A
DISSERTATION REPORT
ON

"ETHANOL PREPARATION AS A FUTURE FUEL AND ITS FUEL GRADING"

PROJECT DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT
FOR
BACHELOR DEGREE IN APPLIED PETROLEUM ENGINEEERING

By

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CERTIFICATE

This is to certify that the project report on "ETHANOL PREPARATION AS A FUTURE FUEL AND ITS FUEL GRADING" submitted to UPES, Dehradun by Mr Rajeev Yadav in partial fulfillment of the requirements for the degree of Applied Petroleum Engineering & academic session (2003-2007) is a bonafide work carried out by him under my supervision & guidance.

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INTRODUCTION

About Ethanol

Ethanol, C2H5OH, (also called Ethyl Alcohol) is the second member of the aliphatic alcohol series. It is a clear colorless liquid, with a pleasant smell. Except for alcoholic beverages, nearly all the ethanol used industrially is a mixture of 95% ethanol and 5% water, which is known simply as 95% alcohol. Although pure ethyl alcohol (known as absolute alcohol) is available, it is much more expensive and is used only when definitely required. Fuel extender (for both gasoline and diesel) or fuel additive for automobiles as ethanol contains 35% oxygen which aids the combustion process

Ethanol fuel

Ethanol fuel is a biofuel alternative to gasoline. It can be combined with gasoline in any concentration up to pure ethanol (E100). **Anhydrous ethanol**, that is, ethanol with at most 1% water, can be blended with gasoline in varying quantities to reduce consumption of petroleum fuels and in attempts to reduce air pollution. Worldwide automotive ethanol capabilities vary widely and most spark-ignited gasoline style engines will operate well with mixtures of 10% ethanol (E10).In Brazil, ethanol-powered and flexible-fuel vehicles are manufactured to be capable of operation by burning **hydrated ethanol**, an azeotrope of ethanol (around 93% v/v) and water (7%). Hydrated ethanol may also be mixed with gasoline in flexible fuel vehicles but a minimum amount of ethanol (granted by legally regulated gasoline type C) is required to avoid problems with the mixture. A few flexible-fuel systems, like Hi-Flex, used by Renault Clio and Fiat Siena, can also run with pure ethanol.

Ethanol is increasingly used as an oxygenate additive for standard gasoline, as a replacement for methyl t-butyl ether (MTBE), the latter chemical being difficult to retrieve from groundwater and soil contamination. At a 10% mixture, ethanol reduces the likelihood of engine knock, by raising the octane rating. The use of 10% ethanol gasoline is mandated in some cities where the possibility of harmful levels of auto emissions are possible, especially during the winter months.Ethanol can be used to power fuel cells, and also as a feed chemical in the transesterification process for biodiesel

Ethanol can be mass-produced by fermentation of sugar or by hydration of ethylene from petroleum and other sources. Current interest in ethanol lies in production derived from crops **(bio-ethanol)**, and there's discussion about whether it is a sustainable energy resource that may offer environmental and long-term economic advantages over fossil fuels, like gasoline or diesel. It is readily obtained from the starch or sugar in a wide variety of crops. Ethanol fuel production depends on availability of land area, soil, water, and sunlight.

In 2004, around 42 billion liters of ethanol were produced in the world, most of it being for use in cars. Brazil produced around 16.4 billion liters and used 2.7 million hectares of land area for this production (4.5% of the Brazilian land area used for crop production in 2005. Of this, around 12.4 billion liters were produced as fuel for ethanol-powered vehicles in the domestic market.

Renewable resource

Ethanol is considered "renewable" because it is primarily the result of conversion of the sun's energy into usable energy. Creation of ethanol starts with photosynthesis causing the feedstocks such as switchgrass, sugar cane, or corn to grow. These feedstocks are processed into ethanol .

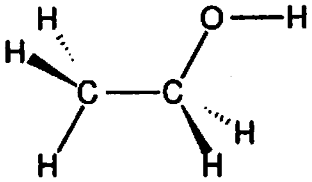
The environmental and economic benefits of non-cellulosic ethanol - including corn ethanol - have been heavily critiqued by many, including Brad Ewing of Environmental Economics & Sustainable Development and Lester R. Brown of Earth Policy Institute The main criticism dwells on the increasing costs of corn for food as the demand for ethanol production increases. It remains to be seen if ethanol production can overcome these problems.

Current, first generation processes for the production of ethanol from corn use only a small part of the corn plant: the corn kernels are taken from the corn plant and only the starch, which represents about 50% of the dry kernel mass, is transformed into ethanol. Two types of second generation processes are under development. The first type uses enzymes to convert the plant cellulose into ethanol while the second type uses pyrolysis to convert the whole plant to either a liquid bio-oil or a syngas. Second generation processes can also be used with plants such as grasses, wood or agricultural waste material such as straw.

Replacement of petroleum

Only about 5% of the fossil energy required to produce bioethanol from corn in the United States is obtained from non-US petroleum Current (2006) United States production methods obtain the rest of the fossil energy from domestic coal and natural gas. Even if the energy balance were negative, US production involves mostly domestic fuels such as natural gas and coal so the need for non-US petroleum would be reduced. Developed regions like the United States and Europe, and increasingly the developing nations of Asia, mainly India and China, consume much more petroleum and natural gas than they extract from their territory, becoming dependent upon foreign suppliers as a result.

PROPERTIES OF THE ETHANOL



In this 3-d diagram of Ethanol, the lines represent single bonds.

During ethanol fermentation, glucose is evolved into ethanol and carbon dioxide.

$C_6H_{12}O_{6(aqueous)}$? $2C_2H_6O_{(aqueous)} + 2CO_{2(gas)}$

During combustion ethanol reacts with oxygen to produce carbon dioxide, water, and heat: (other air pollutants are also produced when ethanol is burned in the atmosphere rather than in pure oxygen

$2C_2H_6O_{(aq)} + 6O_{2(g)}$? $4CO_{2(g)} + 6H_2O_{(l)}$ + heat

It can be seen from these equations that the law of conservation of energy still holds true.

Physical Properties

Ethanol is a colourless liquid with a pleasant smell. It is completely miscible with water and organic solvents and is very hydroscopic.

Melting Point	**-1150C**
Boiling Point	**780C**
Specific Gravity	**0.79.**

Chemical Properties of Ethanol

Combustion of Ethanol

Ethanol burns with a pale blue, non luminous flame to form carbon dioxide and steam.

$$C_2H_5OH + 3O_2 \Longrightarrow 2CO_2 + 3H_2O$$

Ethanol

Oxidation of Ethanol

Ethanol is oxidised

- with acidified Potassium Dichromate, K2Cr2O7, or
- with acidified Sodium Dichromate, Na2Cr2O7, or
- with acidified potassium permanganate, KMnO4,

to form ethanal, (i.e. acetaldehyde).

$$C_2H_5OH \overset{[O]}{\Longrightarrow} CH_3CHO + H_2O$$

Ethanol **Ethanal**

The ethanol is further oxidized to ethanoic acid (i.e. acetic acid) if the oxidizing agent is in excess.

$$CH_3CHO \overset{[O]}{\Longrightarrow} CH_3COOH$$

Ethanal **Ethanoic Acid**

The oxidising agent usually used for this reaction is a mixture of sodium dichromate or potassium dichromate and sulphuric acid, which react together to provide oxygen atoms as follows.

$$Na_2Cr_2O_7 + 4\ H_2SO4 \Longrightarrow Na_2SO_4 + Cr_2(\ SO_4)_3 + 4H_2O + 3[O]$$

Dehydration of Ethanol

When ethanol is mixed with concentrated sulphuric acid with the acid in excess and heated to 170 degC, ethylene is formed. (One mole of ethanol loses one mole of water)

$$C_2H_5OH \xrightarrow[170\ degC]{H_2SO_4} C_2H_4 + H_2O$$

When ethanol is mixed with concentrated sulphuric acid with the alcohol in excess and heated to 140 degC, diethyl ether distils over (two moles of ethanol loses one mole of water) .

$$2\ C_2H_5OH \xrightarrow[140\ deg]{H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

Reaction of Ethanol with Sodium

Sodium reacts with ethanol at room temp to liberate hydrogen. The hydrogen atom of the hydroxyl group is replaced by a sodium atom, forming sodium ethoxide.

$$C_2H_5OH + Na \implies C_2H_5ONa + (H_2)$$

Apart from this reaction, ethanol and the other alcohols show no acidic properties.

Dehydrogenation of Ethanol

Ethanol can also be oxidized to ethanal (i.e. acetaldehyde) by passing its vapour over copper heated to 300 degC. Two atoms of hydrogen are eliminated from each molecule to form hydrogen gas and hence this process is termed dehydrogenation.

C_2H_5OH ==> $CH_3CHO + H_2$

Ethanol Ethanal

Esterification of Ethanol

Ethanol, C2H5OH, reacts with organic acids to form esters.

$$C_2H_5OH + CH_3COOH \xrightarrow{H(+)} CH_3COOC_2H_5 + H_2O$$

Ethanol Ethanoic Ethyl Water

Acid Acetate

Halogenation or Substitution of Ethanol with PCl5

Ethanol reacts with phosphorus pentachloride at room temperature to form hydrogen chloride, ethyl chloride (i.e. chloroethane) and phosphoryl chloride.

$C_2H_5OH + PCl_5$ ==> $C_2H_5Cl + POCl_3 + HCl$

Ethanol Phosphorus Ethyl Phosphorus Hydrogen

Pent chloride Chloride Pent chloride Chloride

Halogenation or Substitution of Ethanol with HCl

$$C_2H_5OH + HCl \xrightarrow{ZnCl2} C_2H_5Cl + H_2O$$

Ethanol Ethyl Chloride

ETHANOL FEEDSTOCK

Agriculture Residues

This source of biomass comes from the leftover organic material from crop harvesting. corn stover, rice straw, and bagasse are all examples of agricultural residues. Presently, some residues are used as animal feed, but there are still significant surpluses in many regions. While using agricultural residues may present a logistical problem due to their seasonal availability, the quantities produced in many regions are large enough that supply problems are not expected. For example, both Illinois and Iowa produce more than 20 million tons of residues annually.

Wood Residues

These are the residues left from cutting logs at sawmills, the leftover branches and barks from logging. Rough estimates indicate more than 70 million tons of residues are produced annually. Though some of the residues are used for pulp and paper, fiberboard, heating or generation of electricity, much of the waste still has little economic use.

Animal Waste

Animal waste comes primarily from large-scale farming operations. There are approximately 100 million dry tons (2005) of animal waste produced annually in the United States alone and large concentrations of hogs, poultry and cattle to support facilities in several areas of North America. These sources are typically very inexpensive to obtain as they are a source of pollution in many regions.

Landfill Gas

Because the amount of municipal solid waste is expected to increase in the future, this will be a ready source of biomass which can be exploited through tapping the gas from landfills. A landfill gas resource generally has an expected reserve life without additional capital requirements of 25-40 years. Consequently, an ethanol facility will enjoy the benefit of long term production and market planning. According to proprietary studies undertaken by Shell Oil, there are in excess of 3,000 active sanitary landfills in the United States.

Production Of Ethanol:

In all, three different class of sources can be used:
a.starch as grain, com and tubers like cassava
b sugar plants (sugar beet or sugar cane)
c cellulose plants (general tree and biomass)

a. Starch based alcohol production:

Process

Alcohols are produced from a large number of different starch crops as barley, wheat, com, potato, sorghum etc. The conversion of starch into alcohol follows the same process of fermentation and distillation as that of sugarcane. The difference lies in additional two steps, namely,

.Milling of the com Removal of by-products, as DDGS, com oil, . com gum etc

Milling of the com is an energy intensive step and is carried by one of the two main processes-

.Wet-milling
.Dry grinding

Wet milling plants are capital intensive but produce high valued by-products whereas dry grind plants cost less but provide lower valued products. Com contains some cellulose which does not *ferment.* A residue called dried distillers grains and solubles (DDGS) is obtained. Presently one bushel of com gives 2.5 gallons of ethano I , 17 lbs of DDGS and 19 lbs of co2. DDGS utilisation/disposal presents *few* problems. The present usage is animal feed but can be converted into high valued products also. The efficiency of ethanol conversion would improve if the following two major technological developments are used-

. Use of enzymes produced by solid state fermentation (SSF), which can breakdown cellulose part also increasing the yield from 2.5 gallons/bu (maxim 2.8 gallonlbu) to 3.52 gallons/bu. This also reduces the DDGS from 17 lbs to 7 lbs/bu and increase its protein content.

Use of high temperature yeast as Thermosac capable to operate at 35-40° C, producing 18-20% ethanol.

.A typical value addition by ethanol conversion is shown in the table below-

2.16.2 Value – Added Benefits, U.S.

Corn 1 bushel	-$2.40
Ethanol 2.8 gallons	+$3.39
Byproducts, DDGS	+$0.60
Value of ethanol & byproducts	+$3.99
Value added	+1.59

Yield and economics would improve when the fermentative abilities of the distillery and the rumen microbes are combined as shown in the table below-

Table 2.11

	TODAY	FUTURE
Alcohol yield		
Per day	2.75/bu	3.52/bu
Per don	98.2	125.69
Revenue @ $1.40/gal	137.48	175.97
DDG produced/bu	17 lbs.	7 lbs.
Yield DDG/ton	607 lbs.	250 lbs.
Price	$0.04 oer lb.	$0.06 per lb.
Revenue	$24.28	$14.99
Total revenue	$161.76	$190.96
Difference		$29.20/ton = $0.81 /bu= $0.29 per gallon alcohol

1 bushel (bu) = 34.8 litres

Corn has four main components: starch, protein, fat and fiber. A large amount of the starch content is hydrolyzed and converted into sugars in the bioethanol production process in our manufacturing plants. Those sugars are then fermented into bioethanol by means of yeasts. However, there is another part known as residual starch that cannot be converted into bioethanol using traditional dry mill process, because it is bound to other molecular structures. The residual starch content can be as high as 10% of the total starch, with 5% as the average level. In short, not all corn starch content is transformed into bioethanol. Part of the content does not transform, another part is degraded, and another is employed for the cellular growth of the yeasts and the forming of other compounds such as glycerin.

On the other hand, as the co-product obtained from the dry-mill bioethanol production process, the DDG (Distiller's Dried Grain) contains all the constituents that have not been converted into bioethanol, including all the proteins, fibers and fats, as well as the non-converted starch. From a theoretical point of view, a bushel of corn (25.2 kg or 56 lbs) could produce 3.02 gallons of bioethanol (12.1 liter); however, average outputs for the industry are around 2.60 gal/bu.

ABRD is developing technologies to achieve higher starch conversion. It is estimated that a 95% fermentation rate could translate into 2.9 gal/bu bioethanol yield. In order to achieve this improvement, a pilot plant is being constructed to carry out an experimental

b. Sugarcane-molasses -ethanol route:

A detailed costing of ethanol production from molasses in the country is given in the table below. Cost of Molasses varies widely across tre different States and in the last six years it has been as low as Rs. 50/- per tonne and as high as Rs. 2000/- per tonne. The sizeable part in the cost is central excise duty, sales tax, transportation cost etc. and the statutory controlled sugarcane and sugar prices, as well as free sale prices coupled with with the release of sugar in the market. If we assume that molasses cost Rs. 1000/- per tonne the feed stock cost will be Rs. 4.5 per litre of ethanol with production of 220 litres ethanol per tonne of molasses. The raw material cost should not represent more than 50% cost of the ethanol production in general and on that basis the ethanol co~t would work out less than Rs. 9/- per litre and would be quite competitive to the present imported cost of gflsoline around Rs. 10-12 per litre.

Table 2.6

Cost of Ethanol Production from Molasses in India

			Stand alone distillery	**Integrated with sugar production**
	Cost of Molasses	Per MT	1000	1000
	Transportation cost	Per MT	150	0
	Total		1150	1000
	Recovery of ethanol/MT molasses	litres	220	220
	Cost of production		**Rs/litre.**	**Rs/litre**
	Molasses cost after milling (Recovery cost)		5.23	4.55
	Steam Cost @ Rice Husk Rs. 500/T		0.25	0
	Power Cost @ Rs. 4.50/Kwhr		0.59	0
	Chemical Cost		0.2	0.2
	Labour cost		0.25	0.25
	Repair & Maintenance		0.15	0.15
	Cost of Replacement of Molecular Sieve		0.02	0.02
	Total Direct costs		**6.69**	**5.17**
	Finance & other costs			
	Indirect costs including overheads		0.56	0.28
	Interest @12% for borrowed capital of Rs. 7.2 cr, (Debt/equity=1.5:1)		0.96	0.96
	Interest @12% for Working Capital for one month of Molasses & Ethanol		0.2	0.2
	Depreciation @ 10% for Rs. 12 cr		1.33	1.33
	Total Finance & other costs		**3.05**	**2.77**
	Total costs		**9.74**	**7.94**

Assumptions:

1. Recovery of 220 litres of Anhydrous Ethanol from one tonne of molasses.

2. Molasses price Rs. 1000 per tonne

3. Annual production of Ethanol @ 30,000 litres per day & 300 working days = 90000 litre/year

3. Alcohol plant assumed to be fully depreciated so capital related charges ignored except that of putting up the facility of making anhydrous alcohol via molecular sieve.

4. Life of Molecular sieve assumed to be 5 years and cost = 3000 kg x Rs.250/kg = Rs.7,50,000/-Avg cost per year Rs. 1,50,000/-.Cost/litre of ethanol = Rs 5/300 ==0.02

5. Power cost of Rs. 4.50/kwh & Rice Husk cost of Rs. 500/MT with steam raising @ 3T([of rice husk.

6. Biogas generation can provide enough energy to meet all energy demand but it has not been taken into account.

7. No taxes (excise or sales etc) on inputs considered.

Preparation of ethanol from molasses:

Fractionating column

A 100-litre capacity cylindrical steel still with 10-ft long x 1-1/2" diameter fractionating column and condenser will suffice for separatimg the ethanol from water. The column should be packed with 1/2"-diameter x 1/2"-long thin black plastic tubes (probably polypropylene or polybutylene) for increasing contact between vapour and liquid inside the column. Make the condenser 6-ft long x 1" diameter with inlets and outlets as shown. This arrangement will easily separate 1-2 litres of spirit per hour.

Stove

Ordinary wood stove using waste wood from the plantation. I used wood gas from wood pyrolysis, with recovery of many useful products: charcoal 30%, acetic acid 6%, wood spirit 1.5%, wood tar 7%, wood gas 25% (burnt under stove). The gas burns well and saves you fuel wood. Wood spirit is excellent auto fuel like ethanol.

Method

Dissolve 1kg molasses containing 50% sugar in 4 litres of water. This will give 10% sugar that is ideal. Add to the plastic container containing the immobilised yeast culture, cap and stand at 25-30 deg C (77-86 deg F). Reaction time is 2-3 days and it is over when bubbling of CO2 ceases. Carefully pour out the alcoholic solution into the still and start the next batch. Once you are familiar with the process you can scale it up 5-fold or more up to the still capacity of 80 litres.

Preparation

Ethanol is prepared as 95% alcohol (i.e. a 95% solution of ethanol in water) by distillation of the solution which results from the fermentation of sugars.

Manufacture

There are two major industrial pathways to ethanol. Ethanol, which is intended for industrial use, is made by the first method, while ethanol intended for food use tends to be made by the second method.

First method:

Reaction of Ethene with Steam

Most of the ethanol used in industry is made, not by alcoholic fermentation, but by an addition reaction between ethene and steam.

C2H4 + H2O ==> C2H5OH

Ethene Steam Ethanol

Second method:

Alcoholic Fermentation

- A solution of sucrose, to which yeast is added, is heated. An enzyme, invertase, which is present in yeast is added and this acts as a catalyst to convert the sucrose into glucose and fructose.,
-
- **invertase**
- **$C_{12}H_{22}O_{11} + H_2O \Longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$**
- **Sucrose Glucose Fructose**
- The glucose, $C_6H_{12}O_6$, and fructose, $C_6H_{12}O_6$, formed are then converted into ethanol and carbon dioxide by another enzyme, zymase, which is also present in yeast.
-
- **zymase**
- **$C_6H_{12}O_6 \Longrightarrow 2C_2H_5OH + 2CO_2$**
- **Ethanol**

The fermentation process takes three days and is carried out at a temperature between 250C and 300C. The ethanol is then obtained by fractional distillation.

Absolute Ethanol

Whatever method of preparation is used, the ethanol is initially obtained in admixture with water. The ethanol is then extracted from this solution by fractional distillation.

Although the boiling point of ethanol, 78.3 degC, is significantly lower than the boiling point of water, 100 degC, these material cannot be separated completely by distillation. Instead, an azeotropic mixture (i.e. a mixture of 95% ethanol and 5% water) is obtained, and the boiling point of the azeotrope is 78.15oC. In a distillation, the most volatile material (i.e. the material that has the lowest boiling point) is the first material to distill from the distillation flask, and this material is the azeotrope of 95% ethanol which has the lowest boiling point. If an efficient fractionating column is used, there is obtained first 95% alcohol, then a small intermediate fraction of lower concentration, and then water. But no matter how efficient the fractionating column used, 95% alcohol cannot be further concentrated by distillation.

The separation of a mixture by fractional distillation occurs because the vapour has a different composition from the liquid from which it distils (i.e. the vapour is richer in the more volatile component). We cannot separate 95% alcohol into its components by distillation, because here the vapour has exactly the same composition as the liquid; towards distillation, then, 95% alcohol behaves exactly like a pure compound.

A liquid mixture that has the peculiar property of giving a vapour of the same composition is called an azeotrope (i.e. a constant-boiling mixture). Since it contains two components 95% alcohol is a binary azeotrope. Most azeotropes, like 95% alcohol, have boiling points lower than those of their components, and are known as minimum-boiling mixtures. Azeotropes having boiling points higher than those of their components are known as maximum-boiling mixtures.

Cellulosic ethanol

Cellulosic ethanol or cellanol is ethanol fuel produced from cellulose, a naturally occuring complex carbohydrate polymer commonly found in plant cell walls. Cellulosic ethanol is chemically identical to ethanol from other sources, such as corn or sugar, and is available in a great diversity of biomass including waste from urban, agricultural, and forestry sources. However, it differs in that it requires an extra processing step called cellulolysis – breaking cellulose down into sugars.

There are at least two methods of production of cellulosic ethanol (see "Production methods", below):

- Cellulolyic method: hydrolysis followed by fermentation of the generated free sugars.
- Gasification, also called synthesis gas fermentation or catalysis (e.g., the Fischer-Tropsch process).

Neither process generates toxic emissions when it produces ethanol.

Cellulosic ethanol production currently exists at "pilot" and "commercial demonstration" scale, including a plant in China engineered by SunOpta Inc. and owned and operated by China Resources Alcohol Corporation (CRAC) that is currently producing cellulosic ethanol from corn stover (stalks and leaves) on a continuous, 24-hour per day basis.One of the benefits of cellulosic ethanol is that it reduces greenhouse gas emissions (GHG) by 85% over reformulated gasoline. By contrast, starch ethanol (e.g., from corn), which most frequently uses natural gas to provide energy for the process, reduces GHG emissions by 18% to 29% over gasoline. Sugar ethanol is cheaper than corn ethanol. Cellulosic ethanol from sugarcane bagasse, reduces greenhouse gas emissions by as much as cellulosic ethanol. In both cases the waste lignin becomes fuel to provide the energy for the process with some excess to provide electricity for the grid.

Converting Orange Peels into Cellulosic Ethanol

Producing approximately 5 million tons of citrus peel waste annually, the Florida orange juice industry has the potential to provide up to 60 million gallons of cellulosic ethanol Although 60 million gallons of cellulosic ethanol per year would not even come close to satisfying U.S. fuel demand, this hasn't stopped companies from seeing the economic and environmental benefits the technology would offer consumers on a regional scale. Really, the citrus waste conversion to ethanol, would be a local biomass source in Florida," said Widmer, noting that amount could meet a local demand for oxygenating fuel additives in central Florida as well as generating additional revenue for citrus growers. The citrus waste, a pectin, cellulose and soluble sugar rich mixture of peel, segment membranes and seeds is available at no cost and in large volumes with potentially no transportation costs since companies like Florida-based Citrus Energy LLC, and newly incorporated Southeast Biofuels, plan to build biorefineries in the local vicinity or co-locate at the citrus processing facility itself. Xethanol, which formed a joint venture with Renewable Spirits last year to create Southeast Biofuels, plans to build a pilot plant this year with the potential to produce up to 50,000 gallons of ethanol from the citrus waste. Citrus Energy LLC, which plans to build a four million gallon per year ethanol biorefinery in Florida, notes the citrus waste to ethanol technology is able to take advantage of a feedstock where the primary costs of growing, harvesting and collection are supported by the existing product stream. Currently, citrus waste from orange juice processing companies is dried into citrus pulp pellets and fed to cattle with little or no return on investment. In addition, during the drying process toxins are released requiring citrus processing companies to install costly equipment to ensure that organic emissions do not escape into the atmosphere.

However, those emissions are negated in the citrus-to-ethanol conversion process since no drying takes place, and the by-products, such as limonene (a valuable ingredients in commercial cleaning products) can be marketed at an additional profit. Approximately half a pound of peel oil is produced for every gallon of ethanol produced, said Widmer. Fermentation of the sugars is done using traditional brewers yeast and the resulting 'beer' has the ethanol separated and converted to fuel grade ethanol using a distillation and dehydration process. However, Widmer notes there are still minor hurdles left to overcome in the laboratory with the citrus to ethanol conversion process. After stripping the alcohol we still end up with a residue that we need to get rid of -- about one-third of the solid is still there and the short term solution right now is to dry that, and produce cattle feed from it.

But with more research, material from the residue left after limonene removal and ethanol production could be turned into other profitable industrial products, such as building-material additives for concrete.

Production methods

There are two ways of producing alcohol from cellulose:

1. Cellulolysis processes which consist of hydrolysis on pretreated lignocellulosic materials followed by fermentation and distillation.
2. Gasification that transforms the lignocellulosic raw material into gaseous carbon monoxide and hydrogen. They are then fed into a special kind of fermenter or to a catalyst bed.

They both include fermentation and distillation as final steps.

Cellulolysis (Biological approach)

There are four or five stages to produce ethanol using a biological approach:

1. A "pretreatment" phase, to make the lignocellulosic material such as wood or straw amenable to hydrolysis,
2. Cellulose hydrolysis (cellulolysis), to break down the molecules into sugars;
3. Separation of the sugar solution from the residual materials, notably lignin;
4. Microbial fermentation of the sugar solution;
5. Distillation to produce 99.5% pure alcohol.

Pretreatment

Although cellulose is the abundant resource in plant materials, its susceptibility has been curtailed by its rigid structure. As the result, an effective pretreatment is needed to liberate the cellulose from the lignin seal and its crystalline structure so as to render it accessible for a subsequent hydrolysis step By far, most pretreatments are done through physical or chemical means. In order to achieve higher efficiency, some researchers seek to incorporate both effects

To date, the available pretreatment techniques include acid hydrolysis, steam explosion, ammonia fiber expansion, alkaline wet oxidation and ozone pretreatment. Besides effective cellulose liberation, an ideal pretreatment has to minimize the formation of degradation products because of their inhibitory effects on subsequent hydrolysis and fermentation processes The presence of inhibitors will not only further complicate the ethanol production and but also increase the cost of production due to entailed detoxification steps. Even though pretreatment by acid hydrolysis is probably the oldest and most studied pretreatment technique, it produces several inhibitors including furfural and hydroxylcarboxylic acids (HMF) which are by far regarded as the most toxic inhibitors present in lignocellulosic hydrolysate. In fact, Ammonia Fiber Expansion (AFEX)is the sole pretreatment which features promising pretreatment efficiency with no inhibitory effect in resulting hydrolysate

Cellulolytic processes

The cellulose molecules are composed of long chains of sugar molecules of various kinds. In the hydrolysis process, these chains are broken down to free the sugar, before it is fermented for alcohol production.There are two major cellulose hydrolysis (cellulolysis) processes: a chemical reaction using acids, or an enzymatic reaction.

Chemical hydrolysis

In the traditional methods developed in the 19th century and at the beginning of the 20th century, hydrolysis is performed by attacking the cellulose with an acid. Dilute acid may be used under high heat and high pressure, or more concentrated acid can be used at lower temperatures and atmospheric pressure. A decrystalized cellulosic mixture of acid and sugars reacts in the presence of water to complete individual sugar molecules (hydrolysis). The product from this hydrolysis is then neutralized and yeast fermentation is used to produce ethanol. As mentioned, a significant obstacle to the dilute acid process is that the hydrolysis is so harsh that toxic degradation products are produced that can interfere with fermentation. Concentrated acid must be separated from the sugar stream for recycle (simulated moving bed (SMB) chromatographic separation for example) to be commercially attractive.

Enzymatic hydrolysis

Cellulose chains can be broken into glucose molecules by cellulase enzymes.

This reaction occurs at body temperature in the stomach of ruminants such as cows and sheep, where the enzymes are produced by bacteria. This process uses several enzymes at various stages of this conversion. Using a similar enzymatic system, lignocellulosic materials can be enzymatically hydrolyzed at a relatively mild condition (50°C and pH5), thus enabling effective cellulose breakdown without the formation of byproducts that would otherwise inhibit enzyme activity. By far, all major pretreatment methods, including dilute acid pretreatment, require enzymatic hydrolysis step to achieve high sugar yield for ethanol fermentation.

Various enzyme companies have contributed significant technological breakthroughs in cellulosic ethanol through the mass production of enzymes for hydrolysis at competitive prices.

Another Canadian company, SunOpta Inc. markets a patented technology known as "Steam Explosion" to pre-treat cellulosic biomass, overcoming its "recalcitance" to make cellulose and hemicellulose accessible to enzymes for conversion into fermenatable sugars. SunOpta designs and engineers cellulosic ethanol biorefineries and its process technologies and equipment are in use in the first 3 commercial demonstration scal plants in the world : Celunol Corporation's facility in Jennings, Louisiana, Abengoa's facility in Salamanca, Spain, and a facility in China owned by China Resources Alcohol Corporation (CRAC). The CRAC facility is currently producing cellulosic ethanol from local corn stover on a 24-hour a day basis utilizing SunOpta's process and technology.

Genencor and Novozymes are two other companies that have received United States government Department of Energy funding for research into reducing the cost of cellulase, a key enzyme in the production of cellulosic ethanol by enzymatic hydrolysis.

Other enzyme companies, such as Dyadic International, Inc. (AMEX: DIL), are developing genetically engineered fungi which would produce large volumes of cellulase, xylanase and hemicellulase enzymes which can be utilized to convert agricultural residues such as corn stover, distiller grains, wheat straw and sugar cane bagasse and energy crops such as switch grass into fermentable sugars which may be used to produce cellulosic ethanol.

Diversa (NASDAQ: DVSA) recently entered the cellulosic market with its acquisition of Celunol, a leading developer of enzymes used for cellulosic ethanol.

Microbial fermentation

Traditionally, baker's yeast (*Saccharomyces cerevisiae*), has long been used in brewery industry to produce ethanol from hexoses (6-carbon sugar). Due to the complex nature of the carbohydrates present in lignocellulosic biomass, a significant amount of xylose and arabinose (5-carbon sugar) also present in the hydrolysate. For example, in the hydrolysate of corn stover, approximately 30% of the total fermentable sugars is xylose. As a result, the ability of the fermenting microorganisms to utilize the whole range of sugars available from the hydrolysate is vital to increase the economic competitiveness of cellulosic ethanol and potentially bio-based chemicals.

In recent years, metabolic engineering for microorganisms used in fuel ethanol production has shown significant progress .Besides *Saccharomyces cerevisiae*, microorganisms such as *Zymomonas mobilis* and *Escherichia coli* have been targeted through metabolic engineering for cellulosic ethanol production.

Combined hydrolysis and fermentation

Some species of bacteria have been found capable of direct conversion of a cellulose substrate into ethanol. One example is *Clostridium thermocellum*, which utilizes a complex cellulosome to break down cellulose and synthesize ethanol. However, *C. thermocellum* also produces other products during cellulose metabolism, including acetate and lactate, in addition to ethanol, lowering the efficiency of the process. Some research efforts are directed to optimizing ethanol production by genetically engineering bacteria that focus on the ethanol-producing pathway.

Gasification process (Thermochemical approach)

Fluidized Bed Gasifier in Güssing Burgenland Austria

The gasification process does not rely on chemical decomposition of the cellulose chain (cellulolysis). Instead of breaking the cellulose into sugar molecules, the carbon in the raw material is converted into synthesis gas, using what amounts to partial combustion. The carbon monoxide, carbon dioxide and hydrogen may then be fed into a special kind of fermenter. Instead of yeast, which operates on sugar, this process uses a microorganism named "Clostridium ljungdahlii"This microorganism will ingest (eat) carbon monoxide, carbon dioxide and hydrogen and produce ethanol and water. The process can thus be broken into three steps:

1. Gasification — Complex carbon based molecules are broken apart to access the carbon as carbon monoxide, carbon dioxide and hydrogen are produced
2. Fermentation — Convert the carbon monoxide, carbon dioxide and hydrogen into ethanol using the *Clostridium ljungdahlii* organism
3. Distillation — Ethanol is separated from water

Alternatively, the synthesis gas from gasification may be fed to a catalytic reactor where the synthesis gas is used to produce ethanol and other higher alcohols as well

Production Process

The basic steps for large scale production of ethanol are: microbial (yeast) fermentation of sugars, distillation, dehydration (required unless distillation is done well and/or repeatedly), and denaturing (optional). Prior to fermentation, some crops require saccharification or hydrolysis into carbohydrates. Saccharification of cellulose is called cellulolysis(see cellulosic ethanol). Other pre-production steps can be necessary for certain crops like corn which requires refinment into starch and liquification.

Fermentation

Ethanol is produced by microbial fermentation of the sugar. Subsequent processing is the same as for ethanol from corn. Production of ethanol from sugarcane (sugarcane requires a tropical climate to grow productively) returns about 8 units of energy for each unit expended compared to corn which only returns about 1.34 units of fuel energy for each unit of energy expended.Carbon dioxide, a potentially harmful greenhouse gas, is emitted during fermentation. However, this is cancelled out by the greater uptake of carbon dioxide by the plants as they grow to produce the biomass.When compared to gasoline, depending on the production method, ethanol releases less or even no greenhouse gases

Catalytic Synthesis

This is the process that Syntec will use to produce ethanol. Syngas can be derived from renewable sources either through reforming of digester gas or biomass gasification. The syngas is then reacted into ethanol through a catalyst at the right pressure and temperature. This process can use a wide variety of feedstock, but has yet to be demonstrated on a commercial scale.

Enzymatic Fermentation

This process adds an extra step to the fermentation process. Enzymes are used to break cellulose and hemi-cellulose into sugars. The sugars are then fermented into ethanol. While this process can use some of the cellulosic feedstock, the additional processing required from using enzymes and the cost of enzymes add to the cost of production.

Dilute Acid Hydrolysis Fermentation

This process uses dilute acid in a two steps process to break down hemi-cellulose and cellulose under high temperature and pressure. The additional acid treatment adds cost to the overall process and it tends to produce large amount of byproducts.

Concentrated acid solution Fermentation

It uses a concentrated acid solution to break down cellulose and hemi-cellulose into sugars. The sugars are fermented as in a normal fermentation process. Recycling of acid is required for economic reasons, an area where research is still ongoing.

Distillation

For the ethanol to be usable as a fuel, water must be removed. Most of the water is removed by distillation, but the purity is limited to 95-96% due to the formation of a low-boiling water-ethanol azeotrope. The 96% m/m (93% v/v) ethanol, 4% m/m (7% v/v) water mixture may be used as a fuel, and it's called **hydrated ethyl alcohol fuel (álcool etílico hidratado combustível**, or **AEHC** in Portuguese). In 2006/2007, an estimated 17 billion liters (4.5 billion gallons) of hydrated ethyl alcohol fuel will be produced, to be used in ethanol powered vehicles Dehydration

BIO-ETHANOL

THE SYNTHESIS GASFROM BIOETHANOL

Introduction

Progress in Ethanol production from almost any biomass pointsthis liquid as one of themost important renewable fuels for direct use in engines. Ethanol, once converted intothe SynGas (mixture of H2and CO) can also energize high-temperature Fuel Cells, beconsidered as source of Hydrogen to feed the low-temperature Fuel Cells, canfuel the decentralized power generation using robust H2- or SynGas-enhanced engines, etc.

Efficient and non-sooting conversion of Ethanol into the SynGasis however difficult andremains still at the R&D stage. We propose anew process of the Partial Oxidation (POX) of Ethanol into SynGasbased on plasma assistance. Very good results of total and soot-free reforming are obtained using our very simple GlidArc plasma system.The GlidArcassisted reformers of various fuels are also a part of ourGas-to-Liquid technology.

Reformer

The principle of a two-zone reformer is described in1. Tests are performed using a 1.3-L(internal volume) reactor presented on Fig. 1.The reformer is thermally insulated fromoutside to keep both zoneshot. We pilot the process *via* temperature measurementsin fivepoints.

Feed

Ethanol (90° grade) or its water solution (70, 60, or 50 wt.%) isdosed by a pump that sucks the liquid from a scale for precise inputflow rate measurements. Atmospheric air at close to 1 bar pressure isused as oxidant at various flow rates. The reactants enter the double-wall reformer where they are preheated in order to integrate a waste heat for better thermal efficiency. The mix is then blown into the GlidArc discharge space. The POX process is then achieved in the post-plasma zone.

To start the cold reformer an injection of a limited amount ofEthanol to the air flowing through the GlidArc plasma of 0.2 kWpower is applied. After 20 minutes of such preheating when the temperature of upper part of the level of the granules reaches 800°C

we increase the Ethanol flow rate getting almost immediately theSynGas. During next 30 minutes the reformer reaches its thermalsteady state. Mostly we run the tests whole day at various air and Ethanol flow rates and then, after the shutdown of the GlidArc power

and Ethanol flow the reformer is cooled at a very limited air flow rate.Almost one hundred complete tests with SynGas analyses wereperformed.

More energy is contained in the ethanol and the other by-products of corn processing than is used to grow the corn and convert it into ethanol and by-products. If corn farmers use state-of-the-art, energy efficient farming techniques and ethanol plants integrate state-of-the-art production processes, then the amount of energy contained in a gallon of ethanol and the other by-products is more than twice the energy used to grow the corn and convert it into ethanol.As the ethanol industry expands, it may increasingly rely on more abundant and potentially lower-cost cellulosic crops (i.e. fast growing trees, grasses, etc.). When that occurs, the net energy of producing ethanol will become even more attractive.

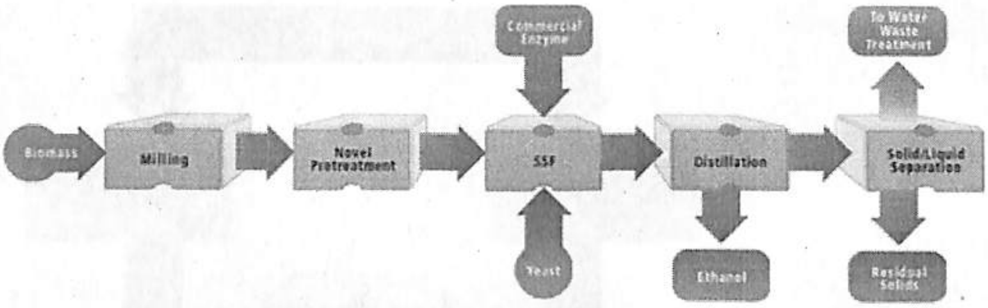
Biomass Enzymatic Hydrolysis

Corn harvesting generates a large amount of biomass residues, which are comprised of stalks, leaves, and cobs. These agricultural residues are normally left in the field and used as an organic source for the soil. A substantial amount of these residues could be collected and used as raw material for bioethanol production, without affecting soil quality.

Compared with dry-mill process, production of bioethanol from agricultural residues, specifically, corn stover. and wheat straw, requires extensive processing to release the polymeric sugars in cellulose and hemicellulose that account for 30 to ?50% and 20? to 35% of plant material, respectively. ABRD is developing a novel biomass-to-ethanol process, with emphasis on thermochemical fractionation and enzymatic hydrolysis to release these sugars for ethanol fermentation. Our process technology is based on the following criteria: ? Best available technology demonstrated at bench scale and preferably at pilot-plant scale; ? Potential for further improvement to be competitive with starch-based bioethanol production; ?

Compatibility with grain bioethanol production process to achieve synergistic gains when integrating the stover-to-bioethanol plant with the grain bioethanol production facility (for example, the two processes could share utilities and even certain process equipment).

ABRD is conducting a two-stage technology effort for the development of the biomass enzymatic hydrolysis process. The first stage is the bench-scale R&D research effort to study the feasibility of the technology and confine the optimal operational conditions range. The second stage is the pilot-plant-scale demonstration of the technology to generate pertinent engineering and operation data that is required for the design of a commercial scale plant. Process simulation using Aspen Plus modeling is being used by ABRD to evaluate the overall technoeconomic performance of the process.

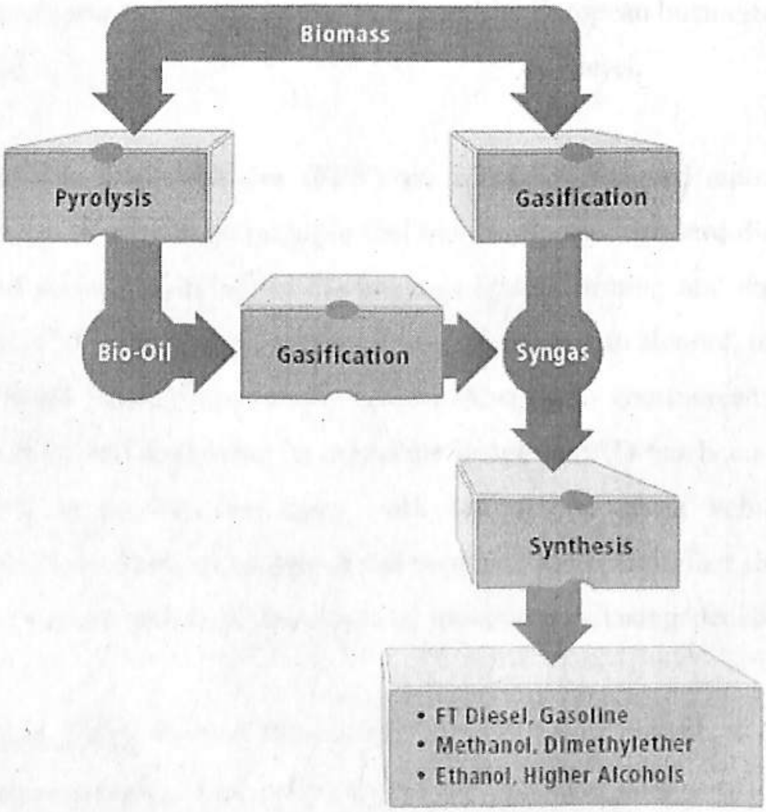


ThermochemicalConversionofBiomass

Agricultural residues like corn stover and straw can be used for production of useful fuels, chemicals and energy. In the thermochemical approach, the biomass first undergoes a severe heat treatment. In the presence of a controlled amount of oxygen, a process called gasification takes place. The product from gasification is called the synthesis gas or syngas, composed mainly from hydrogen and carbon monoxide. If the process is conducted in the absence of oxygen, the process is called pyrolysis which, under certain conditions, might yield predominantly a liquid product named bio-oil.

The syngas can be used in a catalytic process for the synthesis of a variety of products. In a Fischer-Tropsch (FT) process, the syngas will be used for the production of transportation fuels like diesel and gasoline, along with other chemicals. The syngas can be used as well for the synthesis of methanol, ethanol and other alcohols. These in turn can be used as transportation fuels or as chemical building blocks. The bio-oil can be burned for direct energy production in a combustion process or can be gasified to syngas. Another potential use is the extraction of chemicals.

ABRD is studying various routes for the thermochemical conversion of the biomass with the goal of selecting the technology with the most promising technical and economical attributes. In a further stage, an investigation at the pilot-plant scale will provide the data necessary for the design of a commercial-scale plant.



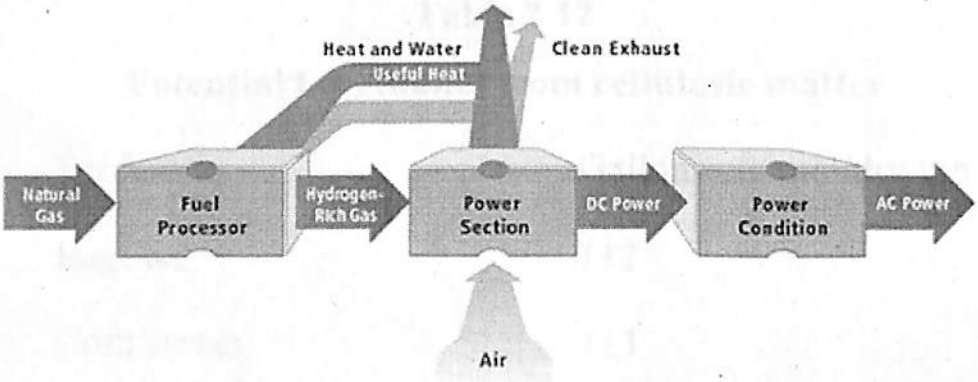
Biothanol Utilization

Bioethanol can be used as a fuel, as an additive to fuel or fuel extender, and as an industrial chemical. Most of the fuel bioethanol in the U.S. and Canada is used as a gasoline extender and an octane enhancer to replace MTBE (Methyl Tertiary-Butyl Ether) by direct blending into gasoline. A 10% volume bioethanol blend (E10), which is called gasohol, can increase octane by two to three points, providing a valuable additive to mid-to-low-octane gasolines. Fuel ethanol can also be used as E85, a mixture of 85% bioethanol and 15% gasoline. E85 is used in Flexible Fuel Vehicles (FFV) specially designed to consume this fuel.

However, in Europe, the bioethanol limit is controlled by the oxygen content limit of 2.7%, which equates to a bioethanol limit of 7.8%. No waiver for bioethanol blends higher than 7.8% is provided. The typical blend of 5% bioethanol is used in some European countries. Instead of using bioethanol, ETBE (Ethyl Tertiary-Butyl Ether) is the renewable oxygenate additive preferred by European refiners and car manufacturers. In order to increase the bioethanol market and demonstrate programs for bioethanol end uses, ABRD conducts research and development in several areas to support its European business, including ETBE, FFV, fuel cell, and E-Diesel, etc.

Flexible Fuel Vehicles (FFV) are specially designed automobiles or light trucks with the ability to operate on multiple fuel blends. Special onboard diagnostics can read the fuel blend, and automatically adjust the engine's ignition timing and air/fuel mixture ratios accordingly. The FFV can use fuels with any ratio of gasoline to alcohol, or use normal gasoline directly. As a world-leading bioethanol producer, Abengoa is continuously promoting the use of bioethanol as fuels and improving its corporate image. ABRD has been involved in experimental tests of FFV to provide consumers with information about vehicle performance, handling, and emissions. Data are collected and analyzed to generate fact sheets to educate and assist general consumers and fleet managers in making purchasing decisions on alternative fuel vehicles.

Fuel Cell: One of the newest markets being looked at for bioethanol uses is fuel cells. Electrochemical fuel cells convert the chemical energy of bioethanol directly into electrical energy to provide a clean and highly efficient energy source. Fuel cells work similarly to batteries except they can run continuously as long as fuel is supplied, and they can obtain 40 to 50% efficiency in conversion of the fuel energy into useable power, compared with approximately 18% efficiency for the average internal combustion engine. Besides high efficiency, other benefits of fuel cell use in the transportation sector include a tremendous decrease in emissions, less vehicle maintenance and the ability to achieve up to 80 mpg. Fuel cell's could eventually be used to supply power to homes, vehicles, and small electronic devices.



Bioethanol is one of the most ideal fuels for a fuel cell. Besides the fact that it comes from renewable resources, highly purified bioethanol can solve the major problem of membrane contamination and catalyst deactivation within the fuel cell, which limits its life expectancy. In order to develop a common vision of the role that bioethanol can play in the developing fuel cell industry, ABRD has been involved in research and development of bioethanol fuel cell technologies. These research activities will ensure that bioethanol remains among the most desirable fuels for fuel cells, delivering all the benefits that the bioethanol fuel cell technologies promise.

Biomass for Bio-ethanol

Ethanol made from cellulosic biomass is called bioethanol. A major challenge is developing biocatalysts capable of fermenting lignocellulosic biomass for efficient industrial application. In the coming years it is believed that cellulosic biomass will be the largest source of bioethanol. The broad category of biomass for the production of ethanol includes agricultural crops & residues and wood. Biomass resources are abundant and have multiple application potential. Among the various competing processes, bioethanol from lignocellulosic biomass appears to have near-term economic potential. The crops residues such as rice straw, bagasse etc are not currently used to . derive desired economic and environmental benefits and thus they could be important resource bases for bioethanol production. The table below indicates potential of such biomass for ethanol production.

Table 2.12

Potential for ethanol from cellulosic matter

Feedstock	Gallons ethanol/dry ton
Bagasse	112
Corn stover	113
Rice straw	110
Forest thinnings	82
Hardwood sawdust	101
Mixed paper	116

TECHNOLOGY

Technologies for Manufacture of Bioethanol

The degree of complexity and feasibility of biomass conversion to ethanol depends on the nature of the feedstock. The three largest components of the biomass sources are cellulose ,hemicellulose, and lignin ranges of which are presented in Table 2.13. Ranges of sugar content in hardwoods, softwoods, and agricultural residues are provided in Table 2.14. Lignin remains as residual material after the sugars in biomass have been fermented to ethanol. Economic use of this byproduct is critical to the financial feasibility of biomass-to-ethanol technology.

Table 2.13:

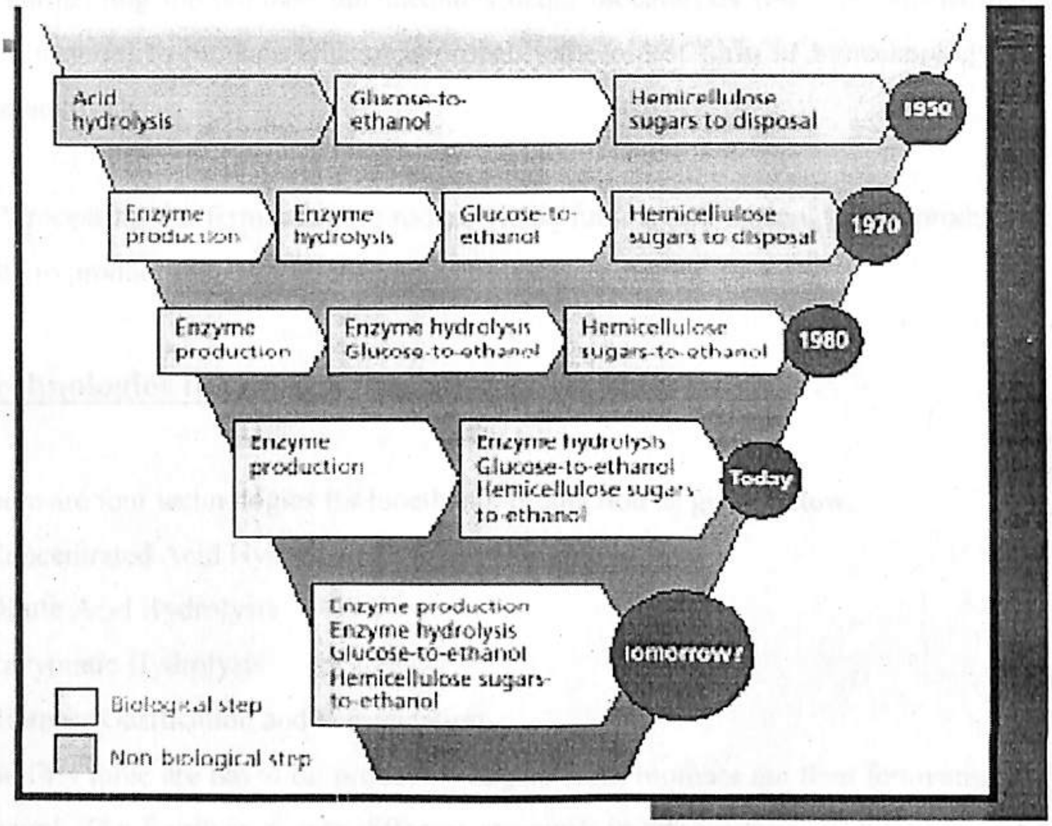
Typical levels of cellulose, hemicellulose and lignin in biomass

Component	Percent Dry Weight
Cellulose	40-60%
Hemicellulose	20-40%
Lignin	10-25%

Table 2.14:

Sugar and Ash Composition of Various Biomass Feedstocks (Weight Percent)

Material	Sugars	Lignin	Ash
Hardwoods	57-78%	15-28%	0.3-1.0%
Softwoods	49-69%	24-27%	0.1-0.4%
Ag Residues	42-81%	11-29%	2-18%



DEVELOPMENTS IN BIOETHANOL PRODUCTION TECHNOLOGIES'

Process steps

There are four basic steps in cony\~rtingbiomass to bioethanol:

1. Producing biomass results in the fixing of atmospheric carbon dioxide into organic carbon.

2. Converting this biomass-o a useable fermentation feedstock (typically someform of sugar) can be achieved using a variety of different process technologies. These processesfor fermentationfeedstoc~(production constitute the critical differences among all of the bioethanol technology optIOns.

3. Fermenting the biomass intermediates using biocatalysts (microorganisms including yeast and bacteria) to produce ethanol is probably the oldest form of biotechnology developed by humankind..

4. 'Processing the fermentation product yields fuel- grade ethanol and byproducts that can be used to produce other fuels, chemicals, heat and/or electricity.

Technologies for production of bioethanol

There are four technologies for bioethanol production as given below.
. Concentrated Acid Hydrolysis
. Dilute Acid Hydrolysis
. Enzymatic Hydrolysis
. Biomass Gasification and Fermentation
The first three are based on producing sugars from biomass ani then fermenting the sugars to ethanol. The fourth is a very different approach involving thermal processing of biomass to gaseous hydrogen and carbon monoxide, followed by fermentation to ethanol.

Concentrated Acid Hydrolysis

This process is based on amcentrated acid decrystallization of cellulose followed by dilute acid hydrolysis to sugars. Separation of acid from sugars, acid recovery, and acid reconcentration are critical unit operations. Fermentation converts sugars to ethanol. The concentrated sulfuric acid process has been commercialized in the past, particularly in the former Soviet Union and Japan. However, these processes were only successful during times of national crisis, when economic competitiveness of ethanol production could be ignored. They cannot be economical because of the high volumes of acid required. Improvements in acid sugar separation and recovery have opened the door for commercial application. Two companies in the United States(Arkenol and Masada) are currently working with DOE and NREL to commercialize this technology

Arkenol holds a series of patents on the use of concentrated acid to produce ethanol. They are currently working with DOE to establish a commercial facility that will convert rice straw to ethanol. Arkenol plans to take advantage of opportunities for obtaining rice straw a cheap feedstock in the face of new regulations that would restrict the current practice of open field burning of rice straw. Arkenol's technology further improves the economics of raw straw conversion by allowing for the recovery and purification of silica present in the straw. NREL is working with Arkenol to develop a recombinant*Zymomonas Mobilis* strain for the project. The facility is located in Sacramento County.

Masada Resource Group holds several patents related to municipal solid waste (MSW)-to-ethanol conversion. DOE and NREL have been working with Masada to support their MSW-to-ethanol plant, which is located in Middletown, NY. The plant will process the lignocellulosic fraction of municipal solid waste into ethanol using technology based on concentrated sulfuric acid process. The robustness of this process makes it well suited to complex and highly variable feedstocks like municipal solid waste to take advantage of relatively high tipping fees available in the area for collection and disposal of municipal solid waste.

Dilute Acid Hydrolysis

Hydrolysis occurs in two stages to maximize sugar yields from the hemicellulose and cellulose tractions of biomass. The first stage is operated under milder conditions to hydrolyze hemicellulose, while the second stage is optimized to hydrolyze the more resistant cellulose fraction. Liquid hydrolyzates are recovered from each stage, neutralized, and fermented to ethanol. There is quite a bit of industrial experience with the dilute acid process. Germany, Japan, and Russia have operated dilute acid hydrolysis percolation plants off and on over the past 50 years. However, these percolation designs would not survive in a competitive market sitwtion. Today, companies are beginning to look at commercial opportunities for this technology, which combine recent improvements and niche opportunities to solve environmental problems.

Enzymatic Hydrolysis

The first application of enzymes to wood hydrolysis in an ethanol process was to simply replace the cellulose acid hydrolysis step with a cellulase enzyme hydrolysis step. This is called separate hydrolysis and fermentation. An important process modification made for the enzymatic hydrolysis of biomass was the introduction of simultaneous saccharification and fermentation (SSF), which has recently been improved to include the co-fermentation of multiple sugar substrates. In the SSF process, cellulase and fermenting microbes are combined. As sugars are produced, the fermentative organisms convert them to ethanol. Enzymati: hydrolysis will be used in IogenlPetro Canada's Ottawa, Canada project and is being explored for BCl's Gridely project. The current high cost of cellulase enzymes is the key barrier to economical production of bioethanol from lignocellulosic material, research is on to achieve a tenfold reduction in the cost of these enzymes.

Cellulase Enzyme Research

The goal is to reduce the cost of using cellulase enzymes in the bioethanol process by employing cutting-edge and efficient biochemical technologies. The current estimate for cellulase ranges from 30 to 50 cents per gallon of ethanol produced. The objective is to reduce cellulase cost to less than 5 cents per gallon of ethanol. This requires a tenfold increase in specific activity or production efficiency or some combination thereof. Nearer-term goals include a threefold increase in cellulase-specific activity (relative to the Trichoderma reesei system) by FY 2005.

manipulation of microbes. This may be possible by genetic

Biomass Gasification and Fermentation

Biomass can be converted to synthesis gas (consisting primarily of carbon monoxide, carbon dioxide, and hydrogen) via a high temperature gasification process. Anaerobic bacteria are then used to convert the synthesis gas into ethanol. Bioresource Engineering Inc. has developed synthesis gas fermentation technology that can be used to produce ethanol from cellulosic wastes with high yields and rates. The feasibility of the technology has been demonstrated, and plans are under way to pilot the technology as a first step toward commercialization. The conversion of a waste stream, the disposal of which is costly, into a valuable fuel adds both environmental and economic incentives. The yields can be high because all of the raw material, except the ash and metal, is converted to ethanol. BRI has developed bioreactor systems for fermentation that results in retention times of only a few minutes at atmospheric pressure and less than a minute at elevated pressure. These retention times result in very economical equipment costs. The biocatalyst is automatically regenerated by slow growth of the bacteria in the reactor.

Development of Microbes

Microorganisms that ferment sugars to ethanol include yeasts and bacteria. Research has focused on expanding the range and efficiency of the organisms used to convert sugar to ethanol. Breakthroughs in fermentation technology in the past decade lead to commercialization of biomass conversion technology For most of this century, researchers assumed that many of the sugars contained in biomass were not fermentable particularly those contained in hemicellulose. This meant that as much as 25% of the sugars in biomass were out of bounds as far as ethanol production was concerned. In the 1970s and 80s, microbiologists discovered microbes that could ferment these sugars, albeit slowly and inefficiently. With the advent of new tools in the emerging field of biotechnology, researchers at DOE labs and at universities acrossUSA, have succeeded in producing several new strains of yeast and bacteria(E. coli;Zymomonas, Saccharomyces) that exhibit varying degrees of ability to ferment the full spectrum of available sugars to ethanol. Today's ethanol producers are turning their attention to com fiber-the shell of the kernel as a source of additional sugars for ethanol production. But, com fiber, like other forms of biomass, contains sugars that are not fermentable by today's industrial fermentation organisms. Research is on to tailor new microbes that can ferment these specific sugars.

Raw materials for making bioethanol

Ethanol producers in the United States produce around 1.5 billion gallons of ethanol each year, mostly derived from com. As demand for ethanol increases, other biomass resources, such as agricultural and forestry wastes, municipal solid wastes, industrial wastes, and crops grown solely for energy purposes, will be used to make ethanol. Research activities over the past 20 years have developed technology to convert these feedstocks to ethanol Fuel ethanol is currently produced from the easily fermented sugars and starches in grain and food processing wastes. Soon, new technologies will be economically viable for converting plant fiber to ethanol. A portion of the agricultural and forestry residues (com stover ,stalks, leaves, branches) which are presently burned or left in the field may therefore be harvested for biofuel production. There will be many benefits by connecting the established com ethanol industry with the elrerging technologies that produce ethanol from agricultural wastes and other types of biomass.

ENERGY REQUIRE TO MAKE ETHANOL

The data in Table 1 for ethanol production are contained in the section titled Processing Energy Input. They are based on the weighted average of both wet and dry milling operations that produce at least 10 million gallons per year.10 Table 3 presents these energy requirements for both wet and dry mills. The data is taken from actual plant operations as of early 1995. Ethanol Processing Energy Use for Wet and Dry Mills

	Average(National)		Best Existing(State)		State of te Art (Farmer)	
	Wet Mill (BTU/gal)	Dry Mill (BTU/gal)	Wet Mill (BTU/gal)	Dry Mill (BTU/gal)	Wet Mill (BTU/gal)	Dry Mill (BTU/gal)
Process Steam	35,400	39,000	29,200	26,500	26,000	26,500
Electricity	17,103 (2.07 kWh)	9,915 (1.2 kWh)	8,676 (1.05 kWh)	4,957 (0.6 kWh)	5,872 (0.9 kWh)	3,915 (0.6 kWh)
Bulk Transport	1,330	1,330	1,100	1,100	800	800
Other (process)	1,450	1,450	1,282	1,282	1,050	1,050
Processing Total	55,283	51,695	40,258	33,839	33,722	32,265

THE ETHANOL AS A FUTURE FUEL

The modern motor fuel grade ethanol industry is only 18 years old. Early plants were very inefficient. Indeed, in 1980 a typical ethanol plant all by itself consumed more energy than was contained in a gallon of ethanol. Some plants used as much as 120,000 BTUs to produce a gallon of ethanol that contained only 84,100 BTUs of energy.

In the last decade many ethanol plants have become much more energy efficient. In 1980, for example, ethanol plants used 2.5 to 4.0 kWh of electricity per gallon of ethanol produced. Today they use as little as 0.6 kWh. The majority of ethanol producers still purchase electricity from outside sources, but newer facilities generate electricity from process steam within the plant.

In the late 1970s, ethanol plants did not recover waste heat. Today they do. Old energy intensive rectification and solvent extraction systems required 12,000 BTUs per gallon of ethanol produced. Newer molecular sieves need only 500 BTUs.11 Larger producers have been using molecular sieves for several years. Now smaller plants (20 million gallons per year and less) are starting to incorporate them.

Best-existing and state-of-the-art ethanol plants can achieve energy reductions through a combination of these technological innovations. Molecular sieves reduce distillation energy significantly; low cost cogeneration facilities produce process steam and electricity; and semi-permeable membranes efficiently remove co-products from the process water to reduce the energy requirements of drying.

Wet mills, which account for 63 percent of all ethanol currently produced, extract higher value co-products than dry mills. Co-products from wet mills include corn oil, 21 percent protein feed, 60 percent gluten meal, germ, and several grades of refined starches and corn sweeteners. In dry milling, co-products can include corn oil and distillers dry grain with solubles (DDGS), which is used as animal feed. Carbon dioxide is a fermentation by-product of both milling processes.

Dry mills derive the DDGS co-product from the process water after fermentation occurs. It then requires a significant amount of energy to dry this co-product into a saleable form. Wet mills derive the majority of the co-products before fermentation through mechanical separators, centrifuges, and screens. All told, wet mills require 60 percent more electrical energy than dry mills on average, while requiring 10 percent less thermal energy. These differences are related specifically to the processing of the co-products, and are illustrated in the "Average" column in Table 3.

An integrated, relatively small-scale dry mill could avoid drying energy requirements for co-products. Reeve Agri-Energy in Garden City, Kansas, operates a 10 million gallon per year plant that feeds wet DDGS to its cattle. This operation uses only about 33,000 BTUs to produce a gallon of ethanol. However, a limited number of locations exist with a sufficient number of nearby livestock to justify such an operation, and it would probably not be economical for larger dry milling operations to adopt such practices.

A wider number of wet mills, on the other hand, may be able to achieve the energy use levels noted in the best existing wet mill category in Table 3.

We conclude that the ethanol industry, on average, uses 53,956 BTUs per gallon to manufacture ethanol. The best existing plants use 37,883 BTUs per gallon. Next generation plants will require only 33,183 BTUs per gallon of ethanol produced.

If we add the amount of energy currently used in growing corn on the average farm to the amount of energy used to make ethanol in the average processing plant today, the total is 81,090 BTUs per gallon (Table 1, Column 1). Under the best-existing practices, the amount of energy used to grow the corn and convert it into ethanol is 57,504 BTUs per gallon. Ethanol itself contains 84,100 BTUs per gallon. Thus even without taking into account the energy used to make co-products, ethanol is a net energy generator.
But an analysis that excludes co-product energy credits is inappropriate. The same energy used to grow the corn and much of the energy used to process the corn into ethanol is used to make other products as well. Consequently, we need to allocate the energy used in the cultivation and

production process over a variety of products. This can be done in several ways.

One is by taking the actual energy content of the co-products to estimate the energy credit. For example, 21 percent protein feed has a calorie content of 16,388 BTUs per pound. The problem with this method is that it puts a fuel value on what is a food and thus undermines the true value of the product.Another way to assign an energy value to co-products is based on their market value. This is done by adding up the market value, in dollars, of all the products from corn processing, including ethanol, and then allocating energy credits based on each product's proportion of the total market value. For example, Table 4 shows the material balance and energy allocation based on market value for a typical wet milling process. Here the various co-products account for 43 percent of the total value derived from a bushel of corn, and thus are given an energy credit of 36,261 BTUs per gallon of ethanol.

Our conclusion is that under the vast majority of conditions, the amount of energy contained in ethanol is significantly greater than the amount of energy used to make ethanol, even if the raw material used is corn.

The difference between high and low heat values represents the heat contribution of the condensation of water during combustion. When ethanol is burned, for example, it produces heat and water vapor. As the water vapor condenses it gives off additional heat. Ethanol has a low heat value(LHV) of 76,000 BTUs/gallon, an estimate which more accurately represents the heat content of the fuel in conventional combustion engines. Ethanol has a high heat value of 84,000 BTUs/gallon. In the United States the energy content of fuels conventionally is expressed on a high heat value(HHV) basis. Interestingly, in Europe LHVs are used. The use of either basis does not affect the conclusions of our analysis such as long as the same heat values are used for all inputs and outputs. The estimate of the net energy gain from cellulosic crop-based ethanol is considered conservative. We believe that as this industry develops, the same learning curve that occurred in the starch based ethanol industry will occur in the cellulosic based ethanol industry, fostering a much more positive net energy gain for ethanol production from cellulose.

ETHANOL-FUEL IN AUSTRALIA

Production

There are currently three commercial producers of fuel ethanol in Australia, all on the East Coast. CSR's Sarina distillery and the Rocky Point distillery are located in Queensland and produce ethanol from molasses feedstock. The Manildra Group also produces fuel ethanol from waste starch and grain at a facility near Nowra, New South Wales. The combined capacity of these three producers has been estimated at less than 150 million litres per annum. A number of other prospective producers have projects at various stages of development

Regulation

Legislation imposes a 10% cap on the concentration of fuel ethanol blends. Blends of 90% unleaded petrol and 10% fuel ethanol are commonly referred to as E10. There is also a requirement that retailers label blends containing fuel ethanol on the dispenser.

Taxation

Domestically produced fuel ethanol is currently effectively exempt from excise tax until July 1, 2011 (an excise of 38.143 cents per litre is payable on petrol). From this date, excise will be increased at 2.5 cents per litre annually until it reaches 12.5 cents per litre in 2015.

Government Support

Federal Government support for fuel ethanol includes a voluntary industry biofuels target (encompassing ethanol, biodiesel, and other biofuels) of 350 million litres per annum by 2010, capital grants to current and prospective producers, fuel excise relief, and an effective tariff on imported ethanol until July 1, 2011.

In 2006, the Premiers of both New South Wales and Queensland proposed mandating the blending of ethanol into petrol.

Marketing

E10 is available through service stations operating under the BP, Caltex, Shell and United brands as well as those of a number of smaller independents. Not surprisingly, E10 is most widely available closer to the sources of production in Queensland and New South Wales. E10 is most commonly blended with 91 RON "regular unleaded" fuel.

Ethanol fuel in Brazil

Gasoline on the left, alcohol on the right at a filling station in Brazil

In Brazil, **ethanol fuel** is produced from sugar cane which is a more efficient source of fermentable carbohydrates than corn as well as much easier to grow and process. Brazil has the tropical climate that is required for the productive culture of sugarcane. Brazil has the largest sugar cane crop in the world, and is the largest exporter of ethanol in the world. High government sales taxes on gasoline, as well as government subsidies for ethanol, have cultivated a profitable national ethanol industry. Nearly all fueling stations in Brazil offer a choice of either gasoline type C or hydrated ethanol.

The National Program for Alcohol

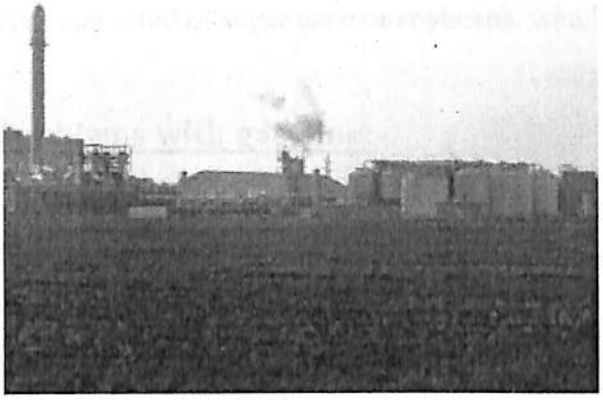
An early poster, prior to flexi-fuel engines, promoting alcohol fuel warns Brazilians not to mix standard petrol with alcohol fuel, and not to use alcohol in unconverted engines With the 1973 oil crisis the Brazilian government, then run by the general Emílio Garrastazu Médici, initiated in 1975 the Pró-Álcool program.The Pró-Álcool or Programa Nacional do Álcool (National Alcohol Program) was a nation-wide program financed by the government to phase out all automobile fuels derived from fossil fuels (such as gasoline in favour of ethanol. It began with the anhydrous alcohol to blend with the gasoline. This mixture has been used since then and is now done with 24% of alcoholand 76% gasoline. The program successfully reduced by 10 million the number of cars running on gasoline in Brazil, thereby reducing the country's dependence on oil imports.

The decision to produce ethanol from fermented sugarcane was based on the low cost of sugar at the time. Other sources of fermentable carbohydrates were tested such as the manioc.

Ethanol fuel in the United States

In 1826, Samuel Morey, experimented with a prototypical internal combustion engine that used ethanol (combined with turpentine and ambient air then vaporized) as fuel. At the time, his discovery was overlooked mostly due to the success of steam power. And while ethanol was known of for decades, it received little attention as a fuel until 1860 when Nicholas Otto began experimenting with internal combustion engines.

In 1859, oil was found in Pennsylvania which provided a new supply of fuel for the United States. A popular fuel in the U.S. before petroleum was a blend of alcohol and turpentine called "camphene", also known as "burning fluid." With the discovery of a ready supply of oil, kerosene's popularity grew.



New energy corporation's 102 mmgy ethanol plant in South Bend, Indiana.

The total energy needed to produce ethanol from corn grain — including fermentation, fertilizing, fuel for farm tractors, harvesting and transporting the grain, building and operating an ethanol plant, and the natural gas used to distill corn sugars into alcohol — is the subject of some debate. Several studies, including one at Berkely and another at Cornell, have shown there is a negative return from the total process. However, no peer-reviewed academic studies show that ethanol production requires more energy than it consumes. According to figures from the state of Minnesota, the ratio for return from corn-based ethanol production is about 1.34:1, or that corn ethanol yields 26% more energy than is used to make it. The return from traditional petroleum-based fuel (gasoline) is .86:1

Ethanol in other countries

Some of the most significant bioethanol fuel programs around the world include that of; Brazil, Colombia, China and the United States.

- Brazil has the largest sugarcane crop in the world, and is one of the largest producers of ethanol in the world. High government sales taxes on gasoline, as well as government subsidies for ethanol, have cultivated a profitable national ethanol industry.
- The United States is largest producer of ethanol with 16 billion liters/year while Brazil produced nearly the same amount (15.5 billion liters).
- Japan imports ethanol from Brazil as part of Brazil-Japan Ethanol.

The United States currently imposes trade restrictions on Brazilian ethanol in order to encourage domestic ethanol production, most of which has so far been based on processing corn consisted of sugar cane or soybeans, which is much less efficient.

Problems with gasoline:

Besides the problem associated with the finiteness of petroleum reserves there is the problem of pollution caused by the engine emissions. Emission of the acid gases cause respiratory problem whereas Nox and CO2 are linked to the climate change problem. CO2 is the major contributor in the GHGs but since all fossil fuels invariably contain carbon there is no way out except increasing the efficiency so that growth in consumption gets retarded. The same is the case with NOx, whose formation during combustion of gasoline or any fuel with air can not be checked. Next is incomplete combustion of the fuel due to very small time to it in the engine and perfect mixing not possible. Partly burnt hydrocarbon emissions from the exhaust of automobile engines are found to be carcinogenic in nature. The problem of incomplete combustion and NOx can be managed by using a catalytic converter in the exhaust. Sulphur compounds, however, poison the catalyst of the converter and so it should not be present in the gasoline. This condition is not compatible with TEL (tetra ethyl lead) which in small quantity is doped in gasoline for Octane improvement..

Octane improvement requirement in gasoline engines:

The average efficiency of Internal Combustion engine is in the range of 30-45%. Among other parameters, compression ratio is an important factor that has a large influence on efficiency. Higher the ratio the better is the efficiency. Problem with gasoline is its knocking tendency when a higher compression ratio is sought in order to achieve higher thermal efficiency. The knocking tendency of the fuel limits the compression ratio of the gas engine that can be used. Different class of hydro-carbons have a difference in their tendency towards resistance to knocking. Oil companies carry out blending of different class of hydro-carbons for increasing the octane rating of the fuel. Still, in the past, they could not achieve a reasonable value of octane number till the discovery of TEL an additive to improve the anti-knocking rating of the fuel dramatically was not made. Addition of TEL in a small quantity became a practice, The harmful effect of the lead led to banning of its use and oil companies were forced to seek other sources of improving the anti-knocking tendency of the gasoline. One is to increase benzene or cyclic compounds in it. Benzene is, however a known carcinogenic material and its content is being limited in the gasoline. Alternatively, MTBE (methyl tertiary butyl ether) and ETBE (ethyl tertiary butyl ether) are being used as additives to improve anti-knocking tendency.

MTBE and ETBE are compounds manufactured from the petroleum source but contain oxygen in addition to hydro-carbons. They are termed as oxygenates and their use improves not only anti-knocking tendency but results in the reduction in other vehicular emissions. The oxygenated fuels bum more completely and so reduce carbon monoxide emission upto 20%.

Problem of the Diesel engine

The major problem with diesel is emission of large particulate matter. US, Environmental Protection Agency, EPA is putting increasingly strict exhaust emissions standard for truck and bus engines. EPA has proposed a gradual reduction of PM reduction from 0.1 glbhp-hr rule in 2002 to 0.01 glbhp-hr in 2006. Even stricter regulations are being initiated in ED. Use of oxygenate is expected to improve combustion efficiency and hence reduction in PM. In India also under the orders of the Supreme Court strict emission norms are being introduced in a phased manner.

.Ethanol as an automotive fuel

While the calorific value of ethanol is lower than that of gasoline by 40% it makes up a part by increased efficiency. So far its use as 100% fuel is concerned it his no problem in designing an engine to run on only ethanol. However, for the reason of compatibility as well as availability its use for blending is only being practised. It can be blended both in diesel as well as gasoline. The advantages and problems associated with the blends are summarised in the following paragraphs.

As can be seen trom above, ethanol improves the octane number, has a higher volumetric efficiency leading to increased power and has advantages of wider flammability limits and higher flame velocity. It has, however, certain disadvantages (i) higher aldehyde emissions, (ii) corrosiveness, affecting metallic parts (iii) higher latent heat of vaporisation causing startability problem, (iv) higher evaporation losses due to higher vapour pressure and (v) requiring large fuel tank due to lower calorific value.

Blends above 15% ethanol would require a few engine modifications to address -

. Corrosion problem of the metal parts.

. Compatible elastomers for oil seals and rubber components.

. Larger orifice for more flow of fuel through carburetor/injector.

. Retarding ignition timing

. increasing compression ratio to take advantage of higher cetane ethanol. number of However, below the 10% value, the disadvantages are not serious and there is no need of modifying the engine, i.e it would be compatible with the blends.

Ethanol as an oxygenate

Ethanol and methanol can serve as oxygenates. Ethanol and MTBE are now the most accepted fuel oxygenates. Compared to MTBE which is petroleum derived and contains 18% oxygen, ethanol is not only renewable but contains 35% oxygen. MTBE is both very water soluble and highly toxic; one teaspoonful being sufficient to contaminate whole water of a large swimming pool. When gasoline is spilled or leaked, it would contaminate ground water. Use of MTBE is going to receive a set back due to recent findings in USA where drinking water is found contaminated with MTBE in a very large section of population (27% of urban water supply) and the state has been asked to phase put MTBE in gasoline. Attempts were made to get a waiver but it was not granted. This clearly leaves the choice to ethanol. Eleven states in USA have acted to curtail MTBE use. With lower use of light vehicles, the MTBE problem may not be as serious as that in USA, still on economical ground, ethanol deserves preference over MTBE.

Oxygenates Permissible in India

Table 2.1

Component	Limit, Percent (V/V), Max
Methanol*	3.0
Ethanol**	5.0
Isporopyl alcohol	5.0
Tertiary butyl alcohol	7.0
Ethers containing five or more carbon atoms	15.0
Other organic oxygenates ***	7.0

* Stabilizing agents essential

** Stabilizing agents may be added

*** Acetone is not permitted.

Table 2.2 Properties Of Conventional & Alcohol Fuels

Characteristics	Diesel	Gasoline	Methanol	Ethanol
Energy content (MJ/kg)	42.5	44.0	20.0	26.9
Heat of vaporisation (KJ/kg)		305		904
Kin Viscosity (mm^2/s)	4.01	0.6		1.5
Boiling point °C	140-360	37-205	65	79
Flash point °C	55-65	-40		13
Auto ignition temperature °C	230	300		366
Flammability limits (%gas in air)	0.0-5.6	1.4-7.6		3.3-19.0
Research octane no.	-25	87-98	106	107
Motor octane no.	-	80-9-	92	89
Cetane no.	45-55	0-5	5	5

Table 2.3 Properites of Most Common Alcohols and Ethers in Oxygenating of Fuels

Property	MeOH	EtOH	MTBE	ETBE	Gasoline
Density, g/ltr	796	789	746	747	730
Boiling point, °C	64	78	55	73	25…230
Heat value, Mj/ltr	15.9	21.2	25.5	27.1	32.6
Carbon, w-%	37.5	52.1	68.1	70.5	86
Oxygen-w-%	49.9	34.7	18.2	15.7	--
Heat of evaporation, kj/l	875	731	240	234	260
Reid vapor pressure, kPa	32	17	54	27	70…100
Vapour pressure in blend, kPa	414	124	62	30	70…100
Octane, RON/MON	133/99	130/96	118/100	118/102	
Blending octane	116	113	109	110	
Solubility in gasoline	Problems	Quite good	Good	Good	

The Oxygenated Fuels Program

Mr. Greenbaum stated that the oxygenated fuels program started before the RFG program as a wintertime program that requires more oxygen to be added to the fuel (2.7 percent by weight oxygen), and is required only in CO non-attainment areas. The data indicate that, with the exception of New York and Los Angeles, all other areas that have this program use ethanol as the oxygenate, and Los Angeles will be moving towards using ethanol given the current decisions in California. In addition, New York is also being redesignated as an area that has attained the standard and, therefore, will not need the winter/oxy program in the future. Mr. Greenbaum asked the Panel to consider whether this is an issue that the Panel needs to discuss and, if so, what should be recommended regarding the program.

It was stated that the New York metropolitan area is comprised of three states, New York, Connecticut, New Jersey. If the Panel recommends any assertions that MTBE must be removed in every state except those three because they are required by mandate, an untenable situation is created for them politically. Those states would like to know that there is some effort to merge the two programs and that there is recognition that what is true for MTBE in groundwater in the summer is equally true for the oxygenated fuels program (OFP) in the winter. Therefore, any recommendations made regarding MTBE should be universal across both programs.

A Panel member stated that the real issue is all other gasolines, including conventional, will be a much bigger issue in the context of low sulfur, low toxic gasolines in the future. This will make the amount of MTBE being used in conventional gasoline look trivial in comparison. There is also a concentration issue that is unique to the conventional gasolines.

It was stated that there may be some apparent trends the midwestern and western CO programs that tend to minimize the concerns with this program, including: (1) many states are coming into compliance; (2) those that are not compliant have reduced their seasons significantly so that all the programs have become shorter; (3) in those areas where there is a continuing problem there is a tendency to increase the amount of oxygen required.

Mr. Grumet presented four slides to demonstrate the pollutants of concern in the Northeast. Through a modeling exercise, the Cumulative Exposure Project demonstrated that there are about 30 toxics of concern, four of which are driving the risk in the Northeast states: acrolein, benzene, 1,3-butadiene, and formaldehyde. Both benzene and 1,3-butadiene are produced predominately by the mobile source sector and, specifically by gasoline combustion. Mr. Grumet noted that the model does not look at the risk associated with diesel fine particles. The second slide presented by Mr. Grumet illustrated that the standard equals .12 mg/m3, which is the level at which one excess cancer risk per million people can be expected. The model reveals that there is a benzene problem. The third slide offered indicates that there is a clear downward trend (almost linear) of pollutants as one moves from urban areas to rural areas with modest industrial activity. This suggests that mobile sources are a dominant source of pollution. Finally, Mr. Grumet presented a slide that showed that in New Hampshire from 1990 to 1991, the CEP predictions are of a factor of 2-3, which illustrates a very impressive modeling result. Mr. Grumet pointed out that, in general, it has been found that RFG areas have substantially lower benzene levels than non-RFG areas on the order of thirty plus percent. Air toxics are a legitimate health concern and diesel and gasoline combustion are primarily responsible for this risk.

THE ETHANOL DEMAND FOR BLENDING

Ethanol can be blended into varying percentages in gasoline, the two most common blends being 10% and 85%.

- E10 - 10% ethanol and 90% unleaded gasoline - is the most common way ethanol is available to motorists. All automakers approve ethanol blends up to this 10% level by warranty, no matter the make or model of the vehicle. About 99% of America's ethanol is retailed as E10.
- E85 - 85% ethanol and 15% unleaded gasoline - is an alternative fuel for use in Flexible Fuel Vehicles (FFVs). FFVs can use unleaded gasoline or any blend of ethanol up to this 85% level.

Some areas of the country use ethanol blends in other percentages; for example, gasoline in California contains 5.7% of ethanol instead of the more common 10% blend.All vehicles are "ethanol-capable" and can use a blend of up to 10% ethanol. Since the 1980s all automakers have covered up to 10% ethanol-blended fuel by warranty, no engine modifications necessary.manufacturers of small engines realize that up to a 10% blend of ethanol is very common in gasoline, so they make their engines compatible with this fuel.

E85 is an alternative fuel comprised of 85% ethanol and 15% unleaded gasoline for use in Flexible Fuel Vehicles (FFVs). FFVs are truly flexible in that they can operate on gasoline or any blend of ethanol up to the 85% blend. On some vehicles this E85-compatibility comes as an option, sometimes as a standard feature.To identify whether a vehicle is flex-fuel, check the owners manual and inside the fuel cap. Visit "Ethanol & Your Vehicle" under the All About Ethanol menu heading to link to a complete list of available FFV models. There are approximately 6 million FFVs on America's roads today, and manufacturers are increasing these numbers each year.

If vehicle is not an FFV, use of any percentage of ethanol higher than 10% is not covered by warranty. People have reported that they use higher percentages of ethanol in regular, unmodified vehicles. A pilot study conducted in mid-2006 suggests that up to 30% ethanol could be used in a non-flex fuel vehicle, but more research is required on this subject - ACE does not endorse this practice.. A vehicle could be converted to operate on E85, but the challenge would be converting it to be a truly flexible fuel vehicle, one that could operate on any blend of fuel up to the 85% ethanol. The good news is that automakers are increasing their lineups of FFVs each model year, so whether you're looking for a new or used vehicle, they are available.

Other blends of ethanol possible besides 10 and 85 percent

There has been some testing and experimentation done with blends of ethanol between 10 and 85 percent. For example, some gas stations in South Dakota have installed blender pumps that dispense regular unleaded, E10, E20 (20% ethanol), E30 (30% ethanol), and E85. The pumps feature two underground tanks, one for unleaded and one for E85, and it mixes the various blends according to what the customer chooses. Because warranties for standard autos currently cover only up to 10% ethanol, these higher blends are for use in Flexible Fuel Vehicles.

A study conducted by ACE in mid-2006 suggests that up to a 30% blend of ethanol could be used in a standard, unmodified vehicle, but more research on the long-term effects of this practice are needed before it can be endorsed. Because so many parties would need to come to the table on the topic of higher ethanol blends - the automakers on warranties, the U.S. EPA on federal regulations, and the retailers on availability - it is important to begin this conversation now and move the process forward so higher ethanol blends can be available in the future.

In 2006, ethanol was blended into 46% of America's gasoline, most in the form of the E10 blend. Ethanol-blended fuel is available from nearly Coast to Coast. In 2006, the U.S. produced and consumed about 5 billion gallons of ethanol.E85 is always labeled at the pump because it is an alternative fuel for use only in Flexible Fuel Vehicles. Because up to 10% ethanol can be used in any vehicle, labeling of this fuel is a decision made locally or by state. Some states require labeling of ethanol blends, and some states say it is not required or that it is voluntary.

The American Coalition for Ethanol supports the consumer's right to know what their gasoline contains, but we do not favor labels that appear more like warning labels. If labeling is not done in an attractive way that shows ethanol's benefits, it can appear more like a warning label and people who are unfamiliar with ethanol will shy away from purchasing this fuel that they believe looks potentially harmful.

A link to a complete list of gas stations offering E85 can be found online in the "Ethanol & Your Vehicle" section of the All About Ethanol menu heading. This site has a searchable map that gives E85 pump locations by state. The number of stations offering E85 is increasing at a rapid pace - today in the U.S. there are more than 1,000 gas stations that offer E85. The number of stations carrying E85 has approximately doubled in the last 24 months, so good progress is being made; however, because the U.S. has about 168,000 gas stations, there is significant work yet to be done. The National Ethanol Vehicle Coalition is a non-profit association that promotes the development of E85 vehicles and infrastructure.

The Energy Policy Act of 2005 contains a new federal tax credit to assist with the installation of equipment and infrastructure to dispense E85 at retail outlets. This new incentive provides a 30 percent federal income tax credit, up to a maximum of $30,000, to assist with the establishment of alternative fuel infrastructure, including equipment necessary to dispense E85. This tax credit became effective in 2006 and is scheduled to expire December 31, 2008.

The technology for storing and dispensing gasoline can be applied to alcohol fuels such as E85 because alcohols and alcohol blends, like gasoline, are liquid fuels at ambient pressures and temperatures. However, only E85-compatible materials should be used in the storage and dispensing systems. Most operating problems with ethanol-fueled vehicles have been traced to contaminated fuel. Consequently, choosing the right materials for fuel storage and dispensing systems and following proper fuel handling procedures are crucial for successfully operating ethanol-fueled vehicles. Although material research and testing is expected to continue, the parts and materials discussed in this guidebook have performed well with E85. They can be obtained from your usual supplier.

Ethanol diesel blends (eDiesel):

In addition to the concern because of reserves of petroleum being limited, the environmental concern is even greater. Diesel generation in general emits large quantity of particulate matter and specially below micron 2.5 which being very small pass the protection system of the body to get lodged in lungs causing reduction in its vital capacity. More seriously than this is the association of the particulate matter with unbumt oil that are potential carcinogenic to human or animals. For this reason, such particles are called respiratory particulate matter and in metro diesel driven vehicles are being phased out. A 15% ethanol blend reduces PM emission, however the blend provides certain technical problems -

The ethanol reduces the flash point of blend to 13 ° C i.e. at the level of pure ethanol which is 50° C lower than that of diesel. For the higher ambient temperature of the country, this disadvantage is not desirable and some additive may be required.

Blend reduces the lubricity of the fuel and increases the wear of the piston rings and injector. In coming years, the sulphur content of the diesel is expected to be lower to 15 ppm and the lubricity of the blend may get further reduced.

Ethanol and diesel fuel do not mix properly. It is found that the presence of water, or extreme cold temperature, causes the mixture to separate. The fuel mixture is known as a micro-emulsion and i; prepared by splash blending in presence of a blending agent. Tolerance of water is influenced by the amount of aromatics level in diesel but generally is of the order of 0.1%. BDiesel owes its commercial aviability to the development of the effective emulsifier, Puranol, invented by Pure Energy Corporation (PEC). Development of more effective emulsifiers is required. The cetane number of the ethanol is just 8 and so reduces the cetane number of diesel on blending.

The calorific value of ethanol is 42% lower than that of diesel on volume basisand would decrese the fuel economy and torque and would need higher injector size to obtain the same peak power. This problem is, however, of not much concern for blends lower than 5%.

Disadvantages

It reduces the flash point up to 13 degree.

It reduces the lubricity of the fuel and increase the wear of the pistons .

It doesn't mix properly with the diesel. The fuel mixture is prepared in the presence of the blending agent.

The cetane number of the ethanol is 8 and so it reduces the cetane number of the diesel on blending.

The calorific value of the ethanol is42% lower than that of the diesel on volume basis and reduce the fuel economy and need higher injector size to obtain the same power.

Gasoline ethanol blend:

The gasoline-ethanol blend is more in practice for the reason of the ability of ethanol to increase octane rating of the fuel without. adding to pollution or unsustainability. The issue of octane improvement has been discussed earlier. Performance parameters of ethanol blends with gasoline are discussed below.

a. Fuel efficiency:

As there is a theoretical decrease in the energy content of gasoline blended with oxygenates, a decrease in mileage, kmlltr of fuel consumed is expected. No definite data is available to correlate the increase in fuel consumption, but with a blend upto 10% not more than 1-3% reduction in vehicular fuel economy in terms ofkmlltr could be expected in the highway driving. It would be insignificant and will not be noticed. On the contrary in urban use a significant increase in fuel efficiency has been reported.

b. Engine performance and drivability:

The higher latent heat of vaporisation of ethanol than that of gasoline is expected to cause startability problem. But 25% blend of ethanol in gasoline is in use in Brazil for the last 25 years without any such problem. The consumption of ethanol in gasoline blend has been more than 10 billion litres there. 10% ethanol blend in gasoline is also in use in USA for the last 18 years and no problem has been encountred as to drivability etc.

c. Material compatibility:

Ethanol is corrosive in nature, absorbs moisture readily and can affect metallic parts (ferrous/non-ferrous). However with the 10% ethanol blend the phillips petroleum study has found no compatibility problem of various components with respect of corrosion tests and swell tests etc. in fuel systems. The experience of using ethanol blended gases in Brazil and USA shows no significant material problems even with older vehicles whereas newer vehicles are having better materials to fight corrosion like flouroelastomers.

d. Emissionissue:

One of the major reasons for using blend is reduction in vehicular emission and eliminating the otherwise emission of lead, benzene, butadiene etc.

e. Hydro-carbon emission:

With better combustion, the ethanol blended gasoline provides a reduction in total hydro-carbon emissions though there is a slight increase in the emission of acetaldehyde.The increase in acetaldehyde emission with 5% ethanol blend has been found marginal, 260 mg vs 233mg per test cycle. With catalyst converters now being used in vehicles reduces aldehydes level by ten times. And therefore the problem is not considered serious. No limits have been set for aldhydes in ethanol by EU, Brazil or USA as emissions are well within tolerable limits. In fact formaldehyde emissions from MTBE are more and greater degree of concerned from health angle,

f Carbon Monoxide emission:

For the same reason as above CO emission also gets reduced as confirmed by many studies.

g. Sulphur Dioxide emission:

As ethanol does not contain sulphur, a corresponding decrease in S02 emission results.

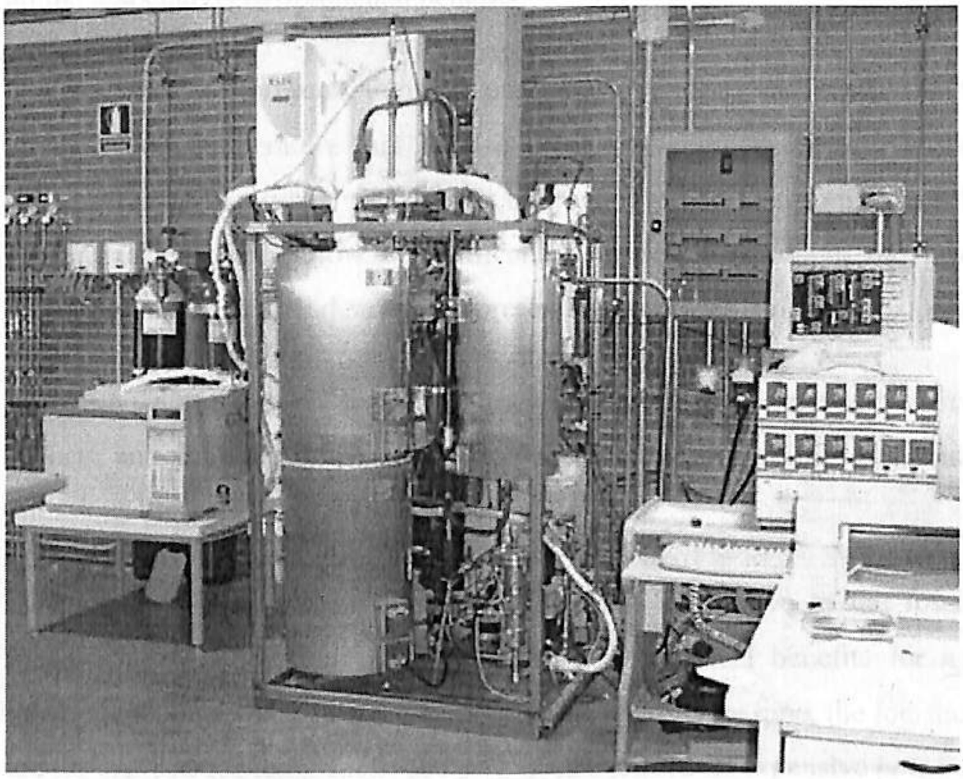
h. Carbon-cycle-emission:

For the ethanol part, it can be taken as zero as it is derived from the plant. Some increase in gasoline emission is likely due to decreased fuel mileage: But in overallconsideration there would be decrease in carbon emission.

Standards For Ethanol Use As Fuel Blending:

Because of low water tolerance of alcohol gasoline blends, ethanol can be blended only in anhydrous form. For 25% blend less than 2% of water can cause seperation. Two stroke engines require oil to be mixed with gasoline. Since oil is not properly miscible with gasoline some additive is required to be added to this.

Ethanol reforming



Hydrogen is an energy carrier with a great growth expected for the future, mainly due to its environmental advantages and suitability for use in fuel cells.

Transport is one of the sectors that need to change its current structure because of its dependence on petroleum and environmental reasons. The use of hydrogen is seen as one of the alternatives, and one of the big challenges is to find a suitable raw material to generate it.

At present bioethanol has been established as one of the best renewable fuel alternatives, being used for the manufacture of ETBE and for direct blending in the fuel stock. If in addition it is developed as a hydrogen source it will represent a firm and solid bridge for the transition towards the so-called "hydrogen economy". It could be done through ethanol reforming, a chemical process to convert bioethanol in hydrogen through a catalytic reaction.

Nevertheless, the development of the "hydrogen economy" has to be carried out under two fundamental premises. First, the costs associated to hydrogen production and distribution must be reduced to much lower levels, enough to make it competitive with other energy carriers. Second, its production from renewable sources has to be of utmost priority to take advantage of all the associated environmental benefits.

Hydrogen as fuel presents logistics problems due to its low energy density, extremely low condensation temperature that require a high power consumption to liquefy it. For these reasons having a system for on-site hydrogen generation from liquid fuels is one of the alternatives that can allow a significant reduction of costs in the production-distribution system, since liquid fuel distribution presents minor costs and risks compared to hydrogen.

Furthermore, the introduction of hydrogen as an energy carrier is justified by environmental aspects, and therefore it is necessary to prioritize all those factors that contribute to decreasing emissions during its production.

Bioethanol as fuel presents clear advantages as alternative to the fossil fuels used in the transportation sector: renewable production, economical benefits for agriculture and rural areas, and energy independence and security. At the same time, the logistics for its distribution are the same as for fossil fuels, and so it does not need an expensive new infrastructure.

Hydrogen generation from bioethanol also presents advantages that need to be emphasized. On one hand, the scale to which can be applied is very wide, from a few kW to large plants of several MW, which allows a variety of applications. On the other hand the generation costs are lower compared to those which at present are associated to hydrogen production from other renewable sources.

So bioethanol is a hydrogen source that presents characteristics suitable to allow the use of hydrogen under favourable conditions. In the first place it allows an important decrease of costs in the production and distribution stages. Secondly its renewable character guarantees all the associated environmental benefits.

In addition, its use as a hydrogen source can be combined with the direct use of bioethanol as fuel, allowing taking advantage of different technologies, reducing costs and favouring the transition from liquid fuels to hydrogen. The biomass origin of the ethanol allows for a high production potential, since the existing estimates state that biomass can produce between 50 and 60% of the renewable energy. So the security of availability in an strategic sector like energy supply is safeguarded this way.

For this reason Abengoa Bioenergía is making an important effort in the development of systems for hydrogen generation from bioethanol. Abengoa Bioenergy is leading different researching works to get a reforming catalyst, that has reach to a patented catalyst which presents fantastic rates of conversion and selectivity, and has designed, constructed and is operating two pilot plants which accumulate thousands of working hours.

At present, a demonstration project is being developed to get knowledge regarding design, operation and costs associated to this technology, and to determine those aspects which need focusing on for optimisation of the process.

FUEL GRADE ETHANOL

For fuel grade ethanol to be blended into diesel fuel (or any internal combustion engine fuel), we believe that the maximum acidity level specification proposed (equivalent to 800 ppm KOH) is nearly 30 times too high. A more appropriate number is 30 ppm as acetic acid measured as a maximum of 1.0 ml of 0.01N NaOH. This is equivalent to 28 ppm as KOH or 0.028 mg KOH/g. Part of the reason for this suggested value is to have a standard product at terminals for blending into either petrol (gasoline) or diesel fuel (distillate). The value of 30 ppm as acetic acid is the current ethanol standard for petrol blending. the mining can be considerable.

Relatedly, if long term durability issues (metallic corrosion) in engines appear after long periods of use, it might not be possible to recover user confidence in these fuels, when a simple reduction in acidity might have sufficed in the beginning. In this regard, use of an appropriate corrosion inhibitor might be pre-added to the ethanol for convenience of the blender, such as is done with DCI-11 at 86 mg/L so that when a 10% blend in petrol is made, the concentration will be correct for the entire blend. Refiners and blenders will have to tell ethanol providers which additive they prefer for diesel fuel.

We recommend the inclusion of the pHe test for acidity, ASTM D6423. While not entirely understood what it is measuring as opposed to other acidity tests, use of this special electrode in the potentiometric determination seems to correlate well with real-world corrosion experience.

Although this is primarily an issue for neat alcohol fuels such as E-85, this test has moved into the mainstream realm of low-percentage blends such as E10 as well.

As a corollary, the pHe test is performed after denaturant is added because of the potential for a high acidity in the denaturing petrol that might be undetected otherwise. This raises the issue of whether denaturant (nominal 1%) should be added to ethanol for diesohol. We believe that the only area of concern to diesohol would be cetane reduction, but petrol is higher in this regard than ethanol, so no degradation would be expected compared to undenatured ethanol. Also, the denaturant would be completely soluble in diesel and might act as a co-solvent for the ethanol.

.Deciding parameter for alcohol content is complicated by more than whether hydrous is used or not, because fuel grade ethanol is not just the chemical species ethyl alcohol. It also has denaturant and various fusel oils such as isomers of amyl alcohol, which are excellent fuels and would help as co-solvents in diesel fuel. Determining oxygen content as a specification for the final diesohol could be a very expensive procedure on a case by case basis. Instead, we think DEH should coordinate with ethanol producers to determine what typical oxygen content for —ethanol" is, and then calculate what final oxygen contents might be for various percentage blends, given that none will be coming from the base diesel. This is if you want to use oxygen as a parameter.For enforcement, there are water-extraction tests that measure the amount of fuel ethanol present in any hydrocarbon fuel that result for careful experiments involving correlation with know
amounts of fuel grade ethanol added, and also noting the temperature. We agree with your last comment that DEH should investigate the possibility of controlling the
quality of ethanol, to be used for making diesohol, separately. As stated already, a copy of the CSR specification is attached as a guide. Then for enforcement purposes, you can correlate extraction tables for ethanol (and other species present) using a typical ethanol product. This is usually a simple observation of amount of aqueous layer increase upon extraction with a known quantity of water.

As evidenced that the solution can take certain amounts of additional water being added without breaking the emulsion. there should be some basic limit on the amount of water present in the hydrous ethanol before blending, however, to prevent the emulsion from breaking and the formation of two distinct layers in the storage tank if water is accidentally introduced. Whether the water is free in the sense of actual droplets as opposed to evenly distributed in solution in the base diesel fuel will become moot when ethanol is added because you now have new conditions where the water will associate itself with the ethanol as closely as possible, whether it was a suspended drop or dissolved originally. In an emulsion technology, most of the water from the diesel fuel (if any) will migrate into the alcohol-water droplets. In a solution technology, addition of anhydrous will stabilize whatever water was present originally as an evenly distributed solution. We do not believe that enough water can be dissolved in base diesel

fuel to be of any consequence in the final diesohol, so if the spec for diesel is 500 ppm, we recommend that it stay there.

As a practical matter, any test you apply to emulsion diesohol for water determination will seek out the water in the emulsion droplets and —count" them. Since the base diesel fuel will benearly dry according to the 500 ppm spec, then you can control the water content in the ethanol

and be assured of final water content as essentially all coming from hydrous ethanol. So far as we know, the Apace technology has worked with 96% ethanol from CSR and what we assume to be 95% ethanol (5% water) from Manildra. We do not know which water content makes a superior emulsified fuel. It is obvious that 4% water is a superior starting place in the sense that you have more protection from phase separation.

It is not necessary, we believe, to have water in anhydrous ethanol at 500 ppm. Ten times that amount, 5000 ppm or 0.5%, will be typical in fuel grade ethanol should it become a standard product, although the specification is actually higher at 1% or 10,000 ppm water. While the higher amount is permitted for petrol, modern molecular sieve dehydrators typically produce 5000 ppm water, and this is what will be commonly available. For the solution-style of diesohol, the resulting mixture has different physical properties than the starting diesel fuel. It will hold more water. The technology providers can advise you on this. In any case, the amount of water in the ethanol will be diluted as it goes into diesel fuel. If the diesel fuel is at 500 ppm water and present at 85%, the ethanol is at 5000 ppm and present at 10%, and the additive package is also 500 ppm water and added at 5% (just an assumption, we have no knowledge of the actual water content of the additives), then the final water content will be 0.85(500) + 0.05(500) +0.1(5000) = 950 ppm water. So far as we know, groups demonstrating this technology in the USA have been using conventional fuel grade ethanol produced for petrol specifications. We recommend, if technology providers concur, that anhydrous ethanol for diesohol be at 5000 ppm or 0.5% water.

We might also point out that average ambient temperatures in Australia are higher than those encountered in the USA, especially in Northern tier States in winter, so water separation will be less of a problem. In all your other areas we have no comment except to say that tests for diesel fuel are probably not applicable for diesohol and so individual testing of the constituents (diesel, ethanol, and additives) is preferred.

PRODUCT SPECIFICATION

ETHANOL100 Fuel Grade with Corrosion Inhibitor

TEST METHOD SPECIFICATION LIMIT DESCRIPTION

Clear, colourless, volatile liquid, hygroscopic, miscible with water and with methylene chloride, free from
matter in suspension and apart from water, consisting essentially of ethanol.

STRENGTH 99.4% (min.) ethanol v/v at 20°C

RELATIVE DENSITY 0.793 (max.)

WATER CONTENT 1.0% by weight (max.)

ALKALINITY Alkalinity to Phenolphthalein – Nil

ACIDITY 1mL of 0.01N NaOH (max.)

CLARITY OF SOLUTION **Dilution of 1mL sample to 20mL water should remain** clear and colourless after 5 minutes.

ALDEHYDES & KETONES 100ppm as Acetaldehyde (max.)

REDUCING SUBSTANCES 30 minutes (min.)

NON-VOLATILE MATTER 2.5mg/100ml (max.)

VOLATILE IMPURITIES Passes Test

pHe6.5 – 9.0

Fuel-Grade Ethanol from Corn Mash

The unit has been developed to produce a fuel-grade ethanol from corn mash in a laboratory to demonstrate how it is accomplished at the industrial level.. The details of the lab are discussed below, followed by descriptions of learning styles used, strategies used, and evaluation techniques:

Fossil fuels are becoming very scarce. Fossil fuels also produce toxic pollutants that contribute to Global Warming and Acid Rain. Ethanol is a fuel that can be produced quite simply from many forms of carbohydrate mash.(i.e. corn, wheat, rice, sugar cane, wood, etc.) Since corn is so very plentiful in the United States at the present time, and probably into the 21st Century, it only seems logical to convert our abundant supplies into fuel-grade ethanol. Furthermore, ethanol burns at high octane and burns clean. In this lab procedure, we use ordinary corn and simple enzymes to produce real ethanol.

Lab Materials needed:

Corn Mash (20 mesh or finer) 200 g
Distilled Water--700Ml
Calcium Carbonate Powder
Celsius and Fahrenheit thermometers
1000mL+ beaker
Autoclave
pipettes
cooling bath
stoppers
rubber hose
ring stands
pH paper

*Alpha Amylase	cheesecloth	pH meter
*Glucoamylase	stirring rods	HCl
Activated Dry Yeast	Fractional Distiller	Balance
Beaker 10 ml	Plastic milk jug (gal.)	hot plate
Ring lamp	Safety goggles	heat mits

*

<u>This lab procedure takes approxiamately 2 hours to complete. Please plan ahead according to your teacher's instructions.</u>

1. Obtain 200 grams of fresh **corn mash**
2. Add 700 mL of distilled water and stir in 1000mL+ beaker.
3. Using Calcium Carbonate or HCL adjust pH of "mash" to 5.8.
4. Add 4mL of Alpha Amylase and stir.(4g of Diastase can be sub.)
5. Autoclave at 225 F for a minimum of 20 minutes.
6. Remove from autoclave and cool to 190 F and add 3 more mL of Alpha Amylase` and stir thoroughly. Stir occasionally for 1 hour.
7. At the end of 1 hour, cool to 90 F and lower pH to 4.2 by adding drops of HCl very slowly. If your mash is in a lump, start over with fresh enzyme.
8. Add 4mL of Glucoamylase to the mash. Then immediately add 3-4g of yeast that has been activated in warm water.
9. Transfer the mixture to a stoppered gallon milk jug that has a pipette rubber hose attached to the top. Stopper the jug and place the hose end in a beaker of water to witness CO2 production. Ferment for 48 hours at 88 F or until all visible CO2 production has ceased. Continue to stir occasionally.
10. Separate the "beer" from the mash by filtering through cheesecloth or a multiple tiered soil sieve into an Ehrlemeyer Flask suitable for distillation.
11. Distill the "beer" at a temp. that does not exceed 90 C, or water will contaminate your ethanol sample.
12. Test your ethanol sample with a lit splint--you should see a blue flame.

Corn mash can be obtained in most parts of the United States at local feed mills and stores. It is simply powdered corn, about the consistency of coarse sand. Cracked corn does not work real well because there is not enough surface area for efficient enzyme action. Other materials can be substituted in place of corn mash; things like corn flour, corn meal, rice, other grains, breakfast cereals, bread, pastas, sport drinks, fruit, and anything that is has a good carbohydrate base to it. Be sure that whatever material is used, that it is ground or powdered to a fine mesh of #20 or smaller. since corn is so inexpensive at this time, that national, even worldwide ethanol production is vital. This lab activity showed that fuel ethanol can be made quite easily and efficiently.

Ethanol is ethyl alcohol, essentially 200-proof grain alcohol. An ethanol production facility, a "plant" or "biorefinery," produces pure fuel-grade ethanol, and then that ethanol is blended in a percentage with gasoline to create a finished motor fuel. A small amount of gasoline is blended into the ethanol at the plant to denature it, or make it unfit for human consumption.

ENVIRONMENTAL EFFECTS

The improvement in air quality in big cities in the 1980s, following the widespread use of ethanol as car fuel, was widely evident; as was the degradation that followed the partial return to gasoline in the 1990s.However, the ethanol program was not perfect and brought a host of environmental and social problems of its own. Sugarcane fields were traditionally burned just before harvest, in order to remove the leaves, kill any snakes and fertilize the fields with ash. The smoke produced each season produces the same amount of carbon polution as the sugarcane would have produced if it was left in the feild to rot, which is relatively little. However, the smoke greatly impacts the sugarcane-growing parts of the country, turning the sky gray and air hazardess throughout the harvesting season. As winds carry the smoke into nearby towns, air pollution goes critical and respiratory problems soar. Thus, the air pollution which was removed from big cities was merely transferred to the rural areas (and multiplied). This practice has been decreasing of late, due to pressure from the public and health authorities. In Brazil, a recent law has been created in order to ban the burning of sugarcane fields, and machines will replace human labor as the means of harvesting cane. This not only solves the problem of pollution from burning fields, but new machines also have a higher productivity than people.

One result of increased use of ethanol is increased demand for feedstocks. Large-scale production of agricultural alcohol may require substantial amounts of cultivable land with fertile soils and water. Clearance of new land often involves burning which can result in a very large emission of carbon dioxide. This may lead to environmental damage such as deforestation or decline of soil fertility due to reduction of organic matter

Many nations have produced alcohol fuel with limited destruction to the environment. Advancements in fertilizers and natural pesticides have all but eliminated the need to burn fields, however chemical pollution from runoff may turn out to be just as harmful to the enviornment as the smoke. To ensure long-term viability for Brazil's ethanol fuel industry, growers must be focused on sustainability rather than short-term productivity.

Fate and Transport of Ethanol in the Environment

Michael Kavanaugh and Andrew Stocking of Malcolm Pirnie delivered a presentation to the Panel that summarized the findings contained in a report prepared for the American Methanol Institute, which evaluated the fate and transport of ethanol in the environment. The purpose of the report was to summarize the scientific literature on the fate, transport, treatment, and toxicity of ethanol in air, soil, groundwater, and surface water as a result of its use as a fuel oxygenate. The study addresses the environmental persistence of ethanol, and the impact of ethanol on water resources. Also included in the report is a summary of the literature describing the advantages and disadvantages of using ethanol to meet fuel oxygenate requirements.

94 percent of ethanol is produced from corn fermentation and must be denatured prior to use. In 1998, 15 percent of all oxygenated gasoline contained ethanol. Ethanol is a highly mobile small chain alcohol with an infinite aqueous solubility. It has a tendency to adsorb moisture when in contact with air. Relative to other oxygenates such as MTBE, ethanol has high oxygen content and heat of vaporization, and low air/water and soil/water partition coefficients. Mr. Stocking further explained the comparative properties of ethanol and other gasoline additives, such as MTBE and benzene, as well as the significance of these properties, including aqueous solubility, vapor pressure, Henry's constant, octanol/water partition coefficient, biodegradability, reactivity, and structure.

Next, Mr. Stocking explained the report's evaluation of the fate of BTEX gasoline components in groundwater in the presence of ethanol. The purpose of this aspect of the study was to determine the likely increase in BTEX plume length due to the presence of ethanol in a gasoline release. The results of these analyses indicate that typical BTEX plumes in California and Texas travel no further than 300 feet from the source. However, the addition of ethanol to gasoline may extend BTEX plumes by 25 to 40 percent, although, areas with higher ethanol concentrations would suggest an increased effect.

Mr. Stocking stated that the conclusions of the study report that, in ground water, ethanol levels depend upon the nature and magnitude of the release. Because ethanol is totally miscible in water, all of the ethanol in gasoline will partition into the water phase. Depending upon the level of dilution, ethanol levels in the ground water can exceed 50,000 mg/L. Probable levels in the vicinity of an ethanol-blended gasoline spill range from 400 to 4,000 mg/L. In addition, ethanol will rapidly biodegrade following release to the environment, but may also cause rapid depletion of electron acceptors and a suspected interference with hydrocarbon biodegradation. Ethanol is preferentially biodegraded compared to other gasoline constituents (e.g., benzene, MTBE). However, if ethanol enters a drinking water supply, ex situ remediation will be difficult.

Finally, Mr. Stocking outlined the data gaps and unknowns that still exist surrounding this issue. For instance, a study has been recently initiated by the MTBE Research Partnership to determine the occurrence of ethanol in water in states using gasohol. In addition, further studies have begun to analyze the impact of ethanol on BTEX plumes in terms of cosolvency and plume elongation. Gaps that require further study include the impact on costs of site characterization and remediation, the impact of ethanol on MTBE plumes, the toxicity of ethanol in a source area, and the treatment of ethanol-impacted drinking water.

The relationship between ethanol cosolvency and benzene concentration is linear and potentially even greater when played out with greater cosolvency. The model did not take into account cosolvency because cosolvency is not assumed to drive the issue.

It is necessary to keep the solubility of neat compounds and the solubility of ethanol separate. It is important to note that the cosolvency effect may not be as important at all sites. Because ethanol biodegrades rapidly and MTBE does not biodegrade as fast, ethanol would not move out in front of BTEX components because it is so soluble and then disappear to allow BTEX to biodegrade. In addition, oxygen is being used up, so while ethanol may move ahead of BTEX initially, it is a small part of the plume.

In the field, a Borden study showed consistent values with those heard in the presentation; the benzene plume was 18-25 percent larger than the other two plumes. However, quantifying the exact length is more difficult. Regarding the implied toxicological effect of the rapid reduction/biodegradation of ethanol, it was noted that in the plume area and at the source area, the reduction of concentration is due to dilution.. It was noted that the taste and odor threshold of ethanol (at 1 ppm) is much higher than MTBE.

Regarding the point at which remediation efforts should be conducted (unless a direct release occurs in close proximity to drinking water wells) ethanol remediation is probably not required.

· In terms of whether soil varieties effect ethanol degradation, the more organic the compound, the faster its degradation rate.

· Regarding denaturants and what they do to ethanol, the Bureau of Alcohol, Tobacco, and Firearms adds denaturants to gasoline to make it poisonous and, therefore, non-drinkable.

· Regarding the remediation/monitoring of leaking tank sites, ethanol cannot be measured using the same standards as BTEX.

FUEL ECONOMY

IN FUEL FLEXIBLE ENGINES

For 2006 vehicles with flexible fuel engines, fuel economy (measured as miles per gallon - MPG- , or liters per 100 km) is directly proportional to energy content Ethanol contains approx. 34% less energy per gallon than gasoline, and therefore will result in a 34% reduction in miles per gallon. For E10 (10% ethanol and 90% gasoline), the effect is small (~3%) when compared to conventional gasoline, and even smaller (1-2%) when compared to oxygenated and reformulated blends However, for E85 (85% ethanol), the effect becomes significant. E85 will produce lower mileage than gasoline, and will require more frequent refueling. Actual performance may vary depending on the vehicle. The EPA-rated mileage of current USA flex-fuel vehicles should be considered when making price comparisons, but it must be noted that E85 is a high performance fuel and should be compared to premium.

However, this analysis applies only to currently designed flex-fuel engines. Ethanol has a much higher octane rating (octane rating of 105 for E85 versus 87 for regular unleaded gasoline). Because currently marketed flex-fuel vehicles must be capable of efficiently burning both gasoline and E85, their engines must be designed to tolerate lower octane rated petroleum-based fuels. Typically this means that the engine must be designed to operate at a lower compression ratio. However, engines that are designed to run on E85 or higher ethanol alone can be designed to better exploit the higher octane rating of the fuel by incorporating higher compression ratios. This results in higher energy efficiencies, though those engines are no longer able to burn conventional gasoline. The higher energy efficiencies of these engines offsets the lower energy content of the alcohol, resulting in approximately the same number of miles per gallon of ethanol fuel as a similar engine designed to run on gasoline. Designing an engine that is capable of running on both E85 and gasoline while changing the compression ratios of the stroke cycle to make maximum use of either fuel is possible, but so far not feasible on a mass-produced scale.

In considering the potential for pollution reduction with ethanol, however, it is equally important to consider the potential for environmental contamination stemming from the manufacture of ethanol. In 2002, monitoring of ethanol plants revealed that they released VOCs (volatile organic compounds) at a higher rate than had previously been disclosed. The Environmental Protection Agency (EPA) subsequently reached settlement with Archer Daniels Midland and Cargill, two of the largest producers of ethanol, to reduce emission of these VOCs. VOCs are produced when fermented corn mash is dried for sale as a supplement for livestock feed. Devices known as thermal oxidizers or catalytic oxidizers can be attached to the plants to burn off the hazardous gases. Smog causing pollutants are also increased by using ethanol fuel in comparison to gasoline.

Economic importance and viability for cellulosic ethanol

For main relevant points, check this article: Barry D. Solomon, Justin R. Barnes and Kathleen E. Halvorsen (2007) Grain and cellulosic ethanol: History, economics, and energy policy, Biomass and Bioenergy, In Press, Corrected Proof, Available online 13 March 2007.

Construction of pilot scale lignocellulosic ethanol plants require considerable financial support through grants and subsidies. On 28th Feb 2007, the US Dept of Energy announced $385 million in grant funding to 6 cellulosic ethanol plants. This grant funding accounts for 40% of the investment costs. The remaining 60% comes from the promoters of those facilities. Hence, a total of $1000 million will be invested for approximately 140 million gallon capacity. This translates into $7/annual gallon in capital investment costs. This seems to be high because these are pilot plants; in the near future, we may expect the costs to be 2.5 - 4 times the capital costs of a corn ethanol plant. Corn to ethanol plants cost roughly $1 - $3/annual gallon capacity.

In contrast, cellulosic ethanol is obtained from cellulose, the main component of wood, straw and much of the plants. Since cellulose cannot be digested by humans, the production of cellulose does not compete with the production of food. The price per ton of the raw material is thus much cheaper than grains or fruits. Moreover, since cellulose is the main components of plants, the whole plant can be harvested. This results in much better yields per acre—up to 10 tons, instead of 4 or 5 tons for the best crops of grain.In June 2006, a U.S. Senate hearing was told that the current cost of producing cellulosic ethanol is US $2.25 per US gallon (US $0.59/litre). This is primarily due to the current poor conversion efficiencyAt that price it would cost about $120 to substitute a barrel of oil (42 gallons), taking into account the lower energy content of ethanol. However, the Department of Energy is optimistic and has requested a doubling of research funding. The same Senate hearing was told that the research target was to reduce the cost of production to US $1.07 per US gallon (US $0.28/litre) by 2012.

l produced from corn as a biomass through industrial fermentation, chemical processing and distillation. It is primarily used in the United States as an alternative to gasoline and petroleum.

In the future corn ethanol may very well become a viable and energy efficient commodity. The advent and promotion of cheaper non-petroleum fertilizers and herbicides. Increased corn acreage and conservation from new techniques of farming. Farming equipment and machinery that runs on E85. Renewable sources of electricity for power and transport. The discovery of new and better enzymes for chemical processing. And new more efficient and coast effective production processes and manufacturing methods being developed with higher yields. The creation of corn ethanol would very well become a much more energy efficient and cost effective process and leave a greatly reduced environmental footprint. These technologies are under development and progressing, and could together easily increase the energy balance of corn ethanol.

Economics of ethanol production:

From sugarcane:

A tonne of sugarcane, on an average, would provide 110 kg of fermentable sugar in the juice. If all the sugar juice is fermented directly, the ethanol yield will be 70 litres taking a sugar loss of 2% in spent wash and specific gravity of ethanol as 0.79.. The present price of sugarcane as fixed by Centre under the minimum statutory price stands at Rs. 695/- per tonne *with* 8.5% *recovery. At* higher recovery which is the case always, the effective price comes to Rs. 900/- per tonne if State Governments does not add furthercost to it. For example, the UP state has added the statutory price by Rs. 45/- per tonne on the Centre's price of Rs. 695/-. Therefore the feed stock price itself comes to Rs. *900170*= Rs. 13/- per litre of ethanol. A minimum of Rs. 2/- per litre would be the

conversion cost i.e. salary and wages of the operational staff. In other words, direct conversion of sugar juice to ethanol will cost more than Rs. 20/- per litre, if we add the capital related charges of investment, profit to the manufacturer, energy cost of making anhydrous alcohol, transport, marketing, blending etc. This may not be financially viable with present ex-factory cost of gasoline. To make it viable following options are available:-

i Sugarcane prices are decontrolled and left for the market to decide. This may result into cane prices lower than Rs. 500/- per tonne.

ii. Combining with sugar production so that major part of cane cost is off-loaded to sugar.This is the present situation also where all the ethanol production from sugarcane is coming through molasses, a by-product in sugar production. A tonne of sugarcane produces 100 kg of sugar as well as 40 kg of molasses the latter will produce around 10 litres of ethanol. Even if sugar is sold at Rs. 10/- per kg it will be sufficient to pay aU the cost of the sugarcane.

iii. Use of by-products bagasse and spent wash *very efficiently*. The spent wash which is produced in large quantity (around 15 litre for 1 lire of ethanol produced) can be subjected to *anaerobic* digestion which not only removes its BOD and COD but will also provide valuable bio-gas (60% methane) which can meet 2/3rd of energy cost of making anhydrous alcohol through conventional route. Using absorption or membrane technology of drying al::ohol above 95% purity, the biogas generation would be sufficient for all its energy demand (if short by any margin, the same could be made from the bagasse based cogeneration facility). The bagasse which is left after crushing can provide electricity through efficient co-generation. As per an estimate, a cane crushing mill with 455 tph crushing capacity can generate 44 MW of power. This comes to about 97 kWh/tonne of cane crushed. At a Rs. 2/- kWh rate of power exported to grid the earning will be far sufficient to meet the cane prices even after meeting the capital rated charges of installing the power generation facility. To realize the energy efficiency as sated above, the followings would have to be set up having the magnitude of the capital investments as indicated -

- Molecularsieve costingaroundRs 2-2.5 crore for 30 kld plant.
- Anaerobicbio-gas productioncostingRs 4-5 crore.
- Steamandpower generationplant (co=-generation) costing around Rs 3 crorelMW.

Fortunately, apart from a low pay back period for return in investments, there are several sources of getting [fiance for setting up the facilities above (to increase efficiency)- .

- Assistance from Asian Development Bank, KfW, Germany, JBIC, Japan
- Assistance from IREDA under renewable energy plan
- Carbon credit of nearly $1O/te of carbon saved under CDM of the Kyoto Protocol.

From other feedstocks:

The other major source can be com, sugrbeet, potatoes etc. Depending on the starch content's in the feedstock, the yield of ethanol would vary. Taking com, it can be at 2.75 tonne of grains per kilolitre of ethanol. The feedstock cost at Rs. 7/- per kg itself would cost Rs. 20/- in one litre of ethanol so produced. The sale of the residue, (i.e. dried distillers grains and solubles which is produced in the quantity of 0.56 kg per litre of ethanol produced would fetch a maximum of Rs. 3.5 @ Rs. 6/- per kg of residue unless the latter is converted to more value added products. Thus the feedstock price after taking the credit of the DDGS sale would not be lower than Rs. 16:5 per litre. The spoiled grain available in large quantity (2-5 lakhs tonnes per year from FCI) would

certainlymake a very cheap alcohol. For others, it is the market price that will determine

the economics. Generally foodgrain price will be dictated by its use for human consumption which, in turn, will be subjected to prices across other grains and alternatives.

R&D work

While a boundary can be drawn to limit R&D activities in the area of ethanol production from agro-crops or biomass in general, but for short term requirement, the following areas of research & development should be stressed mainly towards the compatibility of the use of blends in existing engines:-

Ethanol-gasoline blend:

a. Performance of engine and corrosion of ethanol gasoline blend at higher ethanol percentage above 10%. Because of the low water tolerance of alcohol- gasoline blends, anhydrous ethanol must be used & great care must be exercised to avoid water contamination. For 25 % alcohol blend, less than 2% of water will cause separation. Ethanol can also be used in modified engines, specifically designed and manufactured to operate on ethanol fuel, and will generally be more efficient than modified gasoline engines.

b. Most conventional vehicles on the road today can use EI0 (a 10% ethanol- 90% gasoline blend also known as gasohol) without any special modifications. However,

auto manufacturers are also producing vehicles that are specially modified to run on a higher percentage of ethanol. Generally, the use of ethanol blending reduces the harmful emissions like CO, CO2 & hydrocarbons. However, additional studies are required to understand potential emissions benefits for all engine models and driving cycles. Effect on exhaust treatment devices using ethanol blending should also be established. The main mechanical differences between ethanol and gasoline vehicles lie in the engine calibration and the fuel management system.

Ethanol vehicles come with a special computerized system that monitors the ethanol/gasoline ratio of the fuel, optimizes performance, and adjusts emissions control devices. Ethanol may also

corrode certain materials that are commonly used in automobile parts, such as rubber and plastic. Components that come in contact with tre fuel, such as piston rings, engine block, and valve seals, must be made of ethanol-compatible materials.

c. Suitable additive for ethanol gasoline blend to be used in two stroke engines. The use of ethanol in specially designed two-cycle engines has been demonstrated on a limited basis. The problem of using ethanol in these engines is that the ethanol does not blend well with lubricating oil. To get around this problem, research is under way to find lubricating oils that are not affected by ethanol engines. The study on !r1-use vehicle must also be considered because they are having. totally different configuration compared to new generation vehicles.

d. Andehyde Emission: Aldehyde emissions from ethanol blends are generally higher than those from gasoline. Formaldehyde, the major constituent in aldehyde emissions, is a suspected carcinogen. However, the catalytic converters used vehicles reduce aldehyde emissions to near the level produced when unblended gasoline is combusted. The Royal Society of Canada has concluded that any increases are minute, and harmful effects are remote.

e. E-diesel cannot be safely handled like conventional diesel but must be handled like gasoline. This may necessitate some modifications to storage and handling equipment, as well as vehicle fuel systems. Stability is much less of a concern for micro-emulsions as these have proven stable for extended periods. However, stability of e-diesel micro-emulsions under a range of storage conditions will need to be demonstrated. Emulsifiers are known to extend the stability of ethanol-diesel blends to lower temperatures at ethanol blending levels as high as 15% or even 20% in

conventional diesel. Detailed data on the efficacy of emulsifiers as a function of temperature and fuel aromatic content do not appear to be publicly available & most manufacturers have not optimized emulsifier. A large body of test data acquired in close cooperation with the

OEM's will be necessary to address this issue.Development of better emullsifier for ethanol diesel blend.

f Lubricity of e-diesel: Lubricity is the ability of the fuel to lubricate metal surfaces and is relevant to wear in fuel pumps and other engine components that are lubricated by the fuel. Severely hydrotreated, ultralow sulfur diesel fuels as well as Fischer- Tropsch diesel fuels tend to have low lubricity. This can be remedied through the use of a lubricity additive or by blending with higher lubricity components. Ethanol is not expected to impart increased lubricity to diesel fuel. However, most emulsifier manufacturers claim that the emulsifier itself can impart improved lubricity. This would seem to be substantiated by data made public by PEC that shows premium

lubricity properties (i.e. HFRR of less than 300 micron and SLBOCLE of more than 5200 g [jhtl D. Better quantification of the effect of e-diesel on fuel lubricity for both conventional and ultra-low sulfur fuels is needed. The inclusion of lubricity in an ediesel standard may be desirable.

g. Other problem of e-diesel: Concerns are expressed related to engine performance using e-diesel. These include the idea that the solvency effect of ethanol might loosen deposits in older vehicles causing breakdowns. Another concern is that because of ediesel's higher volatility, there may be a greater incidence of pump and injector cavitation, leading to increased wear and hot restart problems. The lower energy content may require changes to governing strategy to prevent stalling under certain conditions such as steep grades, high temperature, and altitude. While some of these concerns may prove to be unfounded, they will require investigation.

h. Development of more energy efficient and economical process for fermenting cellulose materials into ethmol. In the coming years it is believed that cellulosic biomass will be the largest source of bioethanol. The broad category of biomass for the production of ethanol includes agricultural crops & residues and wood. Biomass resources are abundant and ha ve multiple application potential. Among the various competing processes, bioethanol from lignocellulosic biomass appears to have nearterm economic potential. The crops residues such as rice straw, bagasse etc are not currently used to derive desired economic and environmental benefits and thus they could be important resource bases for bioethanol. A major challenge is developing

biocatalysts capable of fermenting lignocellulosic biomass for efficient industrial application. Some narration on the possibility would be in order which would also highlight the need of research in the area.

Conclusion:

1. Though it is technically feasible to design and run automobiles on 100% ethanol, for the reason of availability and compatibility with vehicles presently in use blending of ethanol with motor spirit needs to make a very modest beginning.

2. Five percent blending has already been introduced in some states. According to the information - availability about production and demand of ethanol for all applications, production of molasses and distillery capacity, 7% blend of ethanol in gasoline is feasible provided facilities to dehydrate alcohol are added to the required extent. The target should be to raise the blending in stages to 10% by the end of the X Plan.

3. Ethanol may be manufactured using molasses as the raw material. If the industry finds it economically feasible, it should be encouraged to produce alcohol also from sugarcane juice directly in areas where sugarcane is surplus.

4. Restrictions on movement of molasses and putting up ethanol manufacturing plants may be removed.

5. Imported ethanol should be subject to suitable duties so that domestically produced ethanol is not costlier than the imported one.

6. Ethanol diesel blending requires emulsifier and also poses certain storage and technical problems. Indian Institute of Petroleum is working on the subject. Ethanol diesel blending should await the solution of the problems.

7. Buyback arrangement with oil companies for the uptake of anhydrous alcohol should be made.

8. To reduce cost of production of ethanol, the following measures may be considered: . Provision of incentives for new economic sized distilleries incorporating state of Integration of distillery with sugar plant to have multiple choice of making sugar, or direct sugarcane to ethanol.
art technology such as, molecular sieve technology for making anhydrous alcohol.

9. The cost of ethanol produced using other raw materials such as grains, potato, sugar beet and straw is estimated to be more than the price of motor spirit and may need subsidy. Economics of ethanol production from other feedstocks as sugar beet, com, potatoes, etc should be studied. It may be left to the industry to use these raw materials for producing ethanol as and when if it finds them economical.

10.R&D may be supported to reduce the cost of ethanol production from different feed stocks.

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