36 billion gallons of renewable fuel is required by 2022. Out of which, 15 billion gallons will be corn-based ethanol. Most of the ethanol produced in USA is derived from corn only. Dry-grind process is more prevalent (RFA, 2008). As a result, ethanol produced from wet-mill are comparatively lower (2.5 gal per bushel) than from dry-grind processes (2.8 gal per bushel) (Ling Tao and Andy Aden, 2009).



Wet-Mill Ethanol Process

Dry-grind Ethanol process Products are: ethanol (2.8 gal.), DDGS (18 lbs.) and CO_2 (18 lbs.). 150 bushel corn yields 413 gallons of ethanol per acre, 2700 pounds of DDGS (Douglas G. Tiffany). These high value co-products have potential to accelerate with the cost of ethanol production. Establishment of large scale industries can make ethanol production more economical. The variation of Ethanol production potential ranges up to 7% depending upon different corn hybrids (Pioneer's report).

Enormous debate over the potential benefits of bio-fuel has taken place for the concept of net energy. Various studies have accounted that ethanol and co-products manufactured from corn yielded a positive net energy and this can be of about 4 MJ/l to 9 MJ/l (Farrell, 2006). The study that ignored co-products but used recent data found a slight positive net energy for corn ethanol. Studies that reported negative net energy ignored the co-products and used some of the obsolete data incorrectly.

India and Ethanol Production

India now has a surplus of corn that can be economically processed into ethanol so as to meet the emerging energy demands of the nation and the world (India and Ethanol Production.mht). International-Planners are planning the construction of 20 regional grain to ethanol conversion facilities in India. They could produce 6,000,000 gallons of ethanol a month, ending India's reliance upon fossil fuel and doubling the income of the average farm workers family so as to make them economically independent. These ethanol production centers will be built in the 20 different states. India now has to import 15 million barrels of ethanol a year. The Indian government has recently offered to underwrite 75% of the development costs of ethanol bio-mass production centers in order to stimulate National ethanol production. The ethanol production centers will produce those 15 million barrels of ethanol for India's needs, which will save India each year more than Rs. 9,000,000,000 ~$760,000,000.

Future Prospects

In view of changing world energy requirements, a research road-map for the bio-refineries is mandatory. This will contribute towards sustainability in terms of energy. Various researchers are trying to come up with cellulosic approaches to maintain the economics of the corn to ethanol process. Progress towards attaining these goals requires new technologies, better quality hybrids, accelerated plant domestication programmes, improved management practices and enough research funding to develop a future renewable energy source. The demands in future bio-refineries will stimulate further advancement in the agriculture to produce more and more improved biomass for ethanol production. Such approaches can lead to a bio-fuel industry that will satisfy improved vehicle efficiency and in overall, will meet the energy security and climate change imperatives of the nation and the world because energy and environment implications of ethanol production are more important than others. Nonetheless, giving up humanity's dependence on decreasing non-renewable energy source is a big challenge in itself that need to be considered by researchers in order to win the end game.

References

Bothast R.J. and Schlicher M.A. (2005). Biotechnological processes for conversion of corn into ethanol. *Appl Microbiol Biotechnol*. **67**: 19-25.

Butzen S. and Haefele D. (2008). Dry grind ethanol production from corn. *Crop Insight*. **18**: 1-4

Cheryan M. (2002). Corn oil and protein extraction method. US Patent 6433146.

Dipardo J. (2000). Outlook for Biomass ethanol production and demand. Energy Information Administration, US Department of Energy, Washington, D.C.

EISA. EISA of 2007 calls for additional production of biofuels. http://www.renewableenergyworld.com/rea/partner/stoel-rives-6442/news/article/2008/01/eisa-of-2007-calls-for-additional-production-of-biofuels-51063; 2007

Farrell A.E. (2006). Ethanol can contribute to energy and environmental. *Science*. **311**: 506-508.

India and Ethanol Production.mht (google.com). http//www.international_planners.com/ethanol-m.htm#

Johnston D.B., Singh V., Eckhoff S.R. (2003). Use of enzymes to reduce steep time and SO2 requirements in a maize wet milling process. US patent 6566125

Kovarik B., Henry F., Charles F. (1998). Kettering and the fuel of the future. *Automot Hist Rev* **32**:7-27.

Ling Tao and Andy Aden (2009). The Economics of current and future biofuels. Invited Review.

Pioneer report (google.com). www.pioneer.com

Ragauskas A.J. (2006). The path forward for biofuels and biomaterials. *Science*. **311**: 484-489.

RFA. Changing the climate, ethanol industry outlook. RFA, Washington, DC; 2008.

Singh V. and Eckhoff S.R. (1996). Effect of soak time, soak temperature and lactic acid on germ recovery parameters. *Cereal Chem*. **73**: 716–720.

Singh V., Moreau R.A., Doner L.W., Eckhoff S.R., Hicks K.B. (1999). Recovery of fiber in the corn dry grind ethanol process: a feedstock for valuable co-products. *Cereal Chem* **76**: 868–872.

भा.कृ.अनु.प.
ICAR

DIRECTORATE OF MAIZE RESEARCH

(Indian Council of Agricultural Research)

Pusa Campus, New Delhi -110 012 (India)

Website: www.maizeindia.org

Email: pdmaize@gmail.com

Phone: 011-25841805, 25842372, 25849725

Fax: 011-25848195