ETHANOL PREPERATION AS A FUTURE FUEL, ITS GRADING & BLENDING CORRELATIONS

By
Vineeta Khurana
Vishwadeep Pandey

College of Engineering
University of Petroleum & Energy Studies
Dehradun

ETHANOL AS A FUTURE FUEL, ITS GRADING & BLENDING CORRELATIONS

A thesis submitted in partial fulfilment of the requirements for the Degree of
Bachelor of Technology
(Applied Petroleum Engineering)

By
Vineeta Khurana – R010204064
Vishwadeep Pandey – R010204065

Under the guidance of
Mrs. Bhawna Yadav Lamba

Approved

Dr. B.P. Pandey
Dean

College of Engineering
University of Petroleum & Energy Studies
Dehradun

UNIVERSITY OF PETROLEUM & ENERGY STUDIES

CERTIFICATE

This is to certify that the project report on " ETHANOL PREPARATION AS A FUTURE FUEL, ITS GRADING AND BLENDING CORELATIONS" submitted to UPES, Dehradun by Vineeta Khurana and Vishwadeep Pandey in partial fulfillment of the requirements for the degree of Applied Petroleum Engineering & academic session (2004-2008) is a bonafide work carried out by them under my guidance & supervision.

Date: 16.05.08

Bhawna
16.05.08

Mrs. Bhawna Yadav Lamba
(Lecturer-COE, UPES)

ACKNOWLEDGEMENT

There are many people to acknowledge when a report like this is completed. Our sincere thanks go to all those who are directly or indirectly involved in this project and took time out of their busy schedules to pour insights into our report.

There is one individual who needs to be highlighted, our guide, **Mrs. Bhawna Yadav Lamba**, since she did too much to pave the way for what we have managed to do. Her insightful feedback has been extremely important without which we would not have succeeded in our endeavor.

We are really indebted to the constant motivation provided by respected **Dr. B.P.Pandey**, Dean who has been a torchbearer and a driving force in bringing up this work.

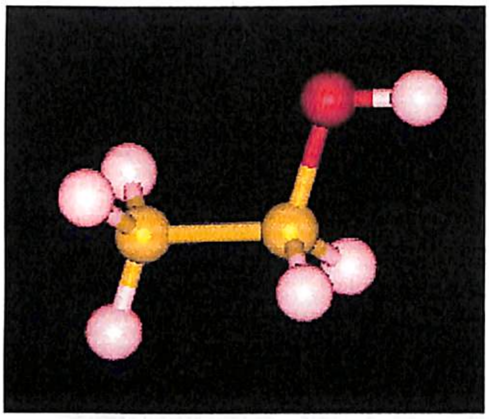
The **University of Petroleum & Energy Studies** must be credited for letting us do a project of our area of interest, keeping faith in us and letting it happen.

Last and most assuredly not least, we are deeply indebted to many people who have helped us indirectly in this project.

TABLE OF CONTENTS

1. INTRODUCTION

Ethanol, C2H5OH (also called Ethyl Alcohol) is the second member of the aliphatic alcohol series. It is a clear colorless liquid, with the 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) ia available, it is much 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.

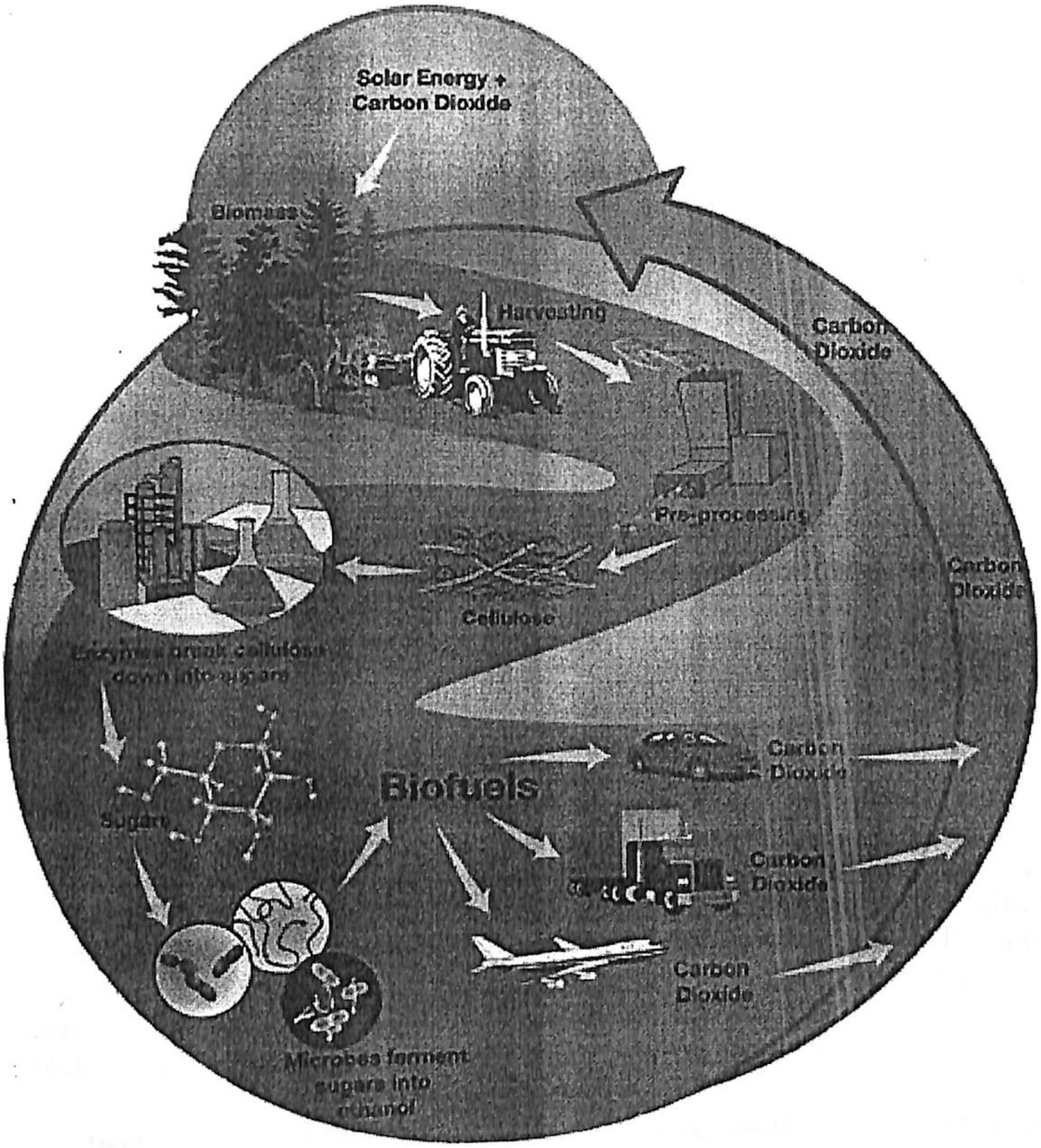
Renewable fuels are alternative source for fuels derived from renewable resources. There has been a lot of attention on renewable fuels lately, mainly due to increasing energy prices.

Ethanol apart from its major use as a beverage is one of the most versatile chemicals and also one of the basic building blocks of the organic chemical industry. Alcohol is generally produced by fermentation of carbohydrates, however, due to the development of petrochemical industry and availability of ethylene currently provides another major route for the formation of ethanol. Ethanol in India is still manufactured through the molasses route. Some of the important chemicals which are prepared through the petrochemical route are still produced through the ethanol route at some places in India.

Two such important complexes are jubilant Organosys Ltd. Gajraula (Uttar Pradesh) and Indian Glycol Ltd, Kashipur (Uttar Pradesh), where a large number of ethanol derivatives is manufactured through the ethanol route.

Ethanol is a grain alcohol that can be burned cleanly as a high-octane fuel. It is used as an oxygenate in gasoline formulations to create cleaner-burning, more efficient fuel. Its molecular formula is variously represented as EtOH, CH_3CH_2OH, C_2H_5OH or as its empirical formula C_2H_6O (which it shares with dimethyl ether).

Typically ethanol is blended with gasoline in a formulation consisting of 10% ethanol and 90% gasoline (known as E10).



Ethanol is also increasingly being used in an E85 formulation (85% ethanol and 15% gasoline) for use in Flexible Fuel Vehicles (FFVs). FFVs can run on E85, gasoline, or any combination of the two, and they are currently offered by most major automotive manufacturers.

Alcohol based chemicals provide feedstock for a variety of industries including synthetic fibres, synthetic resins, pesticides, pharmaceuticals, paints, packaging, dyestuffs, drugs, food processing, formulations, effluent treatment chemicals and explosive industries. Alcohol based industry which had few units in the late 1950s in India is now spread all over the country and has over the years become a mature industry, mostly based on alcohol through the molasses route.

Raw material used for producing ethanol varies from sugar, cereals, sugar beet to molasses in India. Brazil uses ethanol as 100 % fuel in about 20 per cent of vehicles and 25% blend with gasoline in the rest of the vehicles. USA uses 10 % ethanol-gasoline blends whereas a 5% blend is used in Sweden. Australia uses 10% ethanol- gasoline blend. Use of 5% ethanol- gasoline blend is already approved by BIS and is in progressive state of implementation in the country. BIS standards for 10% blend need to be drafted after conducting trials and fixing parameters.

1.1 Physical Properties

The properties of ethanol stem primarily from the presence of its hydroxyl group and the shortness of its carbon chain. Ethanol's hydroxyl group is able to participate in hydrogen bonding, rendering it more viscous and less volatile than less polar organic compounds of similar molecular weight. Ethanol, like most short-chain alcohols, is flammable, colorless, has a strong odor, and is volatile.

Ethanol is slightly more refractive than water with a refractive index of 1.36242 (at λ=589.3 nm and 18.35 °C).

Ethanol is a versatile solvent, miscible in all proportions with water and many organic solvents, including acetic acid, acetone, benzene, carbon tetrachloride, chloroform, diethyl ether, ethylene glycol, glycerol, nitromethane, pyridine, and toluene. It is also miscible with light aliphatic hydrocarbons such as pentane and hexane, as well as aliphatic chlorides such as trichloroethane and tetrachloroethylene. Ethanol's miscibility with water is in contrast to longer chain alcohols (five or more carbons), whose water solubility decreases rapidly as the number of carbons increases.

Hydrogen bonding causes pure ethanol to be hygroscopic to the extent that it readily absorbs water from the air. The polar nature of the hydroxyl group causes ethanol to dissolve many ionic compounds, notably sodium and potassium hydroxides, magnesium chloride, calcium chloride, ammonium chloride, ammonium bromide, and sodium bromide. Sodium and potassium chlorides are slightly soluble in ethanol. Because the ethanol molecule also has a nonpolar end, it also dissolves nonpolar substances, including most essential oils, as well as numerous flavoring, coloring, and medicinal agents.

Several unusual phenomena are associated with mixtures of ethanol and water. Ethanol-water mixtures have less volume than their individual components. A mixture of equal volumes ethanol and water has only 95.6% of the volume of equal parts ethanol and water, unmixed (at 15.56 °C). The addition of even a few percent of ethanol to water sharply reduces the surface tension of water. This property partially explains the tears of wine phenomenon. When wine is swirled in a glass, ethanol evaporates quickly from the thin film of wine on the wall of the glass. As its ethanol content decreases, its surface tension increases, and the thin film beads up and runs down the glass in channels rather than as a smooth sheet.

Ethanol and mixtures with water greater than about 50% ethanol are flammable and easily ignited. This principle was used for the alcoholic proof, which initially consisted on adding gunpowder to given liquor: if the mixture ignited, it was considered to be "100 proof". Ethanol-water solutions below 50% ethanol by volume may also be flammable if the solution is vaporized by heating (as in some cooking methods that call for wine to be added to a hot pan, causing it to flash boil into a vapor, which is then ignited to "burn off" excessive alcohol).

1.2 Chemical Properties

Ethanol is classified as a primary alcohol, meaning that the carbon to which its hydroxyl group is attached has at least two hydrogen atoms attached to it as well.

The chemistry of ethanol is largely that of its hydroxyl group.

Acid-base chemistry

Ethanol's hydroxyl proton is very weakly acidic; it is an even weaker acid than water. Ethanol can be quantitatively converted to its conjugate base, the ethoxide ion ($CH_3CH_2O^-$), by reaction with an alkali metal such as sodium.

$2CH_3CH_2OH + 2Na \rightarrow 2CH_3CH_2ONa + H_2$

Halogenation

Under special conditions, ethanol reacts with hydrogen halides to produce ethyl halides such as ethyl chloride and ethyl bromide:
$CH_3CH_2OH + HCl \rightarrow CH_3CH_2Cl + H_2O$
HCl reaction requires a catalyst such as zinc chloride.

$CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O$
HBr requires refluxing with a sulfuric acid catalyst.

Ethyl halides can also be produced by reacting ethanol with more specialized halogenating agents, such as thionyl chloride for preparing ethyl chloride, or phosphorus tribromide for preparing ethyl bromide.

Ester formation

Under acid-catalyzed conditions, ethanol reacts with carboxylic acids to produce ethyl esters and water:

$RCOOH + HOCH_2CH_3 \rightarrow RCOOCH_2CH_3 + H_2O$

For this reaction to produce useful yields it is necessary to remove water from the reaction mixture as it is formed.

Ethanol can also form esters with inorganic acids. Diethyl sulfate and triethyl phosphate, prepared by reacting ethanol with sulfuric and phosphoric acid respectively, are both useful ethylating agents in organic synthesis. Ethyl nitrite, prepared from the reaction of ethanol with sodium nitrite and sulfuric acid, was formerly a widely-used diuretic.

Dehydration

Strong acid desiccants, such as sulfuric acid, cause ethanol's dehydration to form either diethyl ether or ethylene:

$2\ CH_3CH_2OH \rightarrow CH_3CH_2OCH_2CH_3 + H_2O$

$CH_3CH_2OH \rightarrow H_2C{=}CH_2 + H_2O$

Which product, diethyl ether or ethylene, predominates depends on the precise reaction conditions.

Oxidation

Ethanol can be oxidized to acetaldehyde, and further oxidized to acetic acid. In the human body, these oxidation reactions are catalyzed by enzymes. In the laboratory, aqueous solutions of strong oxidizing agents, such as chromic acid or potassium permanganate, oxidize ethanol to acetic acid, and it is difficult to stop the reaction at acetaldehyde at high yield. Ethanol can be oxidized to acetaldehyde, without over oxidation to acetic acid, by reacting it with pyridinium chromic chloride.

Chlorination

When exposed to chlorine, ethanol is both oxidized and its alpha carbon chlorinated to form the compound, chloral.

$4Cl_2 + C_2H_5OH \rightarrow CCl_3CHO + 5HCl$

Combustion

Combustion of ethanol forms carbon dioxide and water:

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

2. PRODUCTION OF ETHANOL

A variety of feedstock can be used in the production of ethanol, although the technology employed differs from feedstock to feedstock. Most of the world's production of ethanol comes either from sugarcane (from the juice or molasses in sugar production) or from corn.

In the Asia Pacific region, many countries have already evaluated other alternative feedstock for the production of ethanol. The Philippines has three major crops that are being considered for the production of ethanol: sugarcane, corn and cassava. These crops contain sugar and starch that can be processed into alcohol. In Thailand, cassava is already an established feedstock, along with molasses and cane juice. China shall be relying on corn for ethanol.

Globally, Brazilian ethanol is almost entirely from sugarcane, while ethanol in the U.S. is produced using corn as the predominant feedstock. However, comparatively, using sugarcane to produce ethanol remains a cheaper process.

In India, the government is considering allowing the direct production of ethanol from sugarcane juice following the huge surplus of sugar in 2006-07. However, new crops such as sweet sorghum are also being studied as alternative or complementary crops.

Recently; on a smaller scale there has also been some interest in the cultivation of sugar beet in India for the production of ethanol. Sugar beet is a crop of cold temperature regions and a source for about 35% of global sugar production. Compared to sugarcane, sugar beet appears to have a higher recovery rate a lower crop cycle and lower water requirement. The yield is also significant at 3500 liters of ethanol per acre of sugar beet.

Other crops such as corn, maize and sweet sorghum could also be used for the production of ethanol in the country.

2.1 Feedstock

Three classes of vegetative sources (raw materials) can be used:

- starch as grain, corn and tubers like cassava
- sugar plants (sugar beet or sugar cane)
- cellulose plants (general tree and biomass)

Through Sugarcane:

Through sugar cane- sugar route: The major source of ethanol production in the country is via sugarcane-sugar-molasses route. This provides better economy by sale of sugar, molasses becomes the by-product of the sugar. Average sugar cane productivity in India is about 70 MT per hectare and ethanol produced from one MT of sugarcane is 70 litre.

Through sugar beet:

In European countries sugar beet is preferred. Sugar beet has certain advantages over sugarcane. It provides higher yield (12.5 to 17.5 ton per hectare of sugar against 7.5 to 12 ton of sugar per hectare from sugarcane in addition to low requirement of water, lower maturity time and lower power requirement for crushing. Sugar beet cultivation and its processing to ethanol needs to be promoted in the country

Starch based alcohol production:

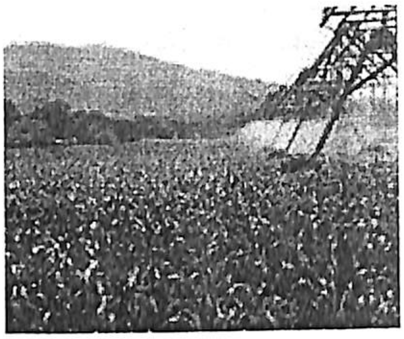
Alcohols are produced from a large number of different starch crops as barley, wheat, corn, potato, sorghum etc. The conversion of starch into alcohol follows the same process of fermentation and distillation as that of sugarcane. Corn can provide about 275 litre of ethanol from one MT. With productivity of 2 MT per hectare, 550 litre of ethanol can be produced from one hectare of corn plantation. In addition to lower yield per hectare of ethanol, corn presents the problem of disposal of residue, but it can be used as animal feed. It can, however, be utilised for value added products which can provide starch based alcohol production economical. Corn oil is edible and its use in India for production of ethanol is not economically feasible.

Ethanol made from cellulosic biomass

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 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 base for bioethanol production. As for example one MT of rice straw or bagasse can give over 400 litre of ethanol.

Cellulosic materials are polymers of sugar and are difficult to decompose by enzymes and need breaking of bonds before hand. Two different routes are being tried. One is by action of chemical (Acid or new generation of enzymes) and the second is the thermal route of gasification. The first route is being generally followed as in paper pulp industry. However, for ethanol production economics are not favorable. The gasification route provides better economics but looks to be very complicated. It is as yet in an experimental stage.

Sugarcane Harvest



Cornfield

Switch Grass

2.2 Alternative Feedstock

In India, currently, ethanol is produced mostly only from molasses, which is a by-product in the manufacture of sugar. A wide range of biomass could be utilized for the purpose of ethanol production if the technology for the production of cellulosic ethanol stabilizes and becomes widely available and commercially viable.

Sweet sorghum

Sweet sorghum in particular shows promise and advantages in comparison to other crops such as sugarcane and maize:

- It has a high content of sweet juice in its stalks. While the juice can be used to produce ethanol, the grains can be used as food or feed.

- Sweet sorghum requires only half the water required to grow maize and one-eighth of the water required to grow sugarcane.
- The cost of cultivation is lesser than that of sugarcane.
- Unlike sugarcane, which is a tropical plant, it can be cultivated in nearly all temperature and tropical climatic areas.
- The fibre obtained from sweet sorghum is similar to bagasse and can be burned as fuel.
- Sweet sorghum will provide farmers with additional sources of income through dry lands, without compromising on food security, as the farmers can continue to use the grain for food purposes.
- It is also a carbon neutral crop. The amount of carbon dioxide the crop fixes is equal to the amount emitted during the entire process of crop growth, conversion to ethanol and the final combustion of ethanol.

Cellulosic ethanol

Currently, not all biomass can be profitably processed into ethanol. Cellulosic ethanol is ethanol fuel produced from lignocellulose, composed mainly of cellulose, hemicellulose and lignin. Lignocellulose, as a raw material is available in a great diversity of biomass, but it requires far greater processing to make the sugar monomers available to the micro-organisms typically used for fermentation. A cellulosic ethanol process would raise the ethanol yields from sugarcane by about one-third per acre by using parts of the sugar plant that are now thrown away as waste.

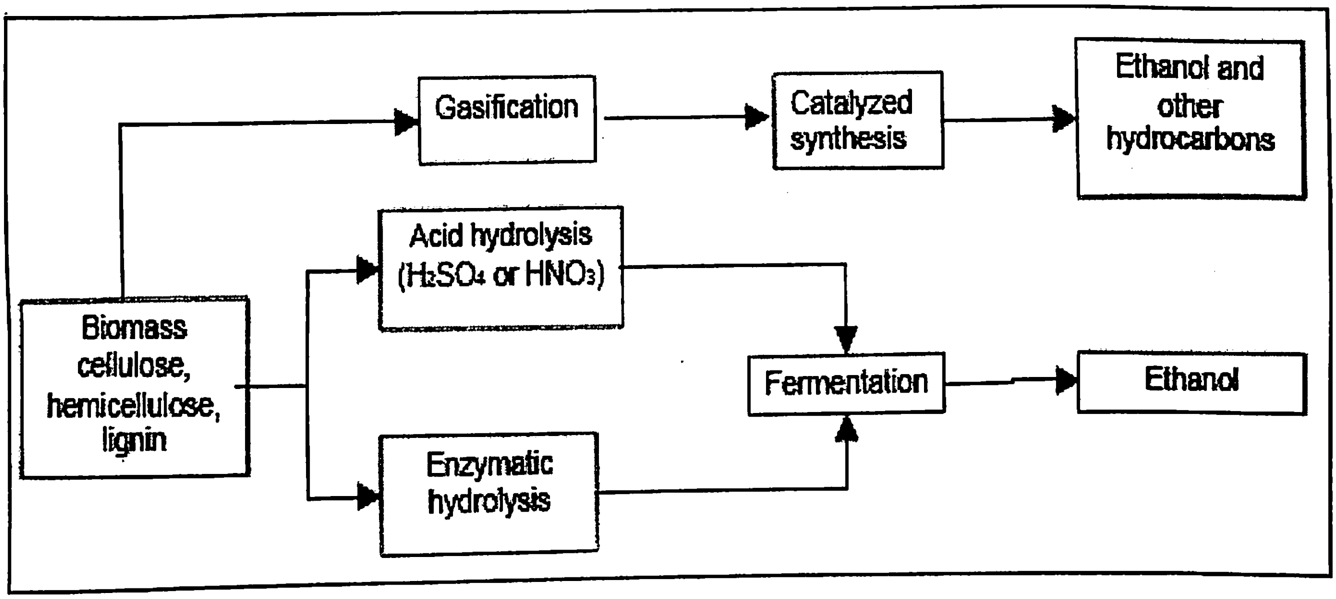
Agricultural residues from crop harvesting also give leftover organic material in the form of corn stover, rice straw and bagasse, which can be used to produce ethanol. There is an element of uncertainty with the logistics in using agricultural residues due to their seasonal availability but most agricultural residues, wood residues such as saw dust, leftover branches and barks from logging can also be used to produce ethanol. Another source that is widely available and inexpensive is animal waste.

A large variety of biomass can be used as feedstock for the production of cellulosic ethanol. India has abundant biomass feedstock such as rice straw, sugarcane bagasse and wheat straw.

However, we must also consider that although theoretically large amounts of this feedstock are available in India, they may not be available in these quantities for the production of cellulosic ethanol as they are used as fodder for animal feed purposes or even as a fuel itself to be burnt. Therefore, collection and availability may be an issue to be considered.

Technologies currently being studied to produce cellulosic ethanol

Although currently, hydrolysis is an expensive process, some companies worldwide have claimed that acid hydrolysis can be made economically viable for the commercial production of ethanol through newer technology, modern control methods and newer materials of construction. Enzymatic fermentation is a process that adds an extra step to the fermentation process. This employs enzymes to break down cellulose and hemicellulose into sugars. These sugars are then fermented into ethanol. The enzymes cellulose simply replaces the sulphuric acid in the hydrolysis step. The cellulose can be used at lower temperatures, which reduces the degradation of the sugars. Process improvements allow simultaneous saccharification and fermentation. Here, the cellulose and fermenting yeast are combined, so that as sugars are produced, the fermentative organisms convert them to ethanol in the same step. A highly promising technology, it is expected be widely used in the long term.



Conversion pathways for making ethanol from cellulosic biomass

Although research is currently taking place on technologies to efficiently utilize some of the alternative feedstock for cellulose conversion, these processes are, by and large, still experimental and currently more expensive to use than the fermentation process.

Converting a wider range of biomass to ethanol will ensure sustainability. The process, however, has to be made more efficient in order to reduce costs of conversion, increase yields and potentially increase the diversity of crops used. There is also considerable research taking place in the area of lignocellulosic ethanol for simultaneous saccharification and fermentation. Research is being carried out to engineer yeast strains with high tolerance, in order to further increase efficiency. Biotechnological and microbiological methods are being actively used in genetic engineering for special strains of yeast and to develop a biotechnological route for the manufacture of cellulosic ethanol.

Currently, to make bioethanol production from cellulose affordable it is necessary to develop a process to break down cellulose to glucose molecules, profitably, and process with fermentation.

3. PROCESS TECHNOLOGY

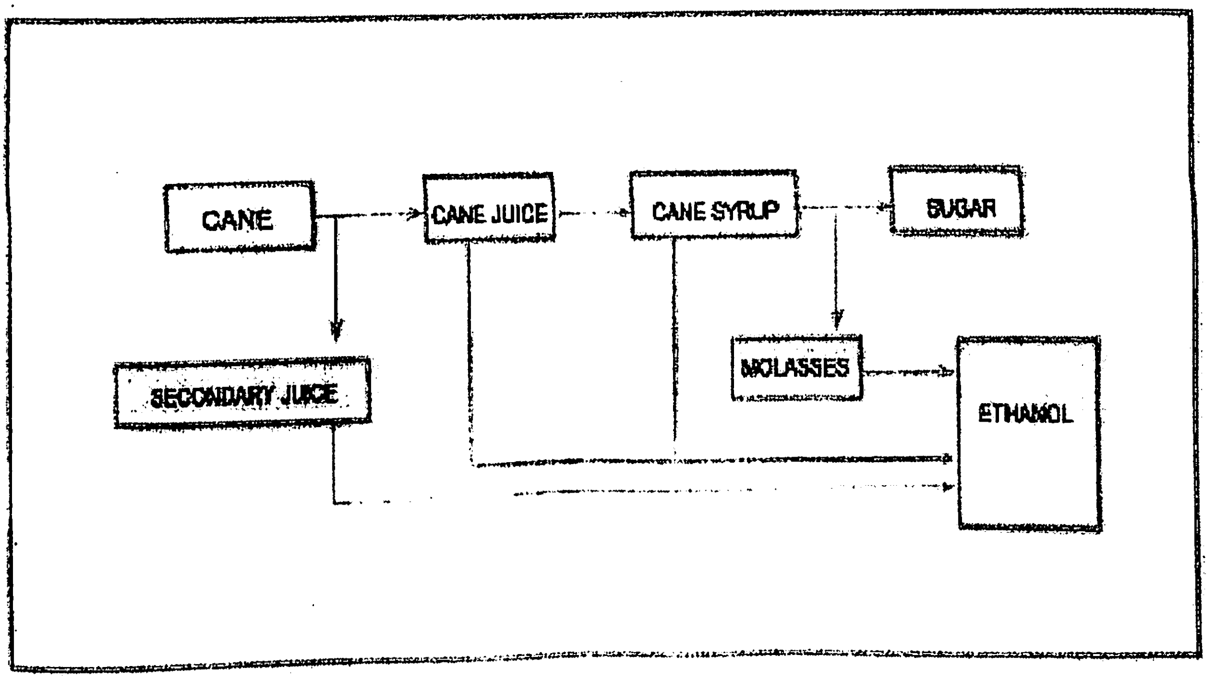
Various routes for manufacture of ethanol are:

- Fermentation
- Milling
- Catalytic hydration of ethylene
- Ethylene esterification and hydrolysis

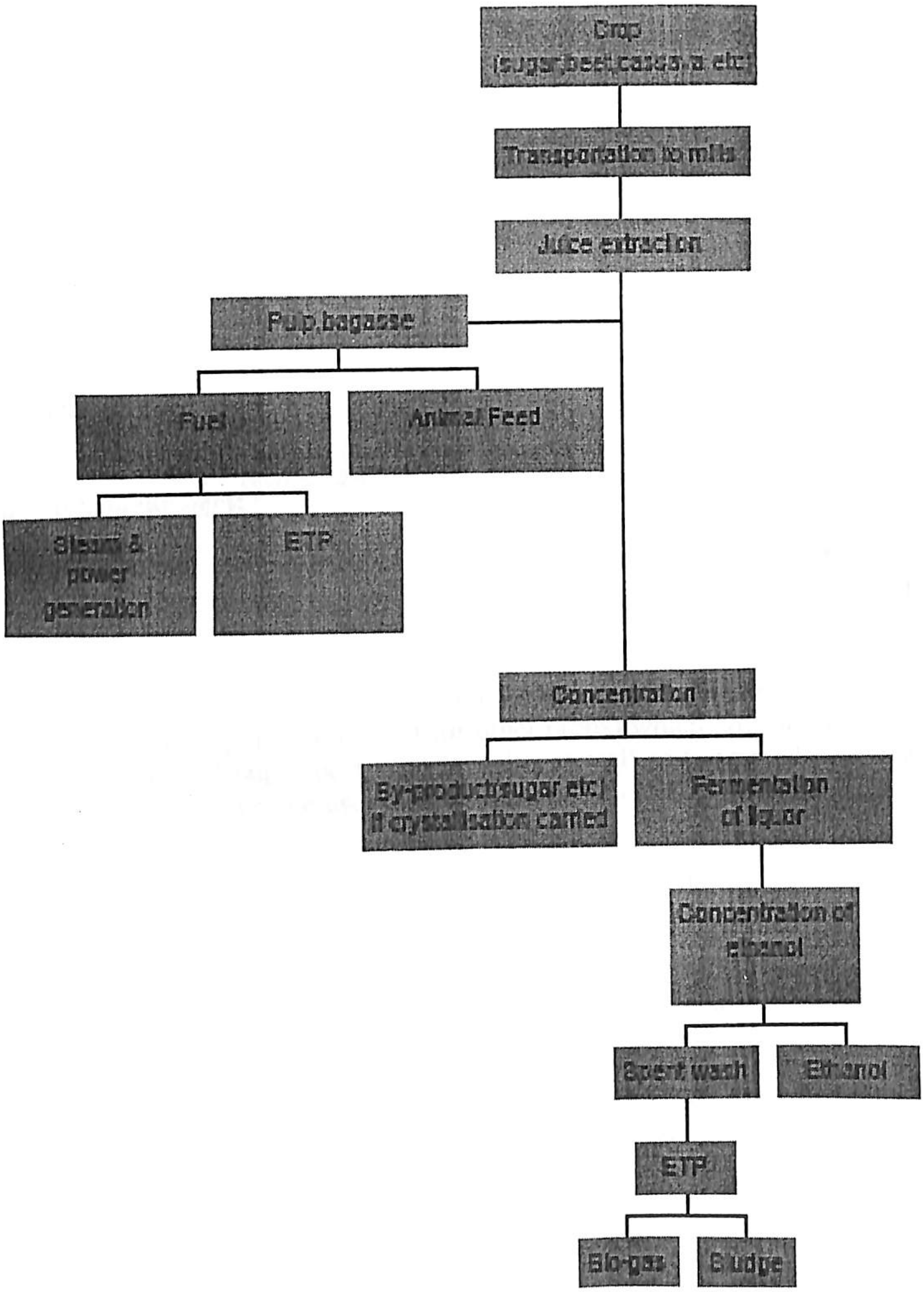
3.1 Fermentation

Ethanol production is very ancient linked with making potable alcohol. The liquor containing corn, grapes juice, molasses etc are fermented by adding yeast to it in batch fermentators for a number of hours (minimum 40 hours) when fermentation gets completed it is distilled to remove water and undesirable compounds for achieving 99%+ purity.

From molasses



Molasses is the residue left after extraction of crystallized sugar and is one of the major by-products of the sugar industry. Ethyl alcohol is produced from molasses by fermentation process utilizing yeast enzymes. The fermentation of diluted acidified molasses is carried out in large wooden or steel fermentation tanks. Further separation of 8-10 percent alcohol is achieved in a series of distillation columns, as alcohol and water at 95 percent concentration form an azeotropic mixture.



Ethanol for use in alcoholic beverages, and the vast majority of ethanol for use as fuel, is produced by fermentation. When certain species of yeast, most importantly, *Saccharomyces cerevisiae*, metabolize sugar in the absence of oxygen, they produce ethanol and carbon dioxide. The chemical equation below summarizes the conversion:

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2$$

The process of culturing yeast under conditions to produce alcohol is called brewing. Ethanol's toxicity to yeast limits the ethanol concentration obtainable by brewing. The most ethanol-tolerant strains of yeast can survive up to approximately 15% ethanol by volume.

The fermentation process must exclude oxygen. If oxygen is present, yeast undergoes aerobic respiration which produces carbon dioxide and water rather than ethanol.

In order to produce ethanol from starchy materials such as cereal grains, the starch must first be converted into sugars. In brewing beer, this has traditionally been accomplished by allowing the grain to germinate, or malt, which produces the enzyme, amylase. When the malted grain is mashed, the amylase converts the remaining starches into sugars. For fuel ethanol, the hydrolysis of starch into glucose can be accomplished more rapidly by treatment with dilute sulfuric acid, fungally produced amylase, or some combination of the two.

Through sugar beet:

In European countries sugar beet is preferred. Sugar beet has certain advantages over sugarcane. The advantages are: lower cycle of crop production, higher yield, high tolerance of wide range of climatic variation, low water and fertilizer requirement (compared to sugar cane, sugar beet requires 35-40 % water and fertilizers). From the table below it will be clear that ethanol yield is higher per year per unit of land even taking only one crop and (no credit for other crops) which will be there in case of sugar beet. Harvesting of sugar beet is also easier as well as requires lower energy for juice extraction. The pulp can be used for cattle field for steam generation.

Comparison of cane and sugar beet

Properties	**Cane**	**Sugar Beet**
Cycle of crop	10-11 months	5-6 months
Yield per acre	25 to 30 tons	35 to 40 tons
Sugar content on weight	12 to 16%	14 to 18%
Sugar yield	3.0 to 4.8 tons/acre year	4.9 to 7.2 tons/acre year
Ethanol yield (100%)	1,700 to 2,700 lit/acre/yr	2,800 to 4,100 lit/acre/yr (with one cycle/yr).

Considering the surplus sugar production in the country it will provide an outlet for the cane production if some sugar is diverted to ethanol production. A part of juice can be directly converted into ethanol thus saving energy and achieving higher yield and reduction in spent wash.

3.2. Starch Based Alcohol Production:

3.2.1. Process

Alcohols are produced from a large number of different starch crops as barley, wheat, corn, 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 corn
- Removal of by-products, as DDGS, corn oil, corn gum etc

Milling of the corn 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. Corn contains some cellulose which does not ferment. A residue called dried distillers grains and soluble (DDGS) is obtained. Presently one bushel of corn gives 2.5 gallons of ethanol, 17 lbs of DDGS and 19 lbs of co2. DDGS utilization/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 gallon/bu) to 3.52 gallons/bu. This also reduces the DDGS from 17 lbs to 7 lbs/bu and increases its protein content.
- Use of high temperature yeast as Thermosac capable to operate at 35-40$_o$ C, producing 18-20% ethanol.

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

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-

	TODAY	FUTURE
Alcohol yield		
Per day	2.75/bu	3.52/bu
Per ton	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

3.2.2. Sweet sorghum as a feedstock

At present, two thirds of world sugar production is obtained from sugar-cane and, one third from sugar beet. These two crops are not in competition, but complementary, being cultivated for their specific requirements in two different climatic belts. In contrast, sweet sorghum can be cultivated in temperate and tropical regions, increasing its potential benefits. Other crops that can yield oligosaccharides (potatoes, cereals, grapes, etc.) are generally not much utilized for bioethanol production (with the exception of corn in the USA). However, particular varieties of sweet sorghum recently developed in China, the USA, and the EU have very attractive and economically promising characteristics. Sweet sorghum can be grown in temperate and tropical regions. Sweet sorghum produces a very high yield in terms of grains, sugar, lignocellulosic biomass (on average a total of 30 dry tons/ha per year) Plantations need less seed than for other crops: 15 kg/ha compared with 40kg/ha for corn, or 150 kg/ha for wheat.

3.3 Ethanol by Vapor Phase Hydration of Ethylene

An ethylene rich gas is mixed with water and heated to about 300 C and passed on to a fixed bed catalytic reactor where catalytic hydration of ethylene takes place.
Ethanol for use as industrial feedstock is most often made from petrochemical feed stocks, typically by the acid-catalyzed hydration of ethylene, represented by the chemical equation

$$C_2H_{4(g)} + H_2O_{(g)} \rightarrow CH_3CH_2OH_{(l)}$$

The catalyst is most commonly phosphoric acid, adsorbed onto a porous support such as diatomaceous earth or charcoal. This catalyst was first used for large-scale ethanol production by the Shell Oil Company in 1947. The reaction is carried out at with an excess of high pressure steam at 300 °C.

The catalyst used is phosphoric acid deposited on silica gel. The reactor effluents are sent to a separator of vapor and liquid. The gases from the separator are cooled scrubbed with water to recover traces of alcohol. The gases are then recycled to the reactor. The alcohol-water mixture is sent to a series of distillation columns where ether is separated in the light-end column and finally 95 percent by volume ethanol-water azeotrope is separated. Purification of ethanol is carried out by catalytic hydrogenation to convert any acetaldehyde formed.

In an older process, first practiced on the industrial scale in 1930 by Union Carbide, but now almost entirely obsolete, ethylene was hydrated indirectly by reacting it with concentrated sulfuric acid to produce ethyl sulfate, which was then hydrolyzed to yield ethanol and regenerate the sulfuric acid:

$$C_2H_4 + H_2SO_4 \rightarrow CH_3CH_2SO_3H$$

$$CH_3CH_2SO_4H + H_2O \rightarrow CH_3CH_2OH + H_2SO_4$$

3.4 Ethanol by Esterification and Hydrolysis

Another route for manufacture of ethanol is through esterification and hydrolysis.

$$C_2H_4 + H_2SO_4 \rightarrow C_2H_5OSO_3H$$

$$2C_2H_4 + H_2SO_4 \rightarrow (C_2H_5O)_2SO_2$$

$$C_2H_5OSO_3H + (C_2H_5O)_2SO_2 + 3H_2O \rightarrow 3C_2H_5OH + 2H_2SO_4$$

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$$

Ethylene and sulphuric acid react at 80 C and 1.5 MPa to form a mixture of ethyl sulphates, which are then hydrolyzed to ethyl alcohol. Ethylene and sulphuric acid react in the absorber from which the mixture of ethylene sulphates thus formed is fed to hydrolyser from which the crude alcohol and sulphuric acid are fed to stripping and caustic scrubbing sections and finally to a series of two distillation columns for the separation of ether and alcohol.

4. ANHYDROUS ETHANOL

By fermentation alone not more than 10% ethanol content can be achieved, whereas the requirement for potable or industry is of getting over 95% purity. The traditional method is distilling the fermented liquor which can provide a purity upto 95%. Water in ethanol is undesirable in its use in gasoline blend and purity over 99% (i.e. anhydrous alcohol) is required. Ethanol forms constant boiling mixture with water at 95.6% that does not allow simple distillation to meet the purpose. As a solution to the problem, azeotrophic distillation through solvent benzene or cyclohexane is used. Azeotrophic distillation, however, increases production cost of ethanol considerably. The cost effective solution is found through the use of molecular sieve to eliminate water by an adsorbent, properly known as Pressure Swing Adsorption- Molecular Sieve Dehydration Technology (MSDH). It uses a synthetic adsorbent to dehydrate alcohol and results into high level of dryness with low energy requirement. Use of vapor phase adsorption has resulted into further energy saving in the process. Fermented wash with approx. 8% v/v ethanol from the wash holding tank is fed to the top of the degasifying column after preheating and spent stillage cooler. Overhead vapor of approx. 40% w/w from the degasifying column is then fed to the bottom of the heads column. Impure spirit with approx. 95% v/v is removed from the vent condenser of the heads column. Heads column bottoms are fed to the alcohol column for recovery of alcohol.

The wash column is heated through the forced circulation reboiler with the condensing vapors from the rectifying column, which is operated under pressure. Analyzer column vapors are condensed and fed to an extractive distillation column. This column is operated with high dilution to enable the removal of fusel oils. Vapors are condensed and sent to the recovery column for alcohol recovery. The alcohol water stream from the bottom of the extractive distillation column is fed to the rectifying column. The rectifier vapors are used to heat the analyzer by using the pressure cascading technique. Ethanol (concentration of 96% v/v) is removed from the top three plates and fed to the demethylizer column for separating methanol. The product Rectified Spirit (RS) is removed from the bottom of the methanol column and cooled in the product cooler. Anhydrous alcohol is produced from 96% RS by molecular sieve technology. Anhydrous ethanol with purity above 99.8–99.9 is produced in the system, using vapor phase adsorption with pressure swing for regeneration. This is the most economical technology for producing anhydrous alcohol.

Fuel ethanol or absolute alcohol is produced by dehydration of rectified spirit or industrial alcohol and can be produced from:
a) Industrial grade alcohol
b) Rectified spirit (RS)
c) Extra-neutral alcohol (ENA)

Commercially available technologies for dehydration of rectified spirit can be classified in to two broad headings-

1. Molecular sieve technology

2. Pervaporation (Membrane technology)
3. Azeotropic distillation

4.1. Molecular Seive Technology

Molecular sieve technology works on the principle of pressure swing adsorption wherein water is first removed by adsorbing on surface of 'molecular sieves' and then cyclically removing it under different conditions including steaming.

Molecular sieves are synthetic zeolites typically 3A zeolite. Zeolites are synthetic crystalline aluminosilicates. This material has strong affinity for water. They adsorb water in cold condition and desorb water when heated. This principle is used to dehydrate ethanol. The crystalline structure of zeolites is complex and gives this material the ability to adsorb or reject material based on molecular sizes. Water molecule can enter the sieve and be adsorbed, but larger alcohol molecule will not be retained and will go through the bed.

There can be two beds in parallel. Once a particular bed is saturated with water, it is heated with steam so that adsorbed water is desorbed from the bed. Till that time, other bed is used for dehydration.

Low steam consumption and low power consumption as compared to distillation characterize this type of system.

Molecular sieve dehydration:

The salient features of the process are given herewith:

Dehydration with Molecular Sieve Process

The rectified spirit from the rectifier is superheated with steam in feed super-heater. Super-heated rectified spirit from feed super-heater is passed to one of the pair of molecular sieve beds for several minutes. On a timed basis, the flow of superheated rectified spirit vapor is switched to the alternate bed of the pair. A portion of the anhydrous ethanol vapor leaving the fresh adsorption bed is used to regenerate the loaded bed. A moderate vacuum is applied by vacuum pump operating after condensation of the regenerated ethanol water mixture. This condensate is transferred from recycle drum to the Rectified Column in the hydrous distillation plant Via Recycle pump. The net make of anhydrous Absolute alcohol draw is condensed in product condenser and passed to product storage.

The life of molecular sieve may be around five to seven years. However, the operating cost is considerably less than **azeotropic distillation.**

Molecular sieve ethanol dehydration technology for fuel ethanol

Most of the ethanol dehydration plants for production of absolute alcohol are based on Azeotropic distillation. It is a mature and reliable technology capable of producing a very dry product. However, its high capital cost, energy consumption, reliance on toxic chemicals like benzene and sensitivity to feedstock impurities, has virtually eliminated the use of azeotropic distillation in modern ethanol plants. Benzene has been used as entrainer of choice of ethanol dehydration but it is now known to be a powerful carcinogen.

4.1.1. Advantages of Molecular Sieve technology

1. The basic process is very simple, making it easy to automate which reduces Labour and training requirements.
2. The process is inert. Since no chemicals are used, there are no material handling or liability problems, which might endanger workers.

Molecular sieves can easily process ethanol-containing contaminants, which would cause immediate upset in an azeotropic distillation system. In addition to ethanol, a properly designed sieve can dehydrate a wide variety of other chemicals, thereby providing added flexibility in future operating options.

The molecular sieve desiccant material has a very long potential service life, with failure occurring only due to fouling of the media or by mechanical destruction. A properly designed system should exhibit a desiccant service life in excess of 5 years.

It can be configured to function as a stand-alone system or to be integrated with the distillation system. This lets the customer make the trade-off between maximum operating flexibility versus maximum energy efficiency.

If fully integrated with the distillation system, steam consumption rate only slightly above the absolute theoretical minimum for the separation can be achieved.

A properly designed molecular sieve can reliably dehydrate 160-proof ethanol to 190 + proof, making strict control of rectifier overhead product quality unnecessary.

4.1.2. Process Description:

From Feed Tank, rectified spirit is pumped to the Stripper / Rectifier Column. A partial steam of vapors from the Column are condensed in Condenser and sent back to the column as reflux. Rest of the vapors are passed through a super-heater and taken to the Molecular Sieve units for dehydration. The vapor passes through a bed of molecular sieve beads and water in the incoming vapor stream is adsorbed on the molecular sieve material and anhydrous ethanol vapor exists from the Mol. Sieve Unit.

Hot anhydrous ethanol vapor from the Mol. Sieve Units is condensed in the Mol. Sieve Condenser. The anhydrous ethanol product is then further cooled down in the product cooler, to bring it close to the ambient temperature. The two Mol. Sieve units operate sequentially and are cycled so that one is under regeneration while the other is under operation, adsorbing water from the vapor stream. The regeneration is accomplished by applying vacuum to the bed undergoing regeneration. The adsorbed from the molecular sieves material desorbs and evaporates into the ethanol vapor stream. This mixture of ethanol and water is condensed and cooled against cooling tower water in the Mol. Sieves Regenerant Condenser. Any uncondensed vapor and entrained liquid leaving the Mol. Sieve Regenerant Condenser enters the Mol. Sieve Regenerant Drum, where it is contacted with cooled regenerant liquid.

The cooled regenerant liquid is weak in ethanol concentration, as it contains all the water desorbed from the Molecular Sieve Beds. This low strength liquid is recycled back to the Stripper Column for recovering the ethanol. The water leaves from the bottom of the column and contains only traces of alcohol.

4.2 Pervaporation:

It is nothing but a form of ultra-filtration where a hydrophilic membrane is used to filter out water from the mixture of alcohol and water.

Here, membranes are used to filter out water out of the ethanol - water mixture. Ultra filtration, nano-filtration and reverse osmosis principles are used here. Also, the size of the membrane depends on the flux of water molecules through it. Hence, if higher purity of ethanol (>99.2 per cent), is required, we get two streams - absolute alcohol stream and weak alcohol stream. The weak alcohol stream has to be distilled to recover ethanol.

4.3 Azeotropic Distillation:

Rectified spirit of industrial alcohol has around 5 per cent v/v water content. This cannot be removed further by simple binary distillation. This is because ethanol forms azeotrope with water at that temperature at atmospheric pressure and temperature.

To dehydrate ethanol further, a third substance called as entrainer (cyclohexane, benzene, toluene, ether, ketone etc) is added to the mixture of ethanol and water.

Entrainer breaks the azeotropic point of ethanol and water, i.e. it alters the relative volatility of water making it more volatile. A typical distillation assembly consists of two distillation columns namely, Dehydration column and Recovery column and a decanter.

During distillation of such a mixture, entrainer forms a ternary azeotrope with water and ethanol and comes at the top of the dehydration column. Water free ethanol comes out from bottom of the dehydration column. The ternary azeotrope coming out from top of the column is heterogeneous in nature and separates into two layers in the decanter. The organic layer contains predominantly entrainer.

It is recycled back to the dehydration column as reflux. The aqueous layer contains some dissolved ethanol and small amount of entrainer. It is send to the recovery column for recovery of this dissolved ethanol and entrainer. Thus the total entrainer is recycled back and only small make up is required to account for losses in vent and drain. This configuration is energy intensive.

5. BIOETHANOL

Raw materials for making bioethanol

Ethanol producers in the United States produce around 1.5 billion gallons of ethanol each year, mostly derived from corn. 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 (corn 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 corn ethanol industry with the emerging technologies that produce ethanol from agricultural wastes and other types of biomass.

5.1 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.

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

5.2 Review of Technologies for Manufacture of Bioethanol

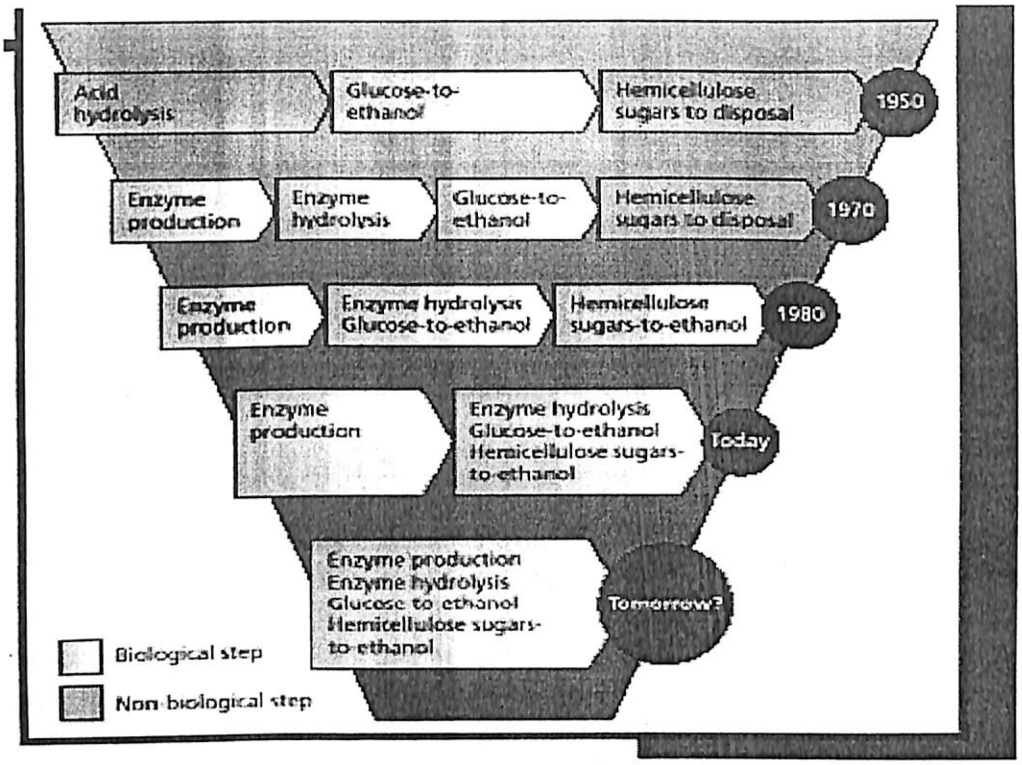
The degree of complexity and feasibility of biomass conversion to ethanol depends on the nature of the feedstock. The three largest components of the biomass sources are cellulose, hemicellulose, and lignin ranges of which are presented in Table. Ranges of sugar content in hardwoods, softwoods, and agricultural residues are provided in Table. 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.

Typical levels of cellulose, hemicellulose and lignin in biomass

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

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 converting biomass to bioethanol:

1. Producing biomass results in the fixing of atmospheric carbon dioxide into organic carbon.
2. Converting this biomass to a useable fermentation feedstock (typically some form of sugar) can be achieved using a variety of different process technologies. These processes for fermentation feedstock 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.

5.3 Technologies

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 and 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.

5.3.1 Concentrated Acid Hydrolysis

This process is based on concentrated 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 pla ns 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.

5.3.2 Dilute Acid Hydrolysis

Hydrolysis occurs in two stages to maximize sugar yields from the hemicellulose and cellulose fractions 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 situation. Today, companies are beginning to look at commercial opportunities for this technology, which combine recent improvements and niche opportunities to solve environmental problems. BC International (BCI) and the DOE have formed a cost-shared partnership to develop a biomass-to-ethanol plant. The facility will initially produce 20 million gallons per year of ethanol. BCI has utilized an existing ethanol plant located in Jennings, LA. Dilute acid hydrolysis will be used to recover sugar from bagasse, the waste left over after sugar cane processing. A proprietary, genetically engineered organism will ferment the sugars from bagasse to ethanol. Tembec and Georgia Pacific are operating sulfite pulp mills in North America, which utilize a dilute acid hydrolysis process to dissolve hemicellulose and lignin from wood, and produce specialty cellulose pulp. The hexose sugars in the spent sulfite liquor are fermented to ethanol. The lignin is either burnt to generate process steam or convertedto value-added products such as dispersing agents, animal feed binders, concrete additives, drilling mud additives, and soil stabilizer.

5.3.3 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. Enzymatic hydrolysis will be used in Iogen/Petro Canada's Ottawa, Canada project and is being explored for BCI'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. This may be possible by genetic manipulation of microbes.

5.3.4 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 corn fiber—the shell of the kernel as a source of additional sugars for ethanol production. But, corn 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.

5.4 Technological Advancement in the Area of Bioethanol

Ethanol is largely produced through the fermentation of sugars from feedstock such as corn, sugarcane, beet and grains. This process is rather expensive, not only due to high cost associated with the feedstock, but also with the volatility and risk associated with the availability issues of agricultural feedstock. The five major sugars are the five carbon xylose and arabinose and the six carbon glucose, galactose and mannose.

Traditional fermentation processes rely on yeasts that convert six-carbon sugars to ethanol. Glucose, the preferred form of sugar for fermentation, is contained in both carbohydrates and cellulose. Because carbohydrates are easier than cellulose to convert to glucose, the majority of ethanol currently produced in the United States is made from corn, which produces large quantities of carbohydrates. Also, the organisms and enzymes for carbohydrate conversion and glucose fermentation on a commercial scale are readily available.

Most of the technology issues being addressed right now focus at making the production process more efficient and less expensive. In order to address the restraint of expensive feedstock and availability issues, intensive research is going on in the field of cellulosic ethanol to enable the utilization of a larger range of biomass.

In the selection of technology, it is essential, in today's scenario to ensure that the technology currently being utilized will remain widely used for a sustained period of time to negate the necessity of an upgrade in the near future, and also to fight competition from a lower priced product from the manufacturers with a newer and more efficient technology. The technology must be efficient in taking into consideration yield, wastage, effluent treatment, possible recycling of utilities and should be applicable to a wide range of raw materials.

Globally emerging technologies

A large number of plants in Brazil employ the process of azeotropic distillation in the production of ethanol. Here, dehydration is carried out in the presence of an entrainer like benzene or cyclohexane. However, this process is very energy intensive and benzene, a carcinogenic, has been banned in many countries. Sometimes, extractive distillation using ethylene glycol is also used.

An upcoming technology to streamline the dehydration process and now being widely considered is molecular sieves. Molecular sieves, in the form of synthetic adsorbents, bring down energy consumption and ensure a high level of dryness. Earlier systems operated in liquid phase and used thermal swing regenerated process, which did not make them very efficient. Further development on the adsorbent saw introduction of vapor phase operation with pressure swing regeneration system and proved to be highly energy-efficient.

Catalytic synthesis involves the production of ethanol from synthesis gas (a mixture of carbon monoxide and hydrogen) upon reacting with an appropriate catalyst at high temperature and pressure. This process can be used on a variety of feedstock. A recent prospective technology has been the discovery of the anaerobic bacterium Clostridium ljungdahlii.

Ethanol can also be produced from landfill gas. Typically, a landfill gas resource has an expected reserve life of 2540-years without additional capital requirements. Therefore, the ethanol manufacturer can enjoy long term production and market planning.

5.5 Meeting the Ethanol Demand for Blending

The ethanol demand for blending can be calculated from the plan projection of the future growth in gasoline use. The tables below provide the figures for the tenth plan together with the availability.

Ethanol Demand and Supply for Blending In Gasoline

Year	Gasoline demand MMT	Ethanol demand Th KL	Molasses production MMT	Ethanol production			Utilisation of ethanol		
				Molasses Th KL	Cane Th KL	Total Th KL	Potable Th KL	Industry Th KL	Balance Th KL
2001-02	7.07	416.14	8.77	1775	0	1775	648	600	527
2006-07	10.07	592.72	11.36	2300	1485	3785	765	711	2309
2011-12	12.85	756.35	11.36	2300	1485	3785	887	844	2054
2016-17	16.4	965.30	11.36	2300	1485	3785	1028	1003	1754

Notes:

1. Area under cane cultivation is expected to increase from 4.36 mha in 2001-02 to 4.96 in 2006-07 which would add additional cane production of around 50 MMT.
2. About 30% of cane goes for making gur and khandsari. If there is no additional increase in khandsari demand, sugar and molasses production would increase.
3. The present distiller capacity is for 2900 Th kL of ethanol and looks to be sufficent for 5% blend till 12 th plan
4. A growth of 3% in potable use and a 3.5% in chemical and other use has been taken

As per the All India Distillers Association, the present installed capacity of alcohol production in the country is 2900 million litres. With the present availability of molasses to the tune of 9 million tonnes the alcohol production is around 1800 million litres. Out of which around 600 million litres is surplus after meeting the demand of industrial use (540 million litres) and potable use, (650 million litres). This is capable of providing a 5% blend to the gasoline. The present consumption of gasoline is estimated at 8.5 million tonnes requiring 502 million litres for 5% blend. The industry expects that the present capacity able to meet the blending requirement of the gasoline till the end of the Tenth Plan with the terminal years gasoline consumption at 11.6 million tones needing 682 million liters of ethanol for blending where 823 million liters will be surplus from the production of 2300 million liters of alcohol. Decision has already been taken to make it compulsory for a 5% blend of ethanol in gasoline.

Since there is a surplus production of sugar and export not giving much value addition it will not be irrational to convert sugar to alcohol or directly came to alcohol in much more proportion than being carried now. By this a 10% blend of ethanol with gasoline can be maintained for considerable period. Apart from sugarcane, other agroproducts including grains can be used for fermentation. Taking the crop yield in account, sugarcane is the best choice as it is the crop having the highest efficiency of photosynthesis and provides a possibility of 1200 gallons of 99% alcohol from a acre. Potato provides the next highest yield of alcohol on unit area of land; 300 gallons per acre.

From the table it is clear that for meeting 5% blending demand, the ethanol capacity in the country is sufficient. For higher blend and till the demand stabilizes, the crop productivity, or use of bio- mass into converting to alcohol would be much more needed. The Government has taken the decision to make the 5% blending in gasoline as mandatory in phased manner. As stated above, the industry can easily meet the requirement if the land is not diverted from cane production.

Alcohol Production from molasses and Use

(in million litre)

Alcohol year	Molasses Prod. MMT	Production of Alcohol (mil. litre)	Industrial use (mil. litre)	Potable use (mil litre)	Other uses (mil. litre)	Surplus availability of alcohol (mil. litre)
1998-99	7.00	1411.8	534.4	5840	55.2	238.2
1999-00	8.02	1654.0	518.9	622.7	576	455.8
2000-01	8.33	1685.9	529.3	635.1	588	462.7
2001-02	877	1775.2	5398	647.8	59.9	527.7
2002-03	9.23	1869.7	550.5	660.7	61.0	597.5
2003-04	9.73	1969.2	578.0	693.7	70.0	627.5
2004-05	10.24	2074.5	606.9	728.3	73.5	665.8
2005-06	10.79	2187.0	619.0	746.5	77.2	742.3
2006-07	11.36	2300.4	631.4	765.2	81.0	822.8

Potential of ethanol production from sugarcane

Year	Area under cane	Cane prod	Cane utilization			Sugar production		Addl. Alcohol prod. (in million litre)	
			Sugar	Gur & khand	Seed & chew	Target	Revised prod.	From addl. molasses prod.	Addl. cane available for alcohol prod.
2002-03	4.36	309.9	181	92.0	37	182	192	69	475
2003-04	4.53	321.6	188	95.6	38	192	202	99	795
2004-05	4.63	333.3	195	98.3	40	199	212	128	1000
2005-06	4.79	345.1	202	102.1	41	206	223	168	1222
2006-07	4.96	356.8	209	104.8	43	213	233	198	1485

Economics of alcohol 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 further cost 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. 900/70 = 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:-

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

- 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 alcohol 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 -

1. Molecular sieve costing around Rs 2-2.5 crore for 30 kld plant.
2. Anaerobic bio-gas production costing Rs 4-5 crore.
3. Steam and power generation plant (co-generation) costing around Rs 3 crore/MW. Fortunately, apart from a low pay back period for return in investments, there are several sources of getting finance for setting up the facilities above (to increase efficiency)
4. Assistance from Asian Development Bank, KfW, Germany, JBIC, Japan
5. Assistance from IREDA under renewable energy plan
6. Carbon credit of nearly $10/te of carbon saved under CDM of the Kyoto Protocol.

From other feedstocks:

The other major source can be corn, sugrbeet, potatoes etc. Depending on the starch content's in the feedstock, the yield of ethanol would vary. Taking corn, 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 certainly make 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.

6. LABORATORY PRODUCTION OF ETHANOL

6.1 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 description of learning styles 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, sugarcane, wood, etc.). Since corn is so very plentiful in the U.S. at the present time, and probably in 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.

This laboratory procedure takes approximately 2 hours to complete. Plan according to teacher's instructions.

1. Obtain 200 grams of fresh corn mash.
2. Add 700ml of distilled water and stir in 1000ml + beaker.
3. Use Calcium Carbonate or HCl to adjust pH of mash to 5.8.
4. Add 4ml of Alpha Amylase and stir. (4g of Diastase can be sub.)
5. Autoclave at 225F for a minimum of 20 minutes.
6. Remove from autoclave and cool to 190 F and add 3 ml more 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 Glycoamylase 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.
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 temperature 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 is a powdered corn, about the consistency of coarse sand. Cracked corn does not work real well because there is not enough surface area foe 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, soft drinks, fruit, and anything that has good carbohydrate base to it. Be sure that whatever material is used, that is ground or powdered to a fine mesh of #20 or smaller. Since corn is inexpensive at this time, ethanol production is vital.

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.

6.2 Development of Bio-Ethanol from Waste Potatoes

The effect of potato cultivar on bio-ethanol production

Ten Swedish potato cultivars were characterized in a lab scale bio-ethanol process. All potato cultivars were processed in a same way. Experiments were performed in two phases: in the first step, we studied only cultivars numbers 1 and 2, and in the second phase the cultivars 3 to10. Potatoes were processed with skin, except the cultivars 1 and 2 which had also samples without skin.

Lab scale process:

Figure presents the process for production of bio-ethanol from potatoes. Five kg of potatoes were used in each batch. (10 kg of cultivars 1 and 2). Potato tubers were mashed to a particle size of about 5mm. the mash was cooked in water bath for one hour. A portion of the alpha-amylase was added before cooking. After boiling, the mash was cooled to 80-90 C and the rest of alpha amylase was added. After one hour liquefaction, the mash was allowed to cool to 60 C for 30 minutes. Before saccharification the pH of the mash was adjusted from about 6 to 4.2-4.4 with phosphoric acid and the glycoamylase enzyme was added. After 90 minutes saccharification, the mash was cooled to 30 C and the yeast was added. During 6 days fermentation, the mash was mixed regularly. Ethanol was separated from beer with a two phase distillation. The first distillation was in the range of 20-94 C. the distillate was handled with carbon and $CuSO_4$ and then the solution was distilled to a temperature of 90 C. Potato cultivars 3 and 7 were processed two times.

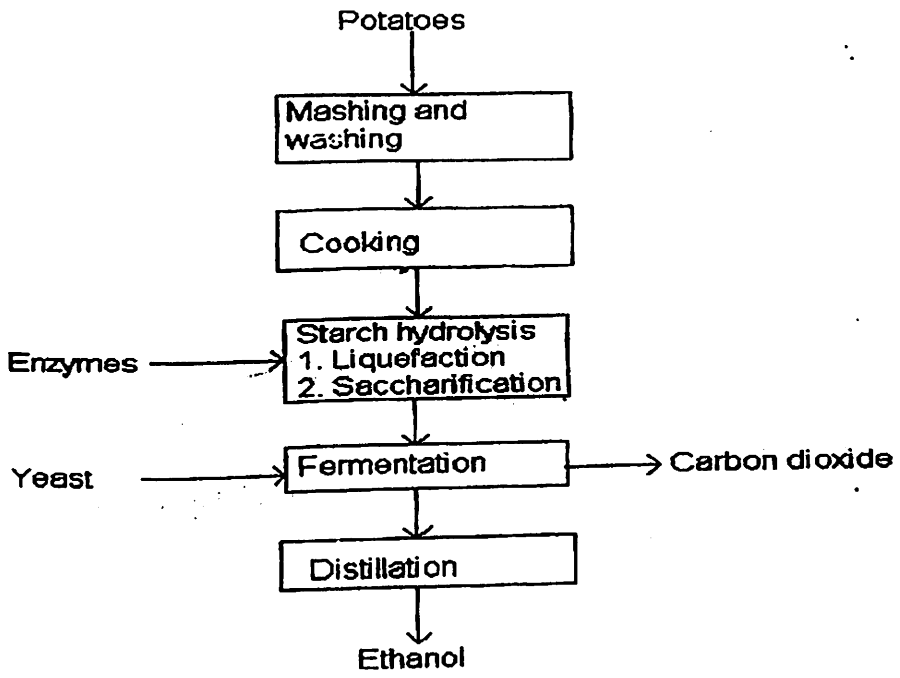


Figure 1. Bio-ethanol production from potatoes.[3]

Properties of waste solution from distillation

Waste solutions from distillation contain quite high concentrations of impurities formed during the fermentation process. Purification of these solutions is not economically viable. However, it is possible to find other application for these bi-products, for instance in industry. The properties analyzed from waste solution of distillation during this study were alcohol content, concentrations of volatile compounds, the heat of combustion ΔHm and the heat of evaporation ΔHvap. Alcohol content was determined with electronic densimetry (AP Paar DMA 40). The method used for the determination of volatile compounds was based on commission regulation (EC) no. 2870/2000. the heat of combustion ΔHm was measured with bomb calorimeter. The low pressure system was used to determine heat of vaporization ΔHvap.

6.3 Ethanol Production by Immobilized Bakery Yeasts

Immobilization of bakery yeast by entrapment calcium alginate gel

A polymeric matrix was prepared using sodium alginate. For this purpose, 300 ml of distilled water was prewarmed at 60 C, and 4.5 gm of sodium alginate (sigma chemical co) was added with continuous stirring until every clot had been dissolved. Commercial pressed bakery yeast, 11.25 gm, was mechanically suspended in 300 ml of the previously prepared 1.5% sodium alginate solution. Figure 2 shows the dropping system for yeast immobilization. An Erlenmeyer flask was filled with the yeast suspension and then emptied by gravity, drop by drop, into a 0.1M CaCl2 solution. The drop volume was calibrated to be 0.04 ml, using an appropriate diameter tube. The calibration was performed by passing distilled water through the tube weighing a fixed number of water droplets. In this way, all the suspension turned into yeast spheres with 10^7 cells per bead. After 15 mins, the beads were washed 4 times with distilled water to eliminate Ca2+ excess.

Alcoholic fermentation of glucose

For fermentation kinetics evaluation, a special device was used (figure 3). It was completely constructed in borosilicate glass. This fermentor was designed to allow only CO2 release. The H2SO4 trap retained only some ethanol molecules that could escape to the gas phase from the fermentation mixture.

The fermentation process was developed as follows:
One batch fermentor was filled with 4000 beads. The other was loaded with 6 g bakery yeast, which represents the amount entrapped in the beads. Then 200 ml of the fermentation medium was added to each fermentor. After connecting the Erlenmeyer flask to the trap filled with H2SO4 solution, the fermentors were immediately weighed and the initial weight was registered. Subsequently, at 1-hr intervals at 35 C incubation without shaking, the weight loss, assumed as CO2 mass, was determined.
The mass (the fermentor mass at time n minus the fermentor mass at time 0) was plotted against the incubation time.

Summary of reagents and equipments used

4.5 gm of sodium alginate in 300 ml distilled water
600ml of 0.1 M CaCl2 in distilled water
11.25 g of commercial bakery yeast (8 X 10^9 colony forming units in sabouraud agar plates/g)
2 fermentors
100 ml H2SO4 0.1M
500 ml fermentation medium
Thermostatic incubator
Magnetic stirrer
Plastic tubes
Balance
General glass laboratory materials

7. ETHANOL PROGRAMME

In the introduction, it has been stated that need for automotive fuel is going to increase and, dependence of internal combustion engine as a source for transport will continue with other technological developments not posing any significant challenge to it.

Among the automobiles, there are two groups of their engines, based on –

- Constant volume cycle which in practice is our gas engines and alternatively called spark ignition engine. The fuel for this kind of engine is gasoline cut of the crude oil.

- Constant pressure cycle which in practice is diesel engine and alternatively called compression ignition engine. The fuel for this kind of engine is diesel a major fraction of crude oil distillation.

While the latter is used for all our heavy vehicles in railway transport, in tractors etc, the former is used for all light vehicles like cars, three wheelers and two wheelers.
Overall efficiency of a gasoline engine is lower than that of a diesel engine, still it offers certain advantages due to its operation based on gasoline, a light fuel. The advantages are in the form of quick start, fast acceleration, no large emission of particulate matter (PM), no frequent major engine over-hauling requirement etc. One of the major concerns of the diesel engine is the emission of 100 to 200 times smaller sized PM than that in the gasoline engine exhaust. Gasoline gives the advantage of making possible two stroke engines for motor bikes, scooters etc without the need of cumbersome valve mechanism.

The demand for light vehicles continues to grow faster than for heavy vehicles. If the diesel and petrol prices are near to each other as is the case in other countries, the tendency of having diesel engines in cars would not be there. The recent price trends show that the gap between the prices of petrol and diesel would close. The demand for auto cycles is growing very fast. With increase in trade and urbanization, a larger segment of population is finding it essential to use two wheelers. The per capita income is growing, and there is a corresponding increase in the use of cars also. The fuel for such engines (spark ignition) is petrol derived by distilling crude oil taking out from the petroleum reserves. It is composed of hydro-carbons which give it a high calorific value of above 10000 kcal/kg. Gasoline has all the desirable properties for storage, ignition, combustion and handling.

However, as narrated earlier, gasoline has two drawbacks which every petroleum derived fuel has namely that it is derived from a depleting resources and that its engines' emission increases the level of NOx, CO2, particulate matter and hydro-carbons in the atmosphere. For the emission of green house gases (GHGs) as NOx and CO2, it is a major contributor to climate change, the greatest concern of the present day.

7.1 Problems with Gasoline:

There are several problems in using gasoline or motor spirit or petrol which are derived from crude oil. Petroleum reserves are finite. Emissions from engines using gasoline or motor spirit such as Nitrogen Oxides, Sulphur Dioxide, Carbon Dioxide and particulate matter cause pollution. Gasoline has knocking tendency which limits the compression ratio of the gas engine. TEL is an additive that improves the anti-knocking rating of the fuel dramatically. The harmful effect of the lead led to banning of its use. Benzene or cyclic compounds also increase the octane rating. Benzene is, however a known carcinogenic material. Alternatively, MTBE and ETBE are used as additives to improve anti-knocking tendency and to reduce other vehicular emissions. The oxygenated fuels burn more completely and so reduce carbon monoxide emission upto 20%.

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.

7.2 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 classes 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 but yl 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 burn more completely and so reduce carbon monoxide emission upto 20%.

7.3 Diesel Engine Problem, Higher Emission of Respiratory Particulate Matter

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 g/bhp-hr rule in 2002 to 0.01 g/bhp-hr in 2006. Even stricter regulations are being initiated in EU. 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.

7.4 Feasibility of Producing Bio-Fuels as Petrol and Diesel Substitutes

While the country is short of petroleum reserve, it has large arable land as well as good climatic conditions (tropical) with adequate rainfall in large parts of the area to account for large biomass production each year. The country, therefore, has very good potential to produce biomass that can be processed in to biofuels that are substitutes of transport fuels.

Ethanol

In India ethanol is currently produced mainly from molasses that is a renewable source and a bio-product of the sugar industry.. It can be also produced from starch as potatoes or even wood. The sugar cane juice and its products both sugar and molasses can be diverted for production of ethanol to be blended in gasoline. However, ethanol has other uses such as beverage and industrial alcohol. The feasibility of producing sufficient quantity of ethanol for blending with motor gasoline is discussed in later part.

8. ETHANOL AS FUEL

8.1 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

BIS specs of 1995 for Motor Gasoline allows oxygenates as follows:

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.

Properties 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	

8.2 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 has 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 practiced. It can be blended both in diesel as well as gasoline. The advantages and problems associated with the blends are summarized in the following paragraphs.

As can be seen from 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 vaporization causing startability problem, (iv) higher evaporation losses due to higher vapor 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 number of ethanol.

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 Properties

Ethanol	Gasoline
Specific Gravity = 0.794	Specific Gravity = 0.72 – 0.78
Boiling Temperature = 77.8°C	Boiling Range = 27 – 225°C
Flash Point = 12.8°C	Flash Point = -42°C
Energy Content = 23,550 kJ/kg	Energy Content = 44,540 kJ/kg
RVP = 15.8 kPa	RVP = 55 – 103 kPa
Blending Octane RON = 120 – 135 MON = 100 – 106	Octane RON = various MON = various

8.3 Ethanol-Based Engines

Ethanol is most commonly used to power automobiles, though it may be used to power other vehicles, such as farm tractors and airplanes. Ethanol (E100) consumption in an engine is approximately 34% higher than that of gasoline (the energy per volume unit is 34% lower). However, higher compression ratios in an ethanol-only engine allow for increased power output and better fuel economy than would be obtained with the lower compression ratio. In general, ethanol-only engines are tuned to give slightly better power and torque output to gasoline-powered engines. In flexible fuel vehicles, the lower compression ratio requires tunings that give the same output when using either gasoline or hydrated ethanol. For maximum use of ethanol's benefits, a much higher compression ratio should be used, which would render that engine unsuitable for gasoline usage. When ethanol fuel availability allows high-compression ethanol-only vehicles to be practical, the fuel efficiency of such engines should be equal or greater than current gasoline engines. However, since the energy content (by volume) of ethanol fuel is less than gasoline, a larger volume of ethanol fuel would still be required to produce the same amount of energy.

8.3.1 Motor Vehicle Operation with Ethanol and Ethanol Blends

Variations in engine performance with changes in fuel/air ratio

Alcohols generally provide better fuel energy economy and lower total exhaust emissions than gasoline when used in internal combustion engines. This has been demonstrated in many engine and vehicle tests, but basically applies to straight or neat alcohols. With regard to fuel economy and exhaust emissions, a 10 volume percent alcohol blend in gasoline (whether ethanol or methanol) exhibits no significant advantage or disadvantage as compared to gasoline.

These statements about blends are, of course, statistical generalizations, but they are amply supported by the great bulk of experimental evidence at hand. Certainly, experimental results will vary slightly from time to time, from test to test, engine to engine, and fuel to fuel. In generally, however, an alcohol blend will not provide any improvement in fuel economy or exhaust emissions that could not be had with gasoline and appropriate engine tuning changes. To see it help to reviews the exhausts emissions from spark ignition engine construction and operating variables on their formations. With this basic understanding, it becomes possible to deduce the results of a change in fuel, from straight gasoline to a low level (say 10% by volume) alcohol blend.

Emissions and Fuel Economy Fundamentals

For a baseline case, consider a typical, multicylinder automotive engine operated on straight commercial gasoline. The combustion emissions from this engine-fuel system will fall into one of five major categories:

1) carbon monoxide
2) various hydrocarbon compounds
3) oxides of nitrogen
4) oxides of sulphur
5) particulates and smoke

Of these, only the first three are regulated, and the last two are much less significant than the others. Very small amounts of sulphur are present in gasoline and some will be burned (oxidized) to sulphates which are classified together as SOx. These vehicle sulphate emissions are not a significant contribution to the general air pollution problem. Particulates are mainly salts of lead and other metals used as antiknock additives. These are expected to decline with time as their use in gasoline is phased out.

Spark ignition engines emit smoke only in poor mechanical conditions (oil burning) or when grossly maladjusted (much excess fuel).

In examining the remaining regulated exhaust emissions, CO, HC, NOx, we find that a crucial factor in their formation characteristics is the relative mixture of the fuel and air (fuel-air ratio or F/A) that is metered to the engine. Based on its chemical composition, each fuel has a precise F/A requirement, expressed in pound of fuel per pound of air, at which the theoretically correct amount of air is available to provide sufficient oxygen to convert al of the carbon in the fuel to carbon dioxides and all of the hydrogen to water vapour with neither fuel or oxygen left over.

The chemically correct or stoichiometric F/A is about 0.069 for a typical gasoline. If the F/A is numerically lower than0.069, the mixture is said to be lean (fuel lean) and unreacted oxygen will left over. If the F/A is numerically larger than 0.069, the mixture is said to be rich or excess fuel will be left over, partially unburned.

Now let us turn our attention to the major exhaust emissions, one by one, and see how variations in F/A influence their concentration in the engine exhaust. Figure is a graph which shows relative amounts of exhaust emissions as a function of F/A.

The amount of carbon monoxide is determined almost entirely by F/A. Mixture richer than stiociometric inevitably lead to higher CO emissions as indicated in figure. With excess fuel present relative to the amount of air (oxygen) available, some carbon atoms will simply be unable to burn completely to CO2 and instead will partially oxidize to CO. This partial oxidation process increases as the mixture gets richer. As the mixture gets leaner, some CO will always be present in the exhaust because fuel and air are never perfectly mixed and apportioned in all the cylinders. But CO emissions can be minimized by operating the engine at leaner than stoichiometric conditions.

Hydrocarbon (HC) emissions from gasoline combustion are mostly unburned fuel (UBF). Gasoline is a complex mixture of hydrocarbon molecules of varying structure end sizes. If an engine is operated at a rich F/A, not all of the fuel can be burned completely in the combustion environment, so rich mixtures raise HC emissions. Perhaps the most important HC producing is flame "quenching". As a flame front at very high temperature (2000 to 5000 F) approaches a relatively cool (200 to 300 F) combustion wall, heat is extracted from it. At some point, usually a few thousandth of an inch from the wall, enough heat is taken from the flame and from the mixture near the wall to put out or quench the flame. The total quench layer over the entire surface area of the chamber may contain an appreciable volume of hydrocarbons (gasoline) that never become hot enough to burn before being expelled in the exhaust. Thus, no engine which burns its fuel in a premixed condition with air can never have zero HC emissions.

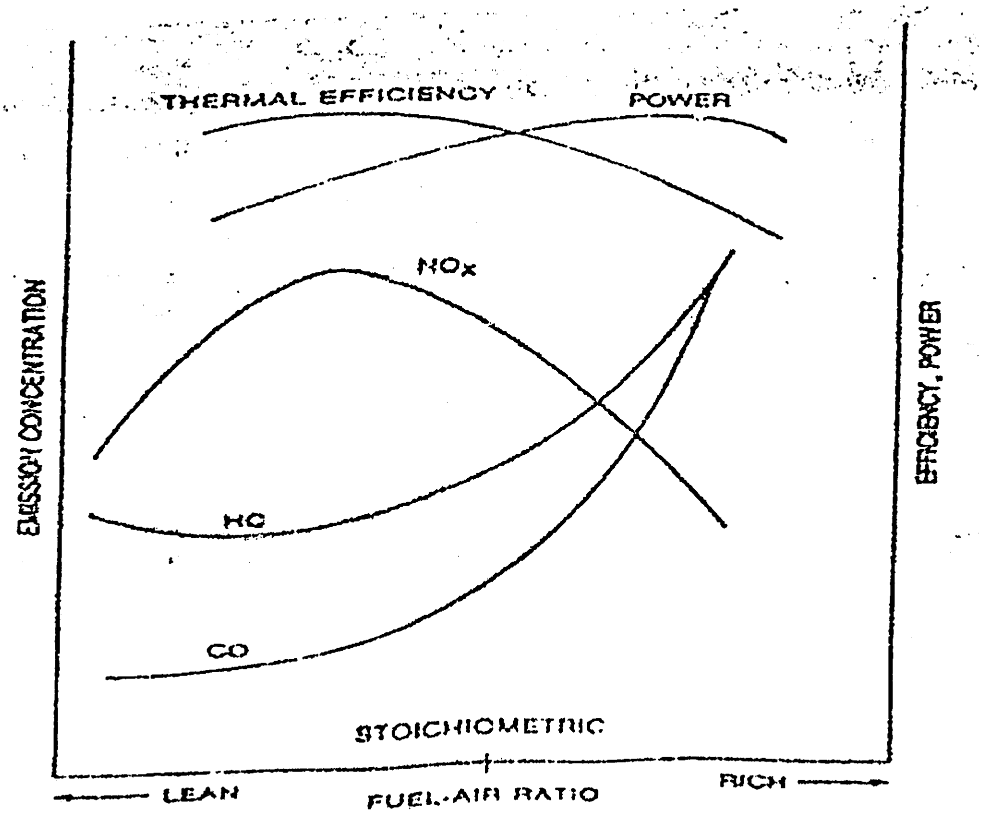
HC emissions decrease as the mixture becomes leaner, as shown in figure, until the misfire limit is approached. Then they start to increase. If mixture becomes so lean that a strong, self-sustaining flame cannot be established or cannot propagate through the entire combustion volume in time available, partially or completely unburned fuel will escape through the exhaust valve.

In the figure HC and CO both tend toward optimum low values at F/A somewhat leaner than stiochiometric. Depending on the engine and the gasoline, these F/As range from about 0.065 to perhaps 0.056. Hydrocarbons reach their minimum where CO is very low. Fuel economy is maximum somewhere in this range also, and for the same basic reason: the engine is making most efficient use of its gasoline, burning it as completely as it can and extracting a maximum of the chemical energy which is converted to heat. Thus thermal efficiency is at a maximum.

The maverick emission specious is NO. It results when normally inert nitrogen (N2), present in the air about 3.76 times the concentration of oxygen, chemically unites with that oxygen. High temperature are needed to make this happen, generally above 2000 F. such temperatures are easily reached and exceeded in the gasoline combustion, and while high temperatures help reduce HC and CO to minimum concentrations, they produce more nitrogen oxides, or NO. The hottest flames theoretically are stiochiometric mixture flames, but it is evident that NO peaks at a somewhat leaner F/A. The increase in free oxygen exerts a stronger influence on NO formation than the slowly falling combustion temperatures as mixtures are leaned slightly fro around 0.069 F/A. When the F/A is leaned progressively away from this value, NO begins falling as excess air "soaks up" the heat of combustion and lowers peak flame temperatures.

Figure shows the effects of F/A on engine power output. Power out put is maximum at a slightly rich F/A mixture, because flame speeds are highest and chemical equilibria most favorable under these conditions. Power drops off as the mixture gets richer than this, due to incomplete combustion of the fuel.

The combination of these factors has a significant influence on automotive design. As figure shows by operating at very lean gasoline-air mixtures all emissions can be reduced at least to near minimum levels. This trend was followed beginning in the late 1960s and early 1970s by virtually all automobile manufacture. At first HC and CO were the target, but as the trend continued and NO emissions standards were enacted, it was found that engines were reaching the limits of their lean-mixture tolerance as shown in figure by the steeper increase in HC emissions. In practice, the result was somewhat worse NO emissions and rough running engines, the victims of misfire, surges and hesitations.



In the mid 70s, as the manufacturers learned to extend the lean mixture tolerance limits of gasoline engines and to lower combustion temperature with inert recycled exhaust gas for NO control, automobile power and smoothness improved. When the catalytic converter was developed, it reinforced this trend toward smoother operation by allowing engines to richer air-fuel ratios. CO and HC engine emissions increased, but because these could be after burned in the catalytic converter, engine performance and efficiency were improved and all exhaust emissions minimized in the catalytic converter before they reached the atmosphere.

Alcohol/Gasoline Blends

With these perspectives on gasoline engine behavior and the historical trends in emissions control in mind, the effects of replacing straight gasoline with alcohol feuls, either 10% alcohol-gasoline blends or straight (neat) alcohols should be considered.

Due to fact that alcohols contain oxygen, they have different stiochiometric F/A than gasoline, i.e.; about 0.155 methanol and 0.111 for ethanol.

When alcohol is added to gasoline to make a 10% blend, the physical qualities of the blend are not changed significantly from those of gasoline. A carburetor will meter the blend the same as it would meter straight. It will deliver to the engine a blend-air mixture at about the same F/A as it was calibrated for on gasoline. The specific F/A will depend on the model year of the car. But if 10% of the blend is ethanol, the blend stiochiometric F/A will be 0.0716

A new parameter, called equivalence ratio (Φ), is often used in place of F/A to facilitate comparisons between different fuels. The equivalence ratio is defined as the ratio of the actual F/A for a specific fuel. Therefore, for stiochiometric mixture the equivalence ratio is 1.0, for lean F/As the equivalence ratio is less than 1.0, and for rich F/As the equivalence ratio is greater than 1.0.

Going back to the example, if the carburetor is calibrated for gasoline at an equivalence ratio of 1.0 and a blend is substituted which contains 10% volume ethanol in gasoline, the equivalence ratio becomes:

$$\frac{0.069(\text{actual F/A})}{0.076(\text{stiochiometric F/A for the blend})} = 0.96$$

Therefore the F/A for the blend is leaner than for gasoline at a fixed carburetor calibration. This phenomenon is called the blend leaning effect and explains why adding alcohol to gasoline does little that cannot be done with straight gasoline by mechanical carburetor adjustment, leaning out the mixture to a lower equivalence ratio. How the engine emission and fuel economy respond to this blend leaning will depend on how rich or lean the engine was running on straight gasoline.

Increase or decreases are possible for NO and HC but if the engine does not become so lean that it stalls, CO can only decrease.

If compared to gasoline at the same equivalence ratio, however, as would be the case if the carburetor were readjusted in the rich direction to maintain the same equivalence ratio after going to a blend, the blend provides essentially identical HC and CO emissions and fuel economy. Such reductions in NO usually occur due to other special characteristics of alcohols (such as cooler burning flame). For a 10% blend, these reductions are roughly 10% of those possible with neat alcohols and thus are quite small.

Straight Alcohols

Combustion of straight alcohols produces substantially less NO than does gasoline at a corresponding equivalence ratio, because of the marked lower combustion temperature. Because alcohols can be burned at lower equivalence ratio than the gasoline without lapsing into misfire and other lean combustion problems, further NO and CO reductions are available and corresponding engine efficiency increases can be obtained. Unburned hydrocarbon fuel (UBF) emissions are still present, but they include some different chemical species then those found in gasoline combustion emissions because alcohols themselves are from a different hydrocarbon chemical family (sometimes knows as partially oxidized hydrocarbons). Operated at the same equivalence ratio, an engine will produce very similar HC and CO emissions on straight gasoline and straight alcohols, with lower NO and higher efficiency from the straight alcohols.

Due to chemical characteristics of the fuel and the related combustion phenomenon, the amount of NO is reduced by about a half to third with straight alcohol. Thermal efficiency is increased in the order of 10%. These relationships occur at all comparable equivalence ratios. Ethanol has about two thirds of energy content of gasoline on an equal volume basis. The volume of ethanol required is half that of gasoline, all other things being equal.

Fortunately, engines can be operated reliably (without misfire) on alcohol at equivalence ratios that are leaner than gasoline, i.e.: the reliable lean operating limit equivalence ratio for alcohols is leaner than the reliable lean operating equivalence ratio for gasoline.

Properties of Ethanol and Ethanol/Gasoline Fuel Mixtures

Property	Comment
Vapor density	Ethanol vapor, like gasoline vapor, is denser than air and tends to settle in low areas. However, ethanol vapor disperses rapidly.
Solubility in water	Fuel ethanol will mix with water, but at high enough concentrations of water, the ethanol will separate from the gasoline.
Flame visibility	An ethanol/gasoline fuel blend flame is less bright than a gasoline flame but is visible in daylight
Specific gravity	Pure ethanol and ethanol/gasoline blends are heavier than gasoline.
Conductivity	Ethanol and ethanol blends conduct electricity. Gasoline, by contrast, is an electrical insulator.
Toxicity	Ethanol is less toxic than gasoline or methanol. Carcinogenic compounds are not present in pure ethanol; however, because gasoline is used in the blend, E85 is considered potentially carcinogenic.
Flammability	Flashpoint for gasoline=-45° F, Flashpoint for pure ethanol= 55° F, Flashpoint for E85= -20 to -4° F, **Considerations:** pure ethanol (UEL=19 percent, LEL=3.3 percent) and E85 (UEL=19 percent, LEL=1.4 percent) have a wider range of flammability than gasoline (UEL=7.7 percent LEL=1.4 percent). Gasoline also has a lower flash point

8.4 Key Parameters for the Development of a Dedicated Engine

The potential of ethanol in terms of greenhouse gas emissions, when produced from biomass, has been outlined above. Moreover, ethanol has some very interesting physical and chemical properties that can be turned into benefits with a dedicated engine, provided some technical difficulties are overcome. The following section describes these advantages and disadvantages of ethanol and gives an example of a preliminary development with a small displacement dedicated engine.

8.4.1. Ethanol properties

Ethanol Physical Properties

	Ethanol	Gasoline (typical)
Molar mass (g/mol)	46.07	102.5
C (%wt)	52.2	86.5
H (%wt)	13.1	13.5
O (%wt)	34.7	0
Density (kg/m^3)	794	735-760
Latent heat of vaporization (kJ/kg)	854	289
Distillation (°C)	78.4	30-190
Net heating value (kJ/kg)	26805	42690
Net heating value (kJ/l)	21285	32020
Stoechiometric ratio	8.95	14.4
RON	111	95
MON	92	85

This table shows that ethanol has some interesting properties to be used as a fuel for spark-ignition engines:

- A very high octane number, which induces a strong resistance to knock and consequently the ability to optimize the engine (compression ratio, spark-advance).
- A density close to the gasoline one.
- The presence of oxygen in the formula, which can provide a more homogeneous fuel/air mixing and consequently a decrease in unburned or partially burned molecule emissions (HC and CO).
- A high latent heat of vaporization enabling a “cooling effect” of air and consequently can enhance the filling efficiency.

On the opposite, some disadvantages have to be considered:

- The oxygen included in the molecule (30%wt) induces an increase in the fuel volumetric consumption.
- The high latent heat of vaporization can induce running difficulties in cold conditions, especially cold start.
- Ethanol leads to azeotropes with light hydrocarbon fractions and can lead to volatility issues.
- Ethanol is miscible with water, which can cause demixing issues when blended with hydrocarbons.
- The high oxygen content of ethanol and its ability to oxidize into acetic acid induce compatibility issues with some materials used in the engine, such as metals or polymers.
- Ethanol combustion in engines induces aldehydes emissions, which can have a negative impact on health.

Octane Number

Ethanol is characterized by high octane numbers (RON and MON). A dedicated engine will consequently be less knock sensitive and its compression ratio can be increased, to enhance the engine efficiency. This physical property is particularly useful to reduce CO2 emissions of spark-ignition engines: yet, one of the most promising ways seems to be the downsizing of engines, with the generalization of small displacement turbocharged engines. Whereas these engines could be generally highly knock sensitive, a substantial improvement could be brought by the use of high octane fuels. A typical correlation that is used for compression ratio calculation gives a value of 1 CR point increase for about 5 points octane [12]. When ethanol is used on a typical spark ignition engine (CR = 9, RON 95), the compression ratio could go up to 13-14, inducing a substantial thermal efficiency increase. So far, most of the developments on dedicated engines selected a compression ratio around 12-12.5, because of they used E85 (85% ethanol mixture) instead of pure ethanol (cold start drivability improvement, see below). Moreover, such high octane numbers are subject to a high uncertainty in their measurements, and also in their physical meanings. Indeed, the ASTM D2699 method for RON values higher than 100 is based on the comparison of the tested fuel with leaded isooctane. One should assume that, even if those 2 fuels may behave the same way in a CFR engine, their radically different physical and chemical properties can induce different behaviors in real engines.

Oxygen Content

The oxygen content in ethanol is around 35%wt. The mass heating value of ethanol is consequently lower than the gasoline one (respectively 27MJ/kg and 42.7MJ/kg). Ethanol higher density tends to reduce the difference in volumic heating values, but a significant difference remains. Besides, another parameter has to be considered: the specific energy, which is the energy released for each unit mass of air consumed in stochiometric conditions. It corresponds to the ratio (heating value/air-fuel ratio). This ratio is around 3 for ethanol and 2.9 for a typical gasoline. Indeed, the oxygen in ethanol reduces the stochiometric ratio, *i.e.* the mass of air which is needed to get the total combustion of a given quantity of fuel. As shown in Table 4, this stochiometric ratio is around 9 for ethanol and 14 for gasoline. As a consequence of this difference, if the engine efficiency remains similar for gasoline and ethanol, the fuel volumetric consumption is inevitably increased when running with ethanol.

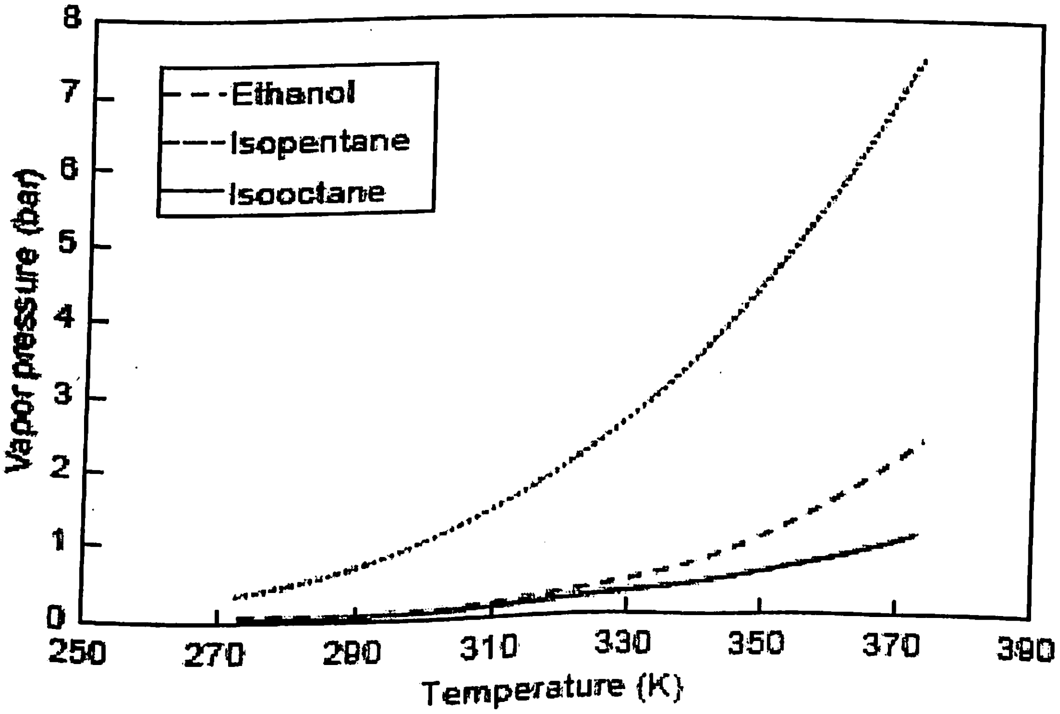
Moreover, the high oxygen content of ethanol has some significant positive aspects, especially when pollutant emissions are considered. As stated above, the use of oxygenated compounds can lead to a more homogeneous combustion by bringing oxygen in the core of the fuel, where the oxygen brought by air can never arrive. A decrease in CO and HC emissions can consequently be measured, but the reduction level varies according to the vehicle type and technology. The impact on HC emissions is also important, but is highly variable because of the high number of parameters implied:

- decrease in air/fuel local heterogeneity (decrease in HC emissions);
- volatility increase (increase in evaporation HC emissions);

– decrease in HC emissions when ethanol is used as a substitution for other high octane molecules such as aromatics (HC precursors).

Volatility

Ethanol by itself has a moderate volatility. Table shows that its boiling point is relatively high (78°C) in comparison with gasoline initial distillation point. Moreover, the vapor pressure, calculated according to Antoine's law, is low for ethanol in comparison with the light fractions of the fuel *(Fig. 2)*. Nevertheless, another physical property must be remembered: ethanol can strongly interact with some hydrocarbons, leading to the formation of azeotropes. Azeotropes are defined as any liquid mixture having constant minimum and maximum boiling points and distilling off without decomposition and in a fixed ratio. Their main characteristic is to have a boiling point radically different from the boiling points of each component on its own, and consequently a different vapor pressure at a given temperature. Ethanol azeotropes have boiling points lower than the initial boiling points of their components. For instance, ethanol and *n*-pentane can give an azeotrope which boiling point is 34°C, lower than the respective boiling points of ethanol (76°C) and *n*-pentane (36°C). The next table summarizes the most common azeotropes formed with ethanol.



Comparison with typical gasoline components

Common ethanol azeotropes characteristics

Molecule	Pure boiling point (°C)	Azeotrope boiling point (°C) with ethanol	Composition of the azeotrope (%wt ethanol)
n-pentane	36	34	5
n-hexane	69	59	21
benzene	80	68	32
cyclohexane	81	65	29.2
toluene	111	77	68
n-octane	126	77	88

The impact of these azeotropes is important when blending ethanol with fuels, by leading to an increased vapor pressure. Of course, this phenomenon is avoided when pure ethanol is used. Nevertheless, as stated above, pure ethanol has a distillation point of 78.4°C, characteristic associated with an important latent heat of vaporization, inducing cold start difficulties. To avoid this phenomenon, E85 (ethanol blended with 15% light hydrocarbons) instead of pure ethanol is a commonly used solution. Moreover, as presented above, most countries prefer to use low ethanol concentrations (lower than10%) in fuels. Azeotrope formation can have an important impact on these kinds of fuels: if the fuel volatility is not correctly controlled, adding ethanol can induce a strong increase in evaporative losses. For refiners, this physical phenomenon means that "plash blending" is difficult with ethanol: ethanol can only be added to selected (low volatility) base fuel.

Water Tolerance

Ethanol and water are miscible in any proportions, while hydrocarbons and ethanol are not miscible. With conventional gasolines containing hydrocarbons, or ethers, the presence of water in the fuel is not a serious concern. In fact, up to 50 ppm at ambient temperature (of course this value depends of the gasoline chemical composition), water remains completely soluble. Over this level, water separates without affecting the hydrocarbon portion and the water layer can be extracted if necessary. On the opposite, in ethanol blends, traces of water can induce a total demixing into two phases: one phase is a mixture of ethanol and water and the other phase contains the hydrocarbons. Demixing traces are not acceptable. Moreover, whereas ethanol can be used as an "octane enhancer" in the fuels, the demixing between the base fuel and ethanol, in presence of water leads to a decrease in the octane number of the base fuel, which could seriously damage the engine.

To avoid this phenomenon, some methods can be used, such as the use of "cosolvents" (for instance TBA (tert-butyl alcohol) in the 1980's in the United States) or a careful check of fuel storing tanks water tightness. Another way to avoid this phenomenon could be the use of pure ethanol [16]. Indeed, water is miscible in ethanol and consequently no demixion phenomenon can occur. Nevertheless, the already mentioned issues linked to engine cold start remain.

Cold Start

Pure ethanol has a moderate volatility. Its high boiling point (78°C) induces difficulties of vaporization in ambient or cold conditions.
Moreover, as it has been outlined previously, ethanol has a very high latent heat of vaporization (3 times higher than typical gasoline). This property induces drivability difficulties: the vaporization of ethanol in cold conditions needs a lot of energy and consequently induces a cooling effect [17]. To lower this phenomenon, some technical solutions can be applied. The most frequently used solution is to use E85 (85% ethanol) instead of pure ethanol. The addition of 15% light hydrocarbon fraction in ethanol induces a strong increase in volatility and consequently an easier engine start. Nevertheless, this modification has to be made carefully to avoid the loss of some of the ethanol advantages (octane number, low HC and CO emissions).
Other solutions have been studied, especially in Brazil. Among these, the most widely spread are the heating of the fuel injection system (and especially the fuel-rail) or the use of a second tank, filled with highly volatile gasoline, to run the engine for a few seconds before switching to ethanol.

8.4.2. Material Compatibility

Polymers

Ethanol induces the swelling and weakening of rubber components, due to the absorption of fuel into rubber. Once absorbed into rubber, the oxygen of the alcohol breaks the rubber's carbon-carbon double bonds. The consequence of swelling and weakening can be a fuel leak that can endanger car users. Swelling and component breakdown can all be solved by the use of compatible materials such as highly fluorinated rubbers. Nylon can also be resistant, but only at low temperature (< 30°C) [19]. This polymer can consequently be used for intake fuel line, provided the fuel temperature remains low.

Galvanic Corrosion

Galvanic corrosion happens when 2 metals are in contact, generally through a conducting electrolyte. For instance, stainless steel and aluminum can undergo galvanic corrosion when placed side by side. Typical fuels (with no additives) have an electrical conductivity between 10–8 to 10–6 µS/cm. Ethanol electric conductivity is 1.35 10–3 µS/cm. Moreover, the oxidation of ethanol into acetic acid induces a rapid increase in electrical conductivity (41 µS/cm for a 0.1M acetic acid solution). The presence of acetic acid can consequently enhance galvanic corrosion and chemical attack. The metals recommended for use with ethanol include carbon steel, stainless steel and bronze. Metals such as magnesium, zinc casings, brass and copper are not recommended. The previous paragraph assumes that ethanol is "dry", which means it contains no water. Yet, as water is miscible in ethanol, ethanol with very high water content has been found in the past (up to 5%vol), with ion concentrations that make it much more aggressive than pure ethanol. The use of anhydrous ethanol is consequently mandatory to avoid engine corrosion. This is the most important limitation to ethanol development, as far as fuel logistic and storage are concerned.

8.5 Preliminary Development of a Dedicated Engine

This section describes the preliminary development of a small displacement dedicated engine. Indeed, if some changes have been done on the engine, it has not been fully optimized. Nevertheless, these results show the potentiality of ethanol.

8.5.1. Engine Initial Characteristics

The selected engine is a small turbocharged engine. Its main characteristics are described in Table below.

Engine characteristic	Value
Cylinder/valves	3 cylinders/6 valves
Displacement	599 cm^3
Compression ratio	9.5: 1
Bore	63.5 mm
Stroke	63 mm

This engine has been fully characterized, with a RON95 EN228 gasoline, then modified as described below.

8.5.2. Engine Modifications

To run with ethanol, the following modifications have been done:

increase in engine compression ratio;
modification of engine fuel system;
modification of cylinder head.

Compression Ratio

The compression ratio has been increased from 9.5 to 12.5 by modifying the piston geometry. A new piston has been designed and produced. Piston rings have also been modified to be more resistant. The new compression ratio (12.5) was selected to optimize engine efficiency. A higher compression ratio could have been used, but tests led on natural gas engines showed that this intermediate compression ratio is a reasonable compromise between engine efficiency and mechanical constraints.
Moreover, to ensure a good resistance to pressure, the connecting rods have also been redesigned with a target of 110 bar of maximum pressure resistance. This new connecting rod design is close to diesel connecting rods. Both pistons and connecting rods were heavier than original parts. As the engine is a 3-cylinder, the crankshaft had to be modified to be reequilibrated.

Engine Fuel System

Ethanol contains approximately 35% oxygen, which does not participate to the heat release during combustion. To maintain high and full load performances, the injection system had to be modified in a way to increase the injection flow by 35%. To reach this objective, the injector hole diameter had to be enlarged by more than 16%. The maximum fuel flow of the initial engine was assumed to be lower than 4 kg/h, which means around 66g/min. With a maximum ethanol flow 35% higher, ethanol injectors must have a static flow of 90 g/min. *Bosch* LPG injectors were selected, with a static flow around 100 g/min, in line with the needs of this engine. The components of these injectors were tested according to their chemical resistance to ethanol and have shown a reasonably good behavior.

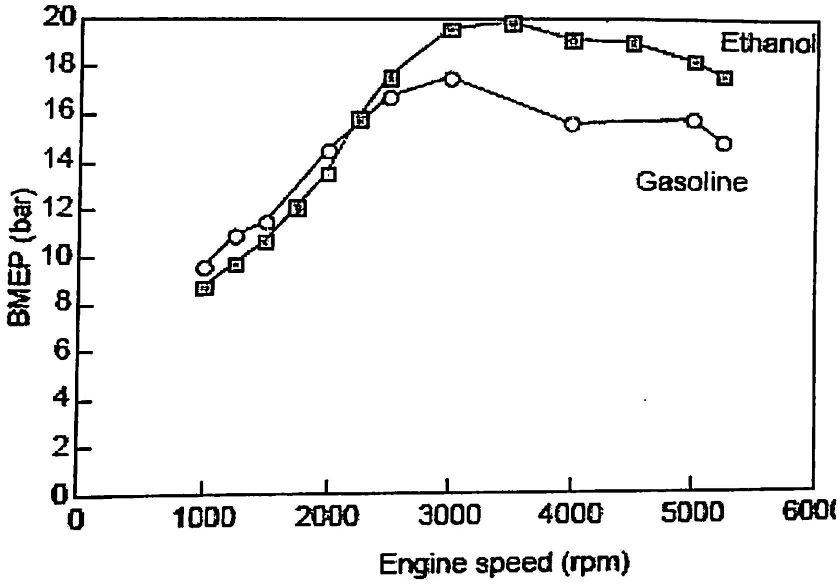
Cylinder Head

Some previous tests had shown a rather poor resistance of exhaust valves and spark plug to ethanol. Indeed, due to a lack of heavy fractions, ethanol does not induce a correct cooling of the exhaust parts and thus could lead to valves fusion on very high speed/high load running conditions. Moreover, very high temperatures can lead to fusion of the spark-plug electrodes. To avoid this phenomenon, the valves were changed to bimaterial "nimonic" valves (nickel-chromium alloy with good mechanical properties and oxidation resistance at high temperatures). The spark plugs have also been changed to more temperature resistant ones.

8.5.3 Results

Full Load

The full load curve obtained with the gasoline and the ethanol versions of the engine are presented in Figure. Ethanol enables a maximum torque of 95 Nm at 3500 rpm, while the gasoline engine is limited to 82 Nm (+15%). The maximum power is consequently increased from 39 kW for gasoline (65 kW/l) to 45 kW for ethanol (75 kW/l). This full load curve is limited by the exhaust temperature (turbine thermal resistance) and the maximum compressor efficiency (waste gate closed).

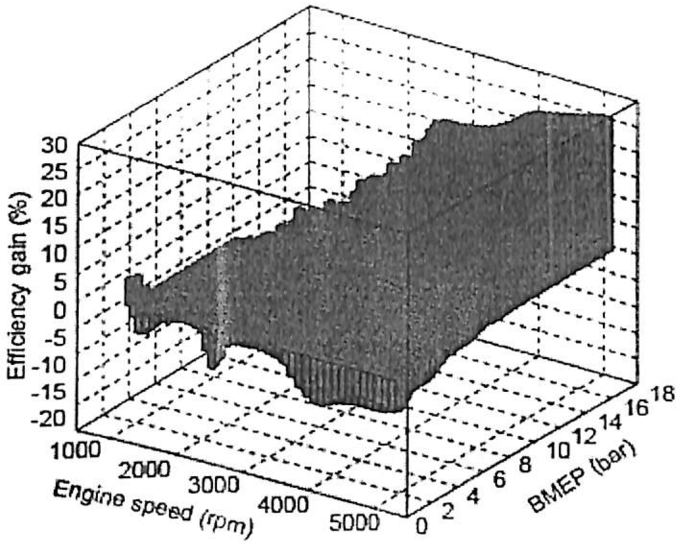


Full load Curve

It has to be outlined that the turbo-charging system was not changed and may not be suitable for ethanol. For instance, the low end torque is slightly lower with ethanol than with gasoline, which could be avoided with a more optimized compressor and an adaptation of the turbine. The study of the cylinder maximum pressure shows that an increase potential remains, as the maximum recorded pressure with ethanol is 95 bar (the engine was modified to reach 110 bar cylinder pressure). Moreover, the full load curve with ethanol has been obtained in stoichiometric running conditions, with an exhaust temperature (before turbine) under 950°C. Figure 4 presents the equivalence ratio and spark advance for gasoline (full load curve) and for ethanol (same performance). The comparison of these curves shows that the spark advance can be increased by 5 to 15 CA and that no mixture enrichment is necessary when using ethanol. This figure shows that ethanol, even without taking the "biofuel" aspect into account, can provide substantial benefits for low CO2 engines (small displacement, high compression ratio, turbocharged).

Engine Efficiency

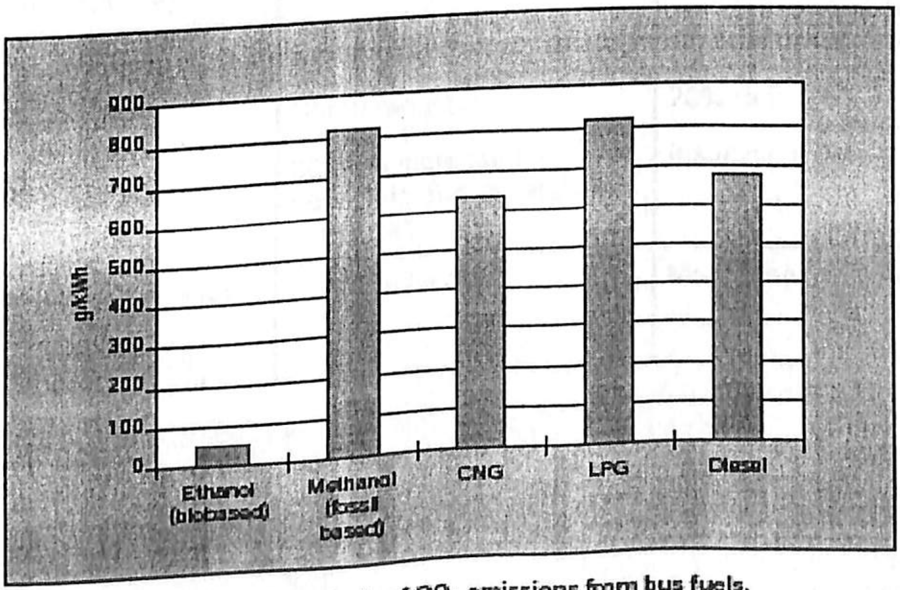
The engine global efficiency was calculated according to the ratio released energy/maximum theoretical energy. The maximum theoretical energy was calculated according to the BSFC and the fuel net heating value (42 800 kJ/kg for gasoline, 26 800 kJ/kg for ethanol). The results obtained for this calculation are presented in the Figures 5 to 7. At low speed/low load running conditions, the efficiency is higher for gasoline than for ethanol but, at high speed / high load, the impacts of the increased compression rate and of the stochiometric running are important and give the advantage to ethanol, as shown in Figure 7.



Engine efficiency gain when running with ethanol

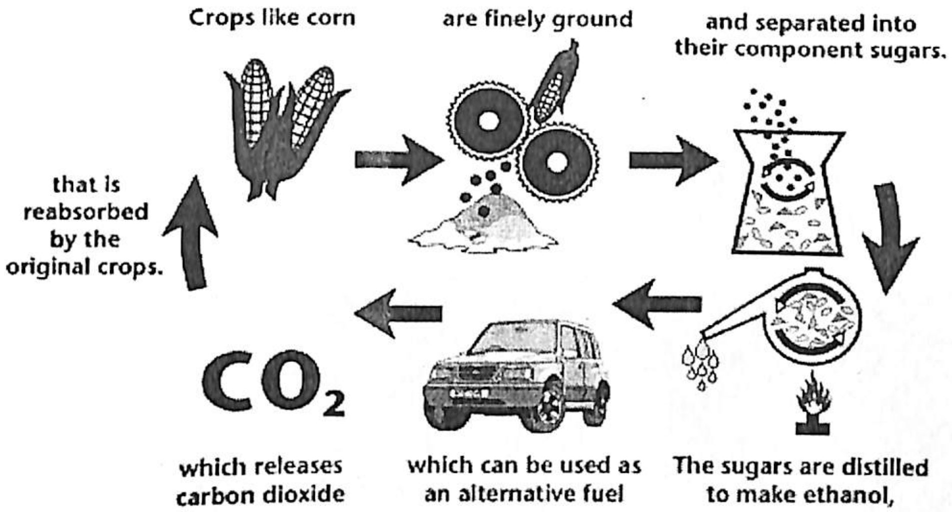
CO2 Emissions

In the frame of its commitment with European Union, ACEA has claimed its will to decrease CO2 emissions of the fleet down to 140 g/km in 2008. Thus, CO2 emissions became one of the key parameters when designing an engine. Ethanol, as a biofuel, has an important potential in terms of lowering CO2 emissions "from well to tank". Nevertheless, its efficiency in the engine has to be checked in order to get the CO2 emissions over the full path. The CO2 emissions of gasoline and ethanol engine are presented in the Figures.



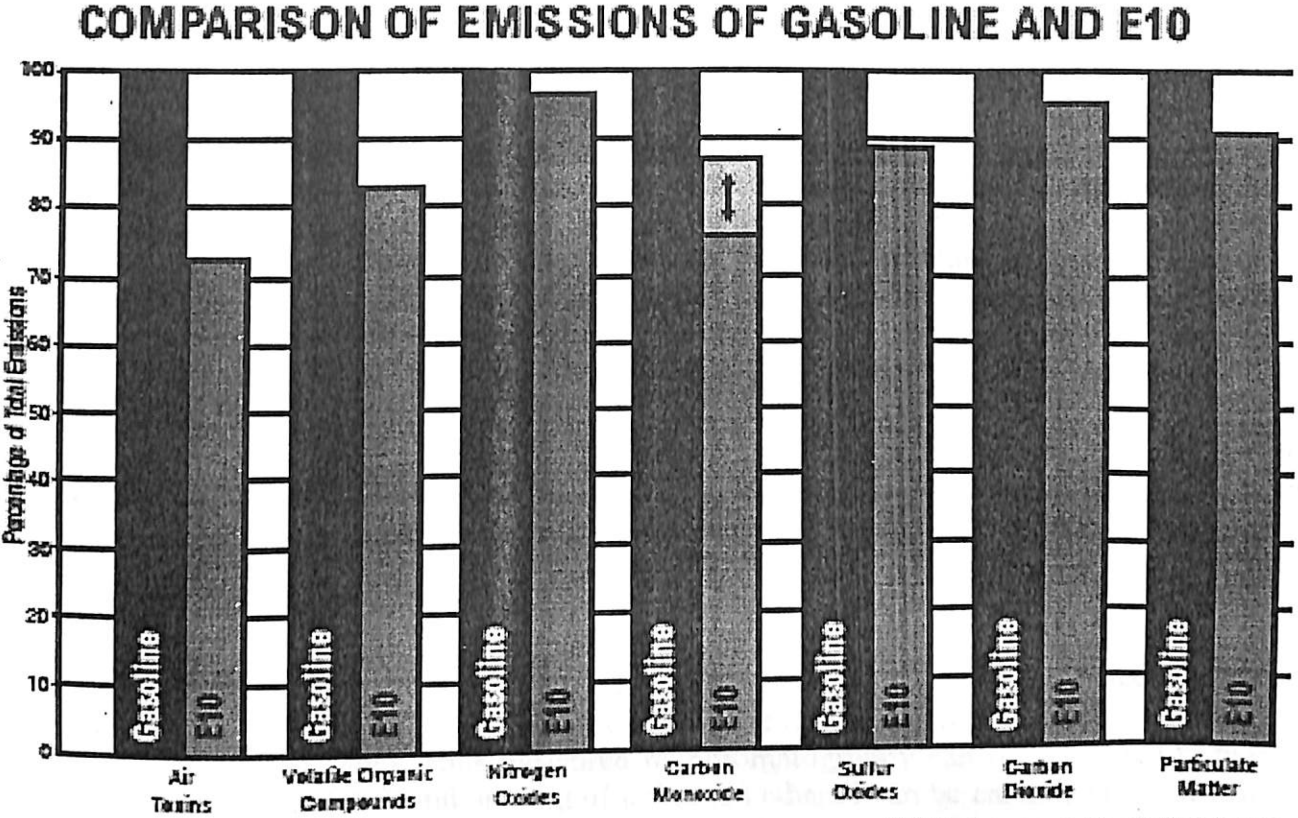
Results from a life-cycle analysis of CO_2 emissions from bus fuels.

THE CARBON CYCLE



Ethanol Emissions as Compared with Gasoline Emissions
(from EPA Fact Sheet EPA420-F-00-035)

Emission	E10	E85
Carbon Monoxide (CO)	25-30% reduction	40% reduction
Carbon Dioxide (CO_2)	10% reduction	14% -102% reduction
Nitrogen Oxides	5% reduction	10% reduction
Volatile Organic Compounds (VOCs)	7% reduction	30% or more reduction
Sulfur Dioxide (SO_2)	Some reduction	Up to 80% reduction
Particulates	Some reduction	20% reduction
Aldehydes	30-50% increase but negligible due to catalytic converter	Insufficient data
Aromatics (Benzene and Butadiene)	Some reduction	More than 50% reduction



U.S. Environmental Protection Agency

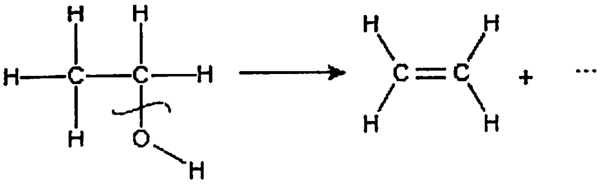
This shows the significant benefits of ethanol on CO2 emissions. An important reduction can be obtained (up to 20%), which can be explained by the high H/C ratio of ethanol (3, against 1.8 for typical gasoline). For instance, for a 2000 rpm-2 bar BMEP, CO2 emissions are 1.22 kg/kWh for gasoline and 1.13 g/kWh for ethanol (–7.4%). To get an evaluation of the benefits on a dedicated vehicle, some simulations have been led. CO2 emissions were calculated on the standard European type-approval driving cycle. The results are summarized Figures 10 and 11. This data processing shows good results for gasoline engine in comparison with type-approval value (120 g/km). The calculation on ethanol engine data shows a 9% reduction in CO2 emissions.

Besides, this assessment has been realized without any change in the vehicle design, and especially with the same gearbox ratios. As demonstrated above, ethanol allows an increase in engine maximum power and torque, enabling further CO2 reduction via a gearbox and transmission optimization.

Pollutant Emissions

HC emissions are difficult to measure accurately with the flame ionization detector typically used for engine pollutant emissions measurement. Indeed, the response factor for oxygenated compounds in these analyzers is low (for instance 1.8 instead of 2 for ethanol, which means that less than 90% of ethanol emissions are analyzed). Assuming that most of the HC emissions are made up of unburned hydrocarbons, the total HC emission level can be corrected by the response factor of ethanol. The value obtained for HC emissions in ethanol configuration is then a maximum estimate (considering that HC emissions are exclusively made up of ethanol).

To minimize this bias and obtain a more accurate HC emission characterization, chromatographic analyses have been achieved, analyzing the chemical species in HC emissions (C1- C8). These analyses have shown that, as far as nonoxygenated hydrocarbons are concerned, ethylene represents more than 50% of HC emissions. This molecule comes directly from ethanol decomposition as shown in the Figure 13.



Ethanol decomposition simplified mechanism.

The comparison of the total HC emission measured with ionization detector and chromatography enables an evaluation of ethanol emissions. Indeed, for the 4 tested running points, the HC emissions measured by chromatography can be compared to the total HC emissions and the total amount of unburned ethanol can be calculated, as shown in Figure 12. This calculation assumes that ethanol (or light aldehydes) is the only component of all HC that are not analyzed here in line by gas chromatography. As far as CO emissions are concerned, ethanol brings a real gain. At low engine speeds, CO emissions with ethanol are approximately reduced to the half in comparison with gasoline. At very high load running conditions, ethanol induces also very low CO emissions in comparison with gasoline, because of its low exhaust temperature, enabling to run the full load curve without any mixture enrichment. Forinstance, at the 5250 rpm-WOT running point, CO emissions before catalyst are divided by 6 when running with ethanol, despite the higher torque and power obtained with ethanol. NOx emissions are less impacted by the use of ethanol, and the results are highly dependant on the running conditions: if for most of the running points, NOx emissions are similar with gasoline or ethanol, some significant differences can be observed for high speed running points.

- At low load, NOx emissions with ethanol are lower than with gasoline, due to differences in the latent heat ofnvaporization and in the combustion speed.
- At high load, the mixture enrichment in gasoline induces a decrease in the combustion temperature and consequently in NOx emissions. As mixture enrichment is not needed with ethanol, NOx emissions are higher. On the other hand, the low exhaust temperatures when using ethanol enable a stoichiometric running among the whole running range, and makes it possible to use a 3-ways catalyst to reduce NOx emissions, even at full load.

Further Optimization

These results show the true benefits brought by ethanol with only a little optimization of the engine: the increased compression ratio induces an important benefit in terms of engine efficiency and CO2 emissions. Still, some points have to be further studied to get a fully optimized engine:

- The tested engine was a PFI engine. To get full benefits from ethanol high latent heat of vaporization via the "cooling effect" (increase in filling efficiency due to the intake air cooling when ethanol is vaporized), a direct injection engine should be used.

- No change was done on the supercharging system. The optimization of this part of the engine could lead to an increased low-end torque.

- Some critical points, such as cold start management or lubricant compatibility, have to be further studied to obtain a fully useable engine.

- Aldehyde emissions have to be considered. As we have worked on engine-out emissions and as even aldehydes have been measured, it is not realistic to conclude on these pollutants without exhaust gas after-treatment.

- The catalyst adaptation has to be checked. Indeed, the low exhaust temperature found with ethanol can induce catalyst light-off difficulties.

8.5.4. Conclusion

In the context of the objective of reducing greenhouse gas emissions, it is worth closely evaluating the use of biofuels in internal combustion engine. First, ethanol characteristics when used pure as fuel in a dedicated engine were reviewed, to determine the balance between its main advantages and disadvantages. Later, after having summarized the main production processes and their relative efficiencies, the main physical properties of ethanol have been analyzed in regard to their positive or negative impact on engine running. Finally, the results obtained on a dedicated engine are presented. The main conclusions are:

- The high diversity of the production paths and feedstock induces highly variable ethanol energy efficiency calculations.
According to the raw material (sugar beet, corn, wheat, etc.), to the agricultural yield and to the transformation process efficiency, the energy balance (energy used/energy produced) has been shown to vary from 0.3 to 1.6

- In a dedicated engine, ethanol-fuel has many advantages, such as its high octane number or its high latent heat of vaporization. These advantages can be valorized in a dedicated engine, provided that some issues are solved (material compatibility, water tolerance, volatility). This ethanol fuel can bring substantial benefits when used in low CO2 engines, such as small displacement turbocharged ones.

- A preliminary optimization of a small displacement turbocharged engine has confirmed the potential benefit of this fuel, with an increase in engine efficiency and a decrease in

CO2 emissions. Some calculation using vehicle simulation models (Amesim®) have shown a net reduction of 9% in CO2 emissions on the NEDC cycle. Moreover, a significant reduction in CO emissions has been noticed.

– Some further optimizations such as cold start strategies.optimized gearbox or dedicated turbo charging system should be foreseen to get a fully useable engine.

– Ethanol-fuel can truly induce a CO2 emission reduction in dedicated engines. Further, as this fuel can be produced from biomass, its “well to wheel” CO2 balance appears to stand at a very interesting level.

Ethanol programs worldwide

Brazil	Requires 25% ethanol blends; provides preferential tax treatment
Argentina	Requires use of 5% ethanol blends over the next five years
Thailand	All gasoline sold in Bangkok must be 10% ethanol
India	Requires 5% ethanol in all gasoline
Australia	Voluntary blending of up to 10% ethanol
Great Britain	Provides incentives for ethanol production at 36 cents per liter
European Union	5.75% (energy content) biofuels target by 2010 (was 2% by 2005)
Canada	Tax benefits for ethanol since 1992 (provincial mandates)

9. ETHANOL BLENDS

9.1 Ethanol-Gasoline Blends

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

- **E10** - which is 10% ethanol and 90% gasoline, the most common way ethanol is available to motorists. All automakers approve ethanol blends upto 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** - which is a mixture of 85% ethanol and 15% gasoline. This mixture has an octane rating of about 105. This is down significantly from pure ethanol but still much higher than normal gasoline 87 octane. The addition of a small amount of gasoline helps a conventional engine start when using this fuel under cold conditions.

E85 does not always contain exactly 85% ethanol. In winter, especially in colder climates, additional gasoline is added (to facilitate cold start). E85 has traditionally been similar in cost to gasoline, but with the large oil price rises of 2005 it has become common to see E85 sold for as much as $0.70 less per gallon than gasoline, making it highly attractive to the small but growing number of motorists with cars capable of burning it. E85 contains approximately 27% less energy per gallon than conventional gasoline, although ethanol typically burns more efficiently. This result in a fuel economy loss of less than the energy content would imply.

E85 is generally the highest ethanol fuel mixture found in the United States. It is common in Sweden, and there are more than 1000 public E85 fuel pumps in the U.S. as of 2006, mostly concentrated in the Midwest, with over half of those in Minnesota.

Comparison of Fuel Properties

Property	Methanol	Ethanol	Gasoline	E85
Chemical Formula	CH3OH	C2H5OH	C4 to C12	--
Octane No. (R+M)/2	100	98 - 100	86 - 94	96
Lower heating Value (Btu/lb.)	8570	11500	18500	12500
Litre Equivalent	1.8	1.5	1	1.4
Km / Litre as Compared to Gasoline	55%	70%	100%	72%
Fuel Tank Size	1.8	1.5	1	1.4

Air/Fuel Ratio	6.45	9	14.7	10

Use of Additives

Although certain sections of D5798 do mention deposit-controlled additives, they currently are not specified. Recent research has shown that FFVs using E85 can produce deposits. The good news is that E85 deposit problems can be addressed with appropriate additives, specially formulated for E85, which are different from gasoline additives.

Gasoline typically contains additive packages to improve performance and keep engines clean. It is tempting to use these same additives in E85.
However, gasoline additives simply are not formulated to meet the specific needs of E85.

E85 Challenges

While typical gasoline-deposits-control additives do not address all of the needs for E85 fuel, there is an even greater concern: the potential harmful effects of using gasoline additives in E85, the high ethanol portion in E85 fuel greatly changes the polarity and solubility characteristics of the fuel as compared to gasoline, and even as compared to 10% ethanol-blended gasoline, which is now common in the US. As a result, typical gasoline-deposit-control additives can have difficulty staying in solution with E85.
If a gasoline additive does not stay in solution in E85, it runs the risk of coming out of solution at various points within the fuel system, potentially creating deposits on filters, fuel injectors and the intake tract of the engine. Recently published studies of additive filtration have shown that gasoline additives can result in E85 filter plugging and severe increases in filtration times. However, at higher ethanol levels (E85), using higher doses of typical gasoline additives can result in a rapid increase in filtration time. In contrast, an additive specifically formulated for E85 will show normal filtration times, regardless of the additive dosage or the ethanol level.

A possible, unintended consequence of using poorly formulated gasoline additives in gasoline additives in gasoline is intake- valve sticking. In this situation, some of the additives can buildup in the annular space between the intake valve stem and the valve guide of the cylinder head. At the low temperature, any build up in this area will become more viscous and inhibit valve spring will be unable to close the intake valve, resulting in compression loss. Consequently, the engine will not start.

Modern gasoline additives are formulated to prevent this problem in normal gasoline. However, recent research has shown that ethanol an make intake- valve sticking even more severe and confirms the need to test gasoline in the full range of fuels in which they will be used, including low-level ethanol blends that are widely available. More important, in the more extreme case of E85, specific additives for E85 that are designed to treat problems without causing unwanted side effects, such as intake-valve sticking, are needed.

Intake-Valve Deposits

A series of 5000-mile tests were conducted on FFVs using varied mixtures of ethanol and gasoline. The results showed that with no additive present, ethanol impacts the amount of intake-valve deposits (IVDs) formed in the engine. At lower ethanol levels, such as E10 (10% ethanol), IVD actually increases to higher levels than in gasoline alone. At higher ethanol levels, the IVD level decreases to the level found in gasoline, or even lower. However, gasoline and E10 blends are commonly treated to reduce these IVD levels to much lower levels. However, E85 does not normally contain deposit-control additives.

Just as all gasolines vary in their severity and ability to form IVDs, batches of E85 also show various severity levels. In a series of 5000-mile tests, three separate batches of gasoline were tested for deposit formation. The results were compared to deposit formation of three separate batches of E85 made from these gasolines. The higher the severity of the gasoline, the higher the severity of the E85 that was used as the hydrocarbon component. The E85-produced IVD was roughly one third to one half of what the gasoline alone produced.

While E85 produces fewer intake-valve deposits than gasoline, gasoline deposits can be controlled with deposit-control additives. Solubility issues preclude using these same additives in E85; however, specially formulated E85 additives can be used to control these deposits. The results using a properly formulated E85 deposit-control additive in the most severe batch of E85 tested.

Combustion chamber deposits

Combustion chamber deposits (CCD) are a secondary concern in gasoline use. Additive packages are formulated to prevent deposits in this area. Test results indicate that CCD thickness actually decreases as levels of ethanol in the blend increase.

NOTE: as those involved in the E85 supply chain gain more knowledge and experience, we can anticipate that the E85 specification, ASTM D5798 will be updated to reflect the current situation on fuel blending and usage. This updated specification will focus on the primary quality issues of making a product suitable for commercial sale, meeting minimum specifications. Beyond minimum performance, recent developments in E85 additive technology enable the formulation of a fuel that delivers greater performance.

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

9.1.1. Flexible-Fuel Vehicles

A **flexible-fuel vehicle (FFV)** or **dual-fuel vehicle** (also sometimes called only *flex-fuel*) is an automobile that can typically use different sources of fuel, either mixed in the same tank or with separate tanks and fuel systems for each fuel. A common example is a vehicle that can accept gasoline mixed with varying levels of bioethanol (gasohol). Some cars (see bi-fuel vehicle) carry a natural gas tank making it possible switch back and forth from gasoline to natural gas.

A flexible fueled vehicle (FFV) has a single fuel tank, fuel system, and engine. The vehicle is designed to run on unleaded gasoline and an alcohol fuel (usually ethanol) in any mixture. The engine and fuel system in a flex-fuel vehicle must be adapted slightly to run on alcohol fuels because they are corrosive.

There must also be a special sensor in the fuel line to analyze the fuel mixture and control the fuel injection and timing to adjust for different fuel compositions. The flex-fuel vehicle offers its owner an environmentally beneficial option whenever the alternative fuel is available. Some 270,000 of the flex-fuel "green" vehicles are expected to be sold in Brazil in 2004, according to industry forecasts.

When ethanol is more than 40 per cent cheaper than gasoline, it becomes attractive to drivers.

9.1.2. Flexible-fuel vehicles in Brazil

Since the oil crisis in the 70's. Brazil has been selling ethanol as a fuel. Car manufacturers modified gasoline engines to support ethanol characteristics (Changes are on compression ratio, amount of fuel injected, replacement of materials that would get corroded by the contact with ethanol, use of colder spark plugs suitable for dissipating heat due to higher flame temperatures, and an auxiliary cold-start system that injects gasoline from a small tank in the engine compartment to help starting when cold) and have been selling ethanol powered cars since then. However, flexible fuel technology started being developed only on the end of the 90's. The flexible fuel car is built with an ethanol ready engine and one fuel tank. The lambda probe, used to measure the quality of combustion in conventional engines, is also required to tell the ECU which blend of gasoline and alcohol is being burnt. So, the controller regulates the amount of fuel injected and spark time: fuel flow needs to be decreased and also self-combustion needs to be avoided when gasoline is used (because ethanol engines have compression ratio around 12:1, too high for gasoline). Those cars can run with arbitrary combinations of gasoline and alcohol (can use both fuels sold in Brazil -ethanol or gasoline with a blend of 20-25% ethanol - pure or blended in any proportion).

In May 2003 Volkswagen built for the first time a production flexible fuel car, the Gol 1.6 Total Flex. Chevrolet followed two months later with the Corsa 1.8 Flexpower, using an engine developed by a joint-venture with Fiat called PowerTrain.

As of 2005, popular manufacturers that build flexible fuel vehicles are Chevrolet, Fiat, Ford, Peugeot, Renault ,Volkswagen, Honda, Mitsubishi, Toyota and Citröen. Flexible fuel cars were 22% of the car sales in 2004, 73% in 2005, and 75% and 90% rates are estimated for 2006 and 2007.

There's another type of flexible fuel vehicle that is not uncommon in Brazil. Those are the cars able to switch from gasoline to natural gas. The term "flex-fuel", however is never used to describe those cars; instead, they are called bi-fueled vehicles or tri-fueled if they are built with an ethanol-gasoline flexible fuel engine (and tetra-fueled if they can run on pure gasoline). These vehicles are always adapted in specialized houses after they are bought. In many capitals, natural gas shares a small part of the fuel market with gasoline and ethanol. It has the advantages of having government incentives for cars with such systems, like annual tax reduction, and being the cheaper cost-per-mile in the country. The disadvantages are a slight reduction of engine power, the small number of gas stations that have this fuel available, having the lowest mileage and the space needed for the cylinder (normally one or two) installation, normally taking up a good amount of space in the trunk.

Trucks and pickups are mostly diesel powered and there's no project on conversion to some kind of flexible fuel system. Instead the tendency is to replace regular diesel with bio-diesel. The currently allowed mixture is 98% diesel and 2% bio-diesel. The mixture of 95% diesel and 5% bio-diesel will become a requirement only in 2013.

FIAT has introduced in 2006 the FIAT Siena Tetra fuel, which can run on 100% ethanol, E25 (Brazil's common gasoline mixture of 75% gasoline and 25% ethanol), pure gasoline (not available in Brazil) and natural gas.

California automobile distributor ZAP, has agreed to be the exclusive North American distributor and has pre-purchased 50,000 cars from Brazilian automotive maker OBVIO!. The first models scheduled to go into production are the flex-fueled 828 and 012 in 2007, soon to be followed by the 828E and 012E equipped with electric drive systems. Models are expected to be available in Canada and the United States in late 2008.

9.1.3. Flexible-fuel vehicles in Europe

For a long time Ford Taurus was the only flexible-fuel vehicle sold in Sweden. It was later replaced by Ford Focus. In 2005 Saab began selling its 9-5 2.0 Biopower (joined in 2006 by its 9-5 2.3 Biopower), and Volvo its S40 and V50 with flexible-fuel engines. In 2007, Saab also started selling a BioPower version of its popular Saab 9-3 line. The Saab-derived Cadillac BLS will also be available with E85 compatible engines in 2008.

There are also plans of selling E85 fuel, and then some flexible-fuel vehicles, in other European countries:

- In October 2005, the Ford Focus FFV became the first flexible-fuel vehicle to be commercially sold in Ireland. E-85 is available throughout a limited number of Maxol service stations in the Republic. Redesigned Ford C-MAX FFV may be sold there in 2007.

- Ford offers the Focus (all three models) since August 2005 in Germany. Ford is about to offer also the Mondeo and other models as FFV versions between 2007 and 2010. - Renault and PSA (Citroen & Peugeot) announced to start selling FFV cars from summer 2007.

The Koenigsegg CCXR is currently the fastest and most powerful flexible fuel vehicle with its twin-supercharged V8 producing 1018hp when running on biofuel (compared to 806hp on 91 octane (US) unleaded gasoline).

9.2 Ethanol-Diesel Blends

The supplementation of diesel fuel with a reliable fuel that is reasonably priced and renewable has been of interest since the oil crisis of early 1970's. Renewable liquid fuels, such as, vegetable oils and alcohols are found to be promising for use in compression ignition and spark ignition engines. Gasohol, a mixture of 10% alcohol and 90% gasoline is already a commercial fuel in over 35 countries. Besides being a biomass based renewable fuel, ethanol is less expensive, has cleaner burning and higher octane rating than various vegetable oils1. The performance studies conducted on a 26.2 kW tractor engine with diesel ethanol blend containing 5% to 50% anhydrous ethanol showed best engine performance on the blend containing 10% ethanol2. Studies on the use of 200°, 190° and 180° proof ethanol denatured with gasoline in a ethanol tractor resulted reduced power output of the engine by 5.5% on 190° proof ethanol and 4.8% on 180° proof ethanol3. The use of a diesel-ethanol blend containing 20% of 170° proof ethanol was recommended for use in a small constant speed CI engine with a view of reduced CO and NOx emissions4. In view of the above, a study was conducted to evaluate feasibility of using lower ethanol proofs for blending with diesel, determine relevant fuel properties of suitable blends and to evaluate performance of a constant speed CI engine on stable ethanol-diesel blends prepared using anhydrous and lower ethanol proof.

9.2.1. Fuel Properties

Relative Density

The relative density of diesel and anhydrous ethanol (200° proof) was found to be 0.8844 and 0.8013, respectively (Table 2). The observations on relative density of fuel types prepared from different proofs of ethanol by blending 20% and 15% ethanol indicate that with decrease in ethanol proof the relative density increases. The fuel type 170/15/85 which is a blend prepared by adding 15% of 170° proof ethanol with 85% diesel has the highest relative density of 0.8426 amongst the blended fuel types.

Viscosity

The dynamic and kinematic viscosity of diesel at 38°C was found to be 4.3346 cP and 4.9012 cS, respectively (Table 2). The dynamic and kinematic viscosity of anhydrous ethanol was

2.2482 cP and 2.8075 cS, respectively. It is evident from Table 2 that viscosity of diesel-ethanol blends is closed to that of diesel.

The kinematic viscosity of 180/20/80/, 180/15/85 and 170/15/85 was only 3.1%, 2.0% and 0.9% lower than that of diesel. It can, therefore, be said that diesel-ethanol blends containing 180° and 170° proof ethanol should have no problems related to atomization of blends by injector when used in CI engines.

Sl No	Fuel Type	Relative Density at 15°C	Dynamic Viscosity at 38°C, cP	Kinematic Viscosity at 38°C cS	Gross Heat of Combustion,	
					kCal/kg	kJ/kg
1	Diesel	0.8844	4.3346	4.9012	10267.4	43123.0
2	Anhydrous ethanol (200°proof)	0.8013	2.2482	2.8075	6696.3	28124.4
3	200/20/15	0.8257	3.6698	4.4445	9830.9	41289.8
4	200/15/85	0.8276	3.7876	4.5766	9997.5	41989.5
5	190/20/80	0.8351	4.0128	4.8051	9798.3	40825.3
6	190/15/85	0.8360	4.0469	4.8405	9874.3	41427.1
7	180/20/80	0.8379	4.1999	5.0124	9687.0	40685.4
8	180/15/85	0.8388	4.2460	5.0620	9841.0	41332.2
9	170/15/85	0.8426	4.2962	5.0987	9767.0	41147.4

Characteristic fuel properties of diesel and diesel-ethanol blends

Gross Heat of Combustion

The gross heat of combustion of fuel types selected was 10267.4 kCal/kg (43123 kJ/kg) for diesel (Table 2). The gross heat of combustion of anhydrous ethanol was found to be 6696.3 kCal/kg (28124.4 kJ/kg). It is evident from the table that 200/20/80, 190/20/80 and 180/20/80 fuel types have the calorific value of 9830.9 kCal/kg, 9798.3 kCal/kg and 9687 kCal/kg, respectively. The fuel types namely, 200/15/85, 190/15/85, and 180/15/85 and 170/15/85 have the calorific value of 9997.5 kCal/kg, 9874.3 kCal/kg, 9841 kCal/kg and 9767 kCal/kg, respectively. The above values, therefore, indicate that the gross heat of combustion of all the selected diesel-ethanol blended fuels were close to diesel fuel.

9.2.2. Conclusions

The feasibility of a diesel-ethanol blend for fuel use depends on phase separation characteristics of the blend. The 15% to 30% ethanol of 200°, 190° and 180° proof ethanol could be blended with diesel. The blending of 170° proof ethanol with diesel was possible when 15% of ethanol was blended by volume. The 150° and 160° proof ethanol were found not suitable for blending with diesel due to distinct phase separation even when only 10% of these proofs were blended. The relative density, viscosity and gross heat of combustion of different diesel-ethanol blends were found to be close to that of diesel. Amongst all the selected diesel-ethanol blended fuels, the fuel type 170/15/85 had the dynamic viscosity only 0.9% lower than the diesel. The gross heat of combustion of the fuel type 170/15/85 was only 5% less than that of diesel. All the selected diesel ethanol blends were found to have similar power producing capabilities under each load conditions. The bsfc of the engine was found to be lower on diesel-ethanol blends when the engine developed its rated power. The thermal efficiency of the engine was found to be higher on diesel ethanol blended fuels as compared to diesel fuel. It appeared that blending of 15% ethanol with diesel is more feasible instead of 20% by volume. The diesel replacement of 15% to 20% is possible by using the different diesel-ethanol blends tested.

9.3 Properties Evaluation

Viscosity – The viscosity of a product is best described as its consistency. Knowing the viscosity of a product across its operational temperature range is important so that suitable pumps etc can be used to transfer it. If a product is too viscous, pumps can struggle to pump it but if it is not viscous enough it can leak past the pump components and seals.

Flash Point (for distillates) – Diesel, gas oil and kerosene all have a minimum flash point specification. The flash point is defined as the temperature at which the fuel ignites when exposed to source of ignition. This property is important in defining the transport and storage requirements for the fuel. As gasoline ignites at very low temperatures the flash test is not required and the product is classified separately from distillates.

Cloud point and Pour Point- Cloud point is the temperature at which a cloud or haze of wax crystals appears at the bottom of the test jar when the oil is cooled under prescribed conditions. Cloud point gives a rough idea of the temperature above which oil can be safely handled without any fear of congealing or filter clogging.

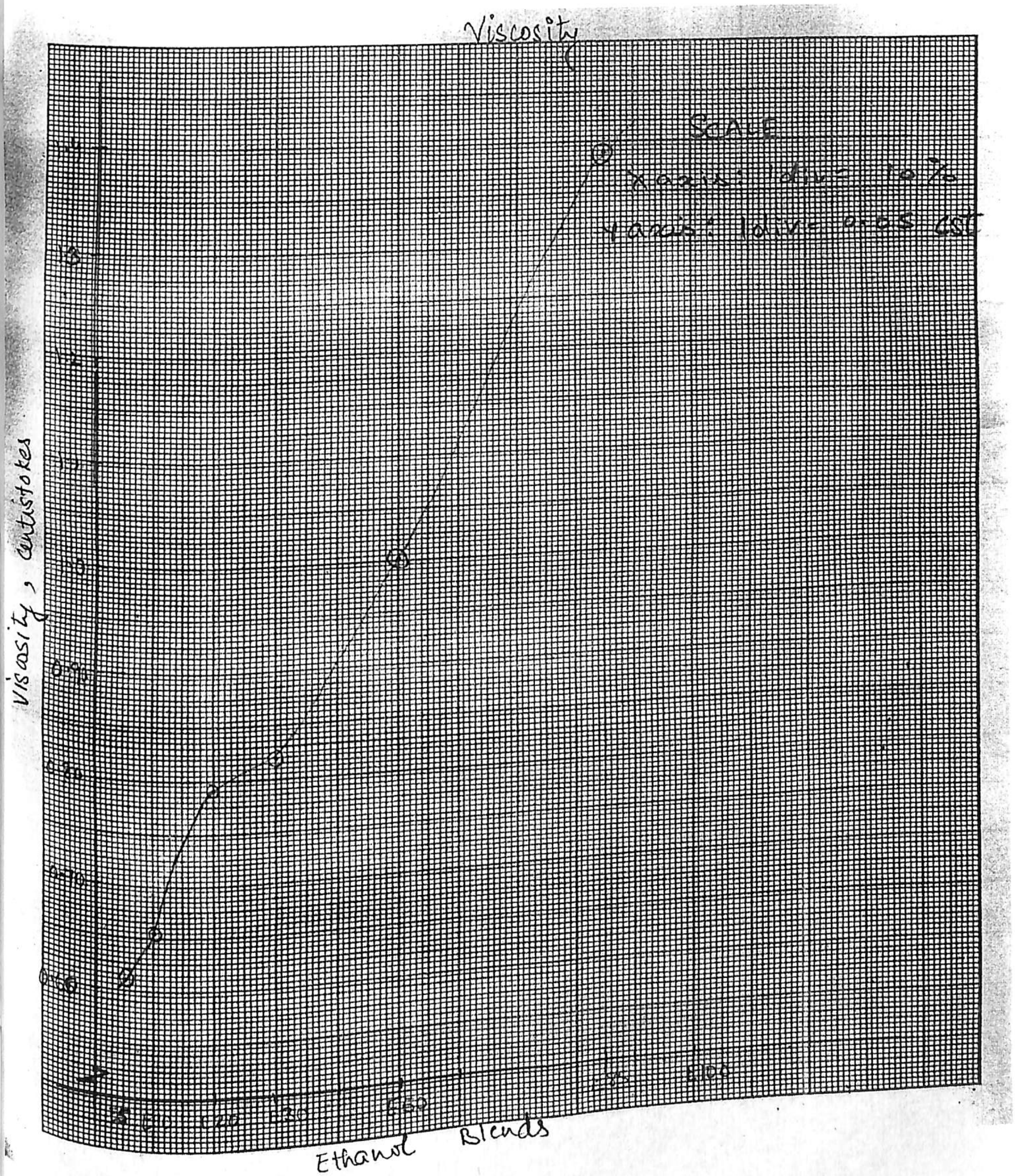
Pour point is the temperature at which a liquid loses its fluid characteristics. It is a rough indication of the lowest temperature at which industrial fluids are readily pumpable. For crude oil and gasoline, pour point is the lowest temperature at which the liquid will pour or flow under test conditions. For diesel fuels, pour point is the temperature at which the amount of wax out of solution is sufficient to gel the fuel when tested under standard conditions.

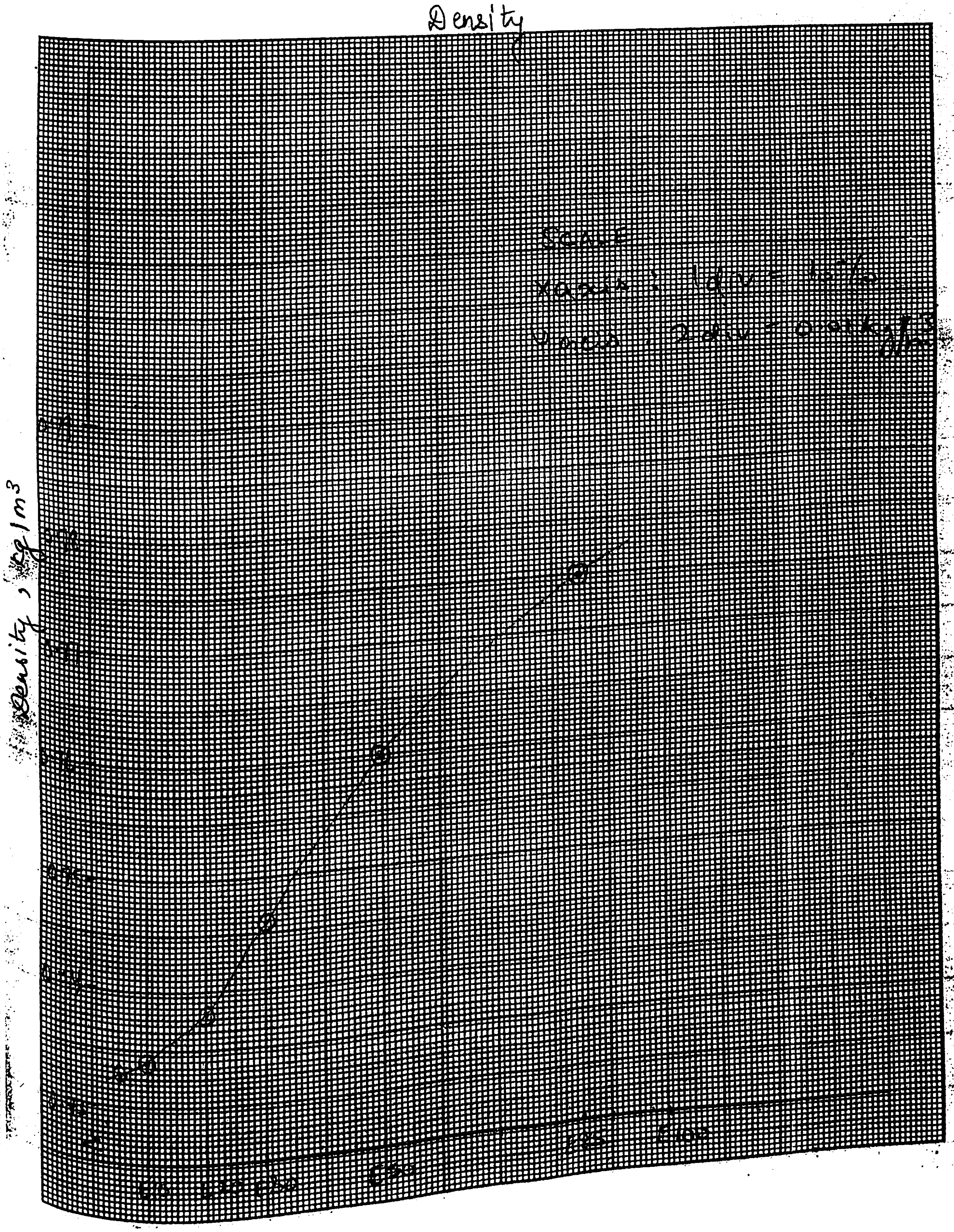
Reid vapor pressure- It is the absolute vapor pressure exerted by a liquid at 100°F. The higher this value, the more volatile the sample and the more readily it will evaporate. Unlike distillation data, vapor pressure provides a single value that reflects the combined effect of the individual vapor pressure of the different petroleum fractions in accordance with their mole ratios. It is thus possible for two wholly different products to exhibit the same vapor pressure at the same temperature - provided the cumulative pressures exerted by the fractions are the same.

Reid Vapor Pressure" is a pressure determined by a conventional analytical method for determining the vapor pressure of petroleum products. In essence, a liquid petroleum sample is introduced into a chamber, then immersed in a bath at 100.degree F(37.8 degree C.) until a constant pressure is observed. Thus, the Reid Vapor Pressure is the difference, or the partial pressure, produced by the sample at 100 F (37.8.degree. C).

Density- Density of a fluid is its mass per unit volume. It is measured over a range of temperatures, usually for convenience at the temperature at which the fuel is to be stored.

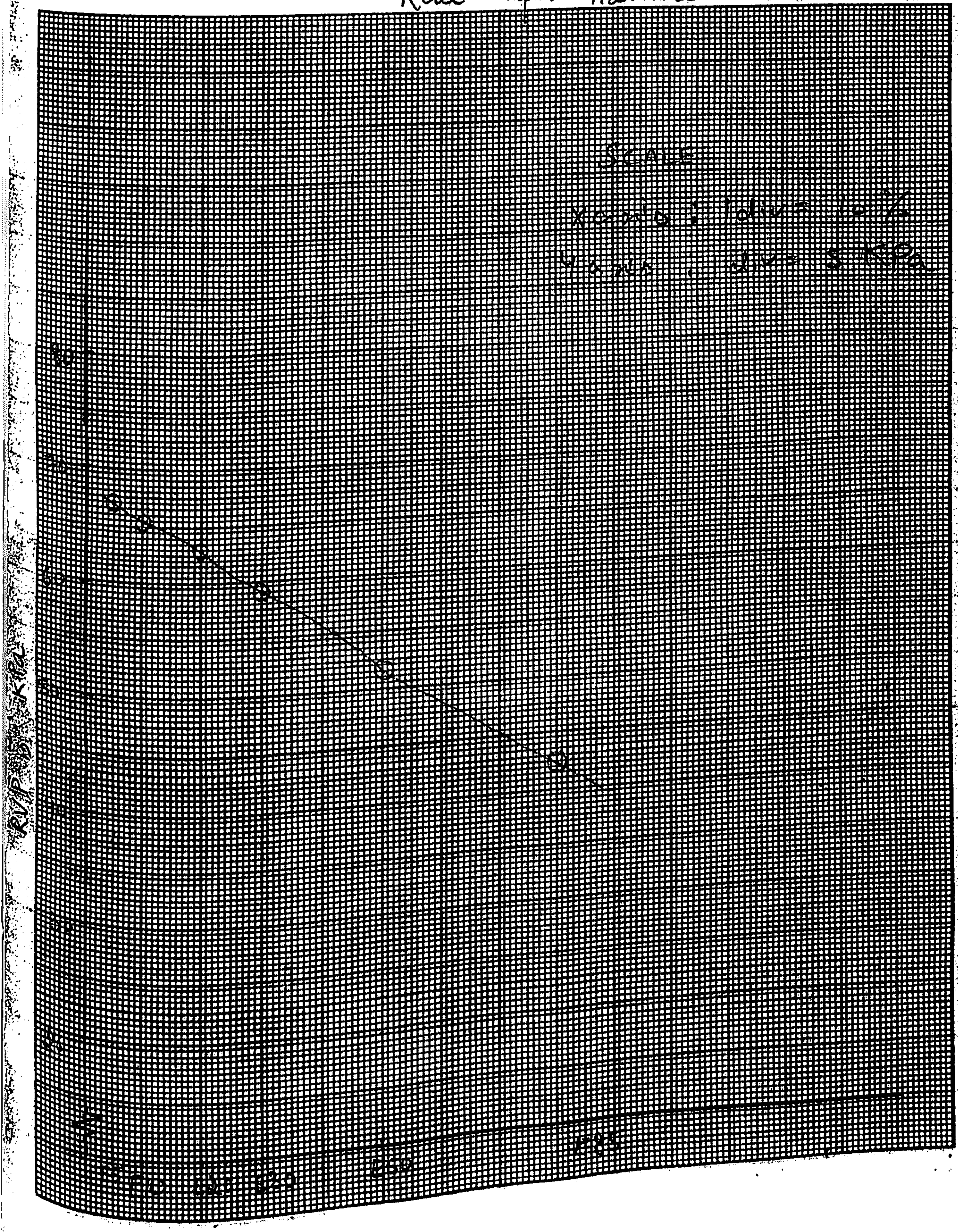
Properties	**E5**	**E10**	**E20**	**E30**	**E50**	**E85**
Density (kg/m3)	**0.732**	**0.734**	**0.738**	**0.744**	**0.760**	**0.778**
Viscosity (cs)	**0.6123**	**0.6593**	**0.7838**	**0.8438**	**1.0024**	**1.389**
Reid Vapor Pressure (KPa)	**67**	**66**	**63**	**59**	**51.4**	**42.4**
Cloud Point (C)	**9**	**6**	-	-	-	-
Pour Point (C)	**-11**	**-14**	-	-	-	-
Flash point (C)	**-39**	**-36**	**-28**	**-21**	**-10**	**6**


Viscosity
SCALE
X axis: 1div = 10%
Y axis: 1div = 0.05 cSt
Viscosity, centistokes
1.4
1.3
1.2
1.1
1.0
0.90
0.80
0.70
0.60
E5
E10
E20
E30
E50
E85
E100
Ethanol Blends

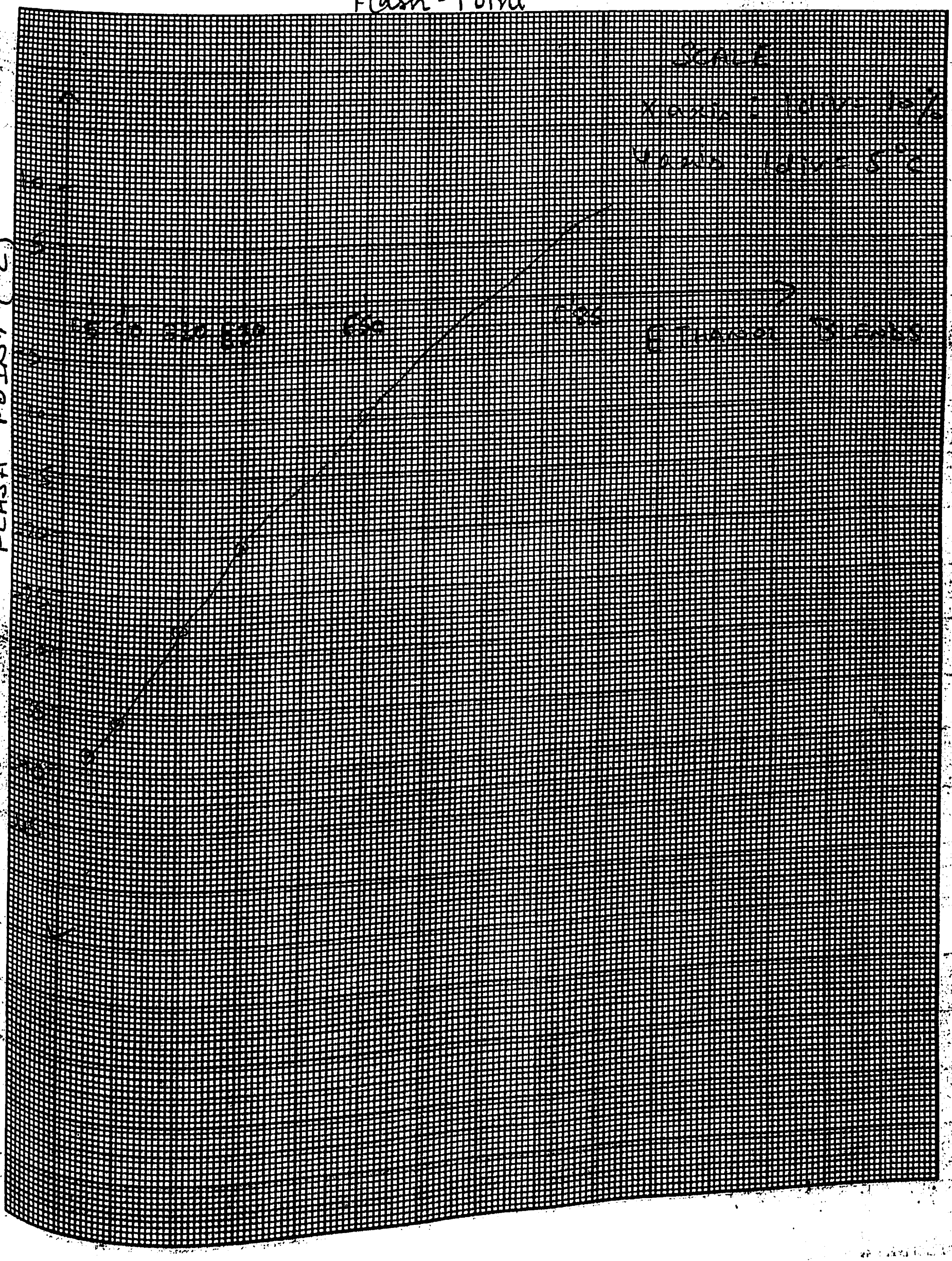


Density

Reid vapor Pressure



Flash - Point


SCALE
X axis : 1 div = 5%
Y axis : 1 div = 5°C
FLASH POINT (°C)
E5 E10 E20 E30 E50 E85
ETHANOL BLENDS

10. ETHANOL ECONOMICS

Economics for ethanol are influenced by a variety of factors including:

1. feedstock price
2. oil price, and
3. government subsidy

The above three factors determine the cost, price, margin, and therefore the attractiveness of the ethanol industry. Oil prices are not impacted by the ethanol industry and cannot be influenced by ethanol supply-demand dynamics. An analysis based on multiple oil price scenarios will have to be conducted to understand ethanol dynamics.

All vehicles have a fuel economy (measured as miles per US gallon -MPG- , or liters per 100 km) that is directly proportional to energy content. Ethanol contains approx. 34% less energy per unit volume than gasoline, and therefore will result in a 34% reduction in miles per US 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.

Year	MS Demand Million Ton	Ethanol requirement for blending Million Ton		
		@ 5%	@ 10 %	@ 20%
2001-02	7.07	0.35	0.70	1.40
2002-03	7.62	0.38	0.76	1.52
2003-04	8.20	0.41	0.82	1.64
2004-05	8.81	0.44	0.88	1.76
2005-06	9.42	0.47	0.94	1.88
2006-07	10.07	0.50	1.00	2.00

The Government has taken the decision to make the 5% blending in gasoline as mandatory in phased manner. From the table it is clear that the present production of ethanol is mainly from molasses. It is projected that in the year 2006-07, 1485 thousand kl of ethanol from sugarcane directly will be produced in addition to 2300 thousand kl from molasses. Thus for meeting the demand of ethanol for 10 % blending, capacity to produce ethanol in the country is sufficient. But for blending purposes anhydrous ethanol is required and the distilleries will have to put up facility to dehydrate ethanol and produce anhydrous ethanol. For higher percentage of blending and till the demand becomes stable, correspondingly higher quantities of ethanol, and consequently more sugarcane and other raw material, would be needed. The target should be to raise the blending in stages to 10% by the end of the X Plan.

10.1 Economics of Production

10.1.1 General

The major factors that affect the ethanol cost are the yield of sugarcane and cycle of production, the sugar contents in the juice, efficiency in juice extraction as well as in fermentation, and lastly utilization of waste. Sugarcane production requires long time as well as high irrigation and chemical fertilizer. This increases the cost of production and puts some question on its competitiveness with other crops.

Lower sugarcane content affects greatly the efficiency of farm production as it provides lower tonnage of sugar for the same inputs "irrigation, fertilizer and labor". Lower sugar content also results in higher extraction cost per tonne of sugar extracted. Next is their efficiency in extracting the juice. Some of the sugar remains in the bagasse.

A higher level of extraction, however, increases the power cost and the effort reaches a trade off. A higher level of extraction obviously reduces the cost of juice and therefore cost of sugar/ethanol. Presently, the fermentation does not provide alcohol content above 10% and lot of energy is wasted in removing the balance water to get anhydrous alcohol necessary for blending in gasoline. A higher level of alcohol by fermentation would automatically reduce the cost of purification.

Two major waste products are generated in the ethanol production from sugarcane

- bagasse:
- spent wash

Bagasse is utilized presently for boiler fuel needed for steam raising while spent wash is an effluent which requires treatment for COD removal before discharge into the land or river. It is possible through anaerobic digestion to utilize the spent wash in production of two valuable commodities – one methane rich fuel gas and another nutrient rich bio-sludge suitable for soil nutrition. The gas production can be sufficient to meet the fuel requirement as well as power for electric derives through co-generation.

10.1.2. 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 the 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 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 cost would work out less than Rs. 9/- per litre and would be quite competitive to the present imported cost of gasoline around Rs. 10-12 per litre.

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
4. 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.
5. 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
6. Power cost of Rs. 4.50/kwh & Rice Husk cost of Rs. 500/MT with steam raising @3T/T of rice husk.
7. Biogas generation can provide enough energy to meet all energy demand but it has not been taken into account.
8. No taxes (excise or sales etc) on inputs considered.

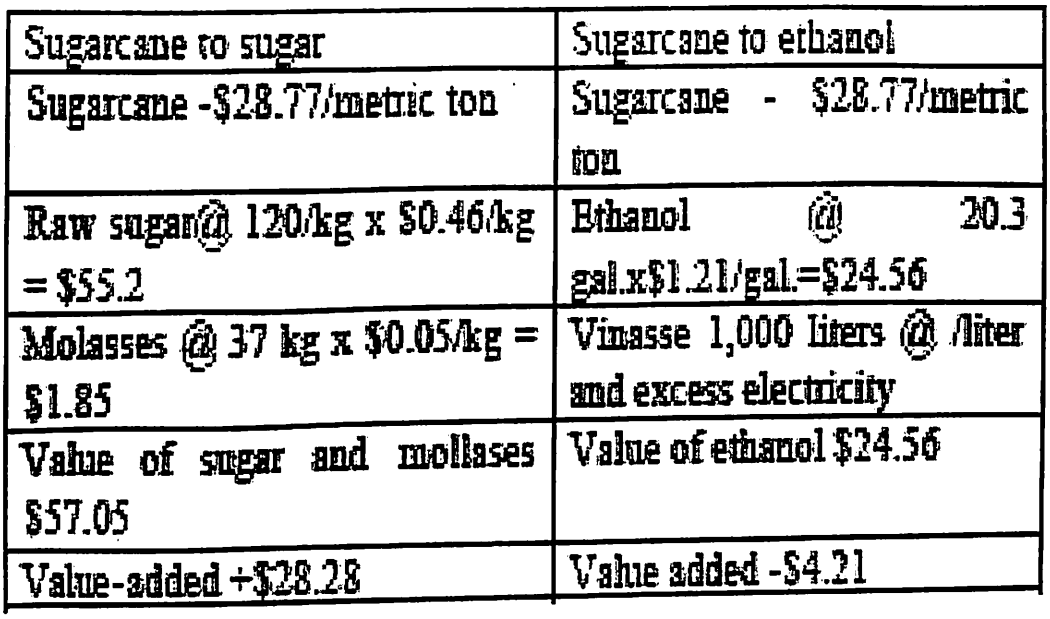
Industry Survey in UP and Uttarakhand:

The present status of industry and prospects of improvement can be gauged from the survey conducted by UP Pollution Control Board (2001) for the 43 distillery units in UP and Uttarakhand, out of which 37 units were functional and 35 among these were molasses based while 1 was based on grain and another on malt. It was found that 22 units have capacity utilization below 74%. There was a wide variation ranging from 4.53 to 6.28 tonne molasses for production of 1 kL of alcohol against the norm of 4.87 mt/kl. Only 14 units have alcohol recovery above the norm of 472.5 litres/MT of TRS (total reducible sugar). A very wide variation in water consumption ranging from 14.69 KL to 512.88 KL per KL of alcohol and 9 units have specific water consumption in excess of 139 KL (norm 15 kl/kl). Again there was a wide variation in energy consumption ranging from 10.17 GJ/KL alcohol to 123.56 GJ/KL as many as 10 units have their specific energy consumption in excess of 24GJ (modal value 18.32 GJ/kl). The survey found variation from 7.92 to 100% of the content of renewable energy in the total energy consumed. 8 units have renewable energy consumption below 77% (model value 93%). 30 units have their specific net external energy consumption below 31 GJ/KL alcohol while one unit was having no need of external energy (model value 9.5 Gj/kl). There was a wide variation among the units ranging from 10.87 KL to 38.34 KL of spent wash per litre of ethanol produced. However, for most of the units it was within 10.87 to 17.7 KL (model value 14.92 kl/kl). For production of biogas from the spent wash, the data from 26 units out of 33 units show a variation from 7.26 Nm3/KL to 54.3 Nm3/KL (model value 30 Nm3/kl) while 2 were not functional.

3.5.3. Economics of Sugarcane to sugar to Ethanol

No definite view can be expressed as economy differs widely depending on the local prices of the products and their respective substitutes. A comparative position in the economics of ethanol production from sugarcane is shown in the tables below as provided by Mr. Hosein Shapouri[1],

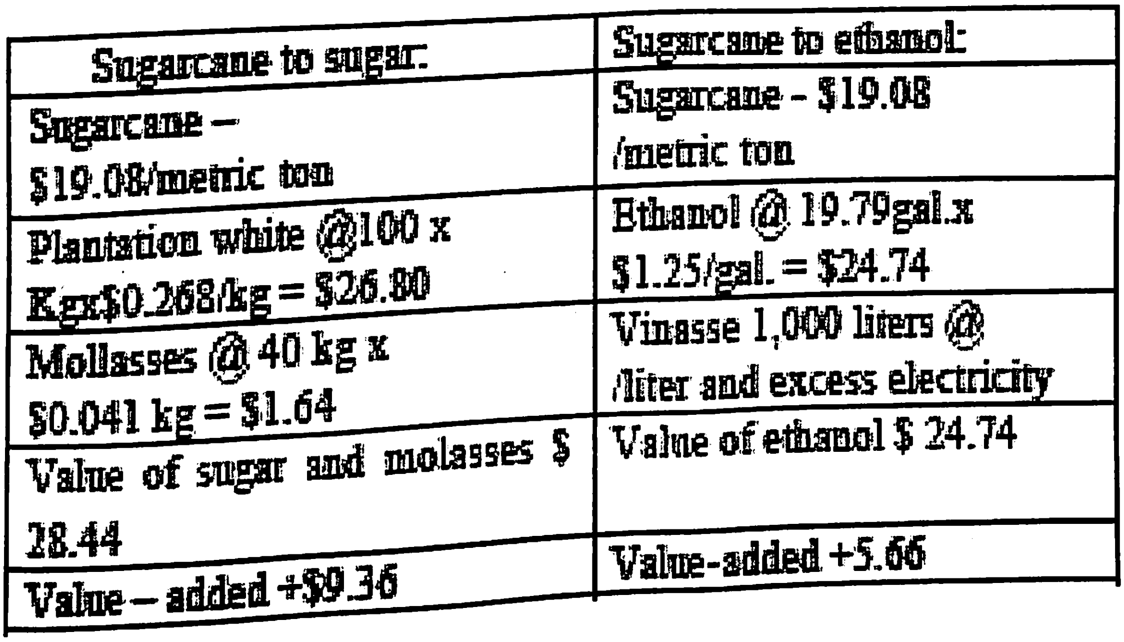
Value Added Benefits (U.S.)



Sugarcane to sugar	Sugarcane to ethanol
Sugarcane -$28.77/metric ton	Sugarcane - $28.77/metric ton
Raw sugar@ 120/kg x $0.46/kg = $55.2	Ethanol @ 20.3 gal.x$1.21/gal.=$24.56
Molasses @ 37 kg x $0.05/kg = $1.85	Vinasse 1,000 liters @ /liter and excess electricity
Value of sugar and mollases $57.05	Value of ethanol $24.56
Value-added +$28.28	Value added -$4.21

Value Added Benefits, India

Source: Nizam Sugars Limited P. Srimannarayana, General Manager, Hyderabad, India.



Sugarcane to sugar:	Sugarcane to ethanol:
Sugarcane – $19.08/metric ton	Sugarcane - $19.08 /metric ton
Plantation white @100 x Kgx$0.268/kg = $26.80	Ethanol @ 19.79gal.x $1.25/gal. = $24.74
Mollasses @ 40 kg x $0.041 kg = $1.64	Vinasse 1,000 liters @ /liter and excess electricity
Value of sugar and molasses $ 28.44	Value of ethanol $ 24.74
Value – added +$9.36	Value-added +5.66

Value Added Benefits, Brazil

Source: UNICA, Sao Paulo Sugarcane, Agroindustry Union, Mr. Luiz Carlos Correa Carvalho, Consultant.

Sugarcane to sugar:	Sugarcane to ethanol
Sugarcane - $6 /metric ton	Sugarcane - $6/metric ton
Raw sugar @ 120kg	Ethanol @20.3 gal. X $ 0.70/gal. = $14.21
Molasses @ 37 kgx $0.03/kg = $1.11	Excess electricity ?
Value of sugar and molasses $16.71	Value of ethanol $14.21
Value-added +10.71	Value – added +$8.21

The conclusion is that under the existing price structure, sugar production provides the highest value addition in all the three countries, US, Brazil and India as indicated in the table below-

Value addition from sugar cane to sugar and ethanol

In $ /MT

	U.S.A.	Brazil	India
Sugarcane to sugar	28.28	10.71	9.36
Sugarcane to ethanol	-4.21	8.21	5.66

11. ENVIRONMENTAL ASPECTS

Energy balance

All biomass needs to go through some of these steps: it needs to be grown, collected, dried, fermented, and burned. All of these steps require resources and an infrastructure.

Opponents of corn ethanol production in the U.S. often quote the 2005 paper of David Pimentel, a retired Entomologist, and Tadeusz Patzek, a Geological Engineer from Berkeley. Both have been exceptionally critical of ethanol and other biofuels. Their studies contend that ethanol, and biofuels in general, are "energy negative", meaning they take more energy to produce than is contained in the final product.

A 2006 report by the U.S. Department Agriculture compared the methodologies used by a number of researchers on this subject and found that the majority of research showed that the energy balance for ethanol is positive. A 2006 study published in *Science* analyzed six studies, normalizing assumptions for comparison; Pimental and Patzek's studies still showed a net energy loss, while four others showed a net energy gain. Furthermore, fossil fuels also require significant energy inputs which have seldom been accounted for in the past.

Ethanol is not the only product created during production, and the energy content of the by-products must also be considered. Corn is typically 66% starch and the remaining 33% is not fermented. This unfermented component is called distillers grain, which is high in fats and proteins, and makes good animal feed.

In Brazil where sugar cane is used, the yield is higher, and conversion to ethanol is somewhat more energy efficient than corn. Recent developments with cellulosic ethanol production may improve yields even further.

Air pollution

Compared with conventional unleaded gasoline, ethanol is particulate-free burning fuels source that combusts cleanly with oxygen to form carbon dioxide and water. The Clean Air Act requires the addition of oxygenates to reduce carbon monoxide emissions in the United States. The additive MTBE is currently being phased out due to ground water contamination; hence ethanol becomes an attractive alternative additive.

Use of ethanol, produced from current (2006) methods, emits a similar net amount of carbon dioxide but less carbon monoxide than gasoline. Current production methods include air pollution from the manufacturer of macronutrient fertilizers. The production of ammonia to produce nitrogen fertilizer consumed about 5% of the world natural gas consumption while China uses coal for 60% of their nitrogen fertilizer production.

If ethanol-production energy came from non-fossil sources the use of ethanol as a fuel would add less greenhouse gas.

Manufacture

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.

Greenhouse gas abatement

Corn ethanol has received much support on environmental grounds primarily because of its role in reducing greenhouse gas emissions. However, the evidence for this claim is mixed.

A recent ten-year forecast of ethanol production by the USDA places 2017 corn ethanol production at 12 billion US gallons and growing at only 2% per year. This estimate, together with a parameter publishing in the Proceedings of the National Academy of Sciences (PNAS), indicates that this near-maximum level of ethanol production will abate GHG emissions by 0.13% (~1/10 of 1%) of current US GHG emissions. However, this does not hold for all greenhouse gases. Another study has suggested that replacement of 100% petroleum fuel with E85 (a fuel mixture comprised of 85% ethanol and 15% petroleum) would significantly increase ozone levels, thereby increasing photochemical smog and aggravating medical problems such as asthma.

This value reflects increases in corn area and the use of 30% of the corn crop for ethanol. It also apparently takes into account anticipated improvements in corn yields and ethanol production. The PNAS value is a 12% reduction in greenhouse gas emission relative to the "net emissions of production and combustion of an energetically equivalent amount of gasoline."

The January 2006 Science article from UC Berkeley's ERG, estimated this parameter to be 13% after reviewing a large number of studies. However, in a correction to that article releases shortly after publication, they reduce the estimated value to 7.4%. None of the other values needed to complete the calculation are controversial.

Land use

Large-scale 'energy farming', necessary to produce agricultural alcohol, requires substantial amounts of cultivated land. Some have claimed that land is acquired through deforestation, while others have observed that areas currently supporting forests are usually not suitable for growing any sort of crops. Related concerns have been raised regarding a decline in soil fertility due to reduction of organic matter, a decrease in water availability and quality, an increase in the use of pesticides and fertilizers, and potential dislocation of local communities.

As demand for ethanol fuel increases, food crops are replaced by fuel crops, driving food supply down and food prices up. Growing demand for ethanol in the United States has increased corn prices by 50% in Mexico. Average barley prices in the United States rose 17% from January to June 2007 to the highest in 11 years. Prices for all grain crops trend upward, reflecting a progressive increase in farm land devoted to corn for the production of produce ethanol fuel. Prices for U.S. corn-based products, including animal feed, also rise. This translates to higher prices for animal products like chicken, beef, and cheese. June 2007 cheese prices rose to $2 per pound on average, increasing 65% over the same period in 2006. As milk prices in the United States, approached $4.00 per US gallon, many American restaurant franchises announced price increases for their products to compensate for rising food costs.

Alternatively, cellulosic ethanol can be produced from any plant material, potentially doubling yields, in an effort to minimize conflict between food needs versus fuel needs. Instead of utilizing only the starch bi-products from grinding wheat and other crops, cellulosic ethanol production maximizes the use of all plant materials, including gluten. This approach would have a smaller carbon footprint because the amount of energy-intensive fertilizers and fungicides remain the same for higher output of usable material. While the enzyme technology for producing cellulosic ethanol is currently in developmental stages, it is not expected to be available for large-scale production in the near future. Moreover, the production of ethanol for fuel raises a number of land scarcity issues, regardless of what production method is employed. Many analysts suggest that biofuel strategies must be accompanied by fuel conservation restrictions.

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 (see production).

The environmental and economic benefits of non-cellulosic ethanol - including corn ethanol - have been heavily critiqued by many, including Lester R. Brown of Earth Policy Institute and Environmental Economics & Sustainable Development. 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.

12. MARKET DYNAMICS

Market drivers

Ethanol Blending Program

The Indian Government with an aim to increase energy security and decrease dependence on fossil fuels has encouraged the blending of 5% ethanol with petrol through a mandate covering 20 states and four union territories. This will ensure a boost in the demand for bioethanol in fuel purposes. If this mandate is successfully implemented in these regions, this would lead to a demand of approximately 550-mn liters of ethanol in the country. By 2011-12, the fuel ethanol demand could be 807-mn liters, if a 5% blending mandate is implemented across the country and 1,628-mn liters for a 10% blending mandate.

Volatile oil prices

Volatile oil prices ensure that a competitive and low profit margin industry such as the transport sector is constantly trying to source cheaper fuels. The market for transport fuels is very price sensitive and rising prices at the pumps, driven by the high mineral oil price, have opened up a market for cheaper alternatives. Fuel ethanol being cheaper than petrol will have an advantage here.

Increasing importance of alternate clean fuels

Persistent growth in transport activity in India is a concern for the environment. India is among the top five global contributors to carbon emissions, growing at an average rate of 3.2%. Ethanol consumption could lead to diversification of energy sources and at the same time a reduction in carbon emissions.

Compatibility with existing fuel infrastructure

The ease of use of ethanol in the existing fuel infrastructure and vehicle fleet has been a major driver behind its rapidly expanding use and acceptance. This gives it a substantial advantage over other 'alternative' fuels such as LPG or natural gas, which require expensive changes to the vehicles and completely different dispensing equipment.

Sugarcane production

India is one of the largest producers of sugarcane and sugar in the world. In India, ethanol is produced primarily from molasses, obtained as a by-product in the manufacture of sugar.

As in the case with major sugarcane producing countries such as Brazil, this larege-scale availability of sugarcane and molasses, in specific, and the strong presence of the sugar industry in India gives some stability to the supply of ethanol, which is normally affected by the cyclical nature of sugarcane production.

Government support and initiatives

Apart from the mandates and the ethanol blending program, the government also offers support to the industry through other initiates such as subsidized financial support for research and development on ethanol production undertaken by public and private sector organizations and even for non-profit organizations and research organizations for identifying feedstock suitable for semi-arid wasteland and for the utilization of crop cellulose waste that can be used for ethanol production.

A national biofuel policy is also under formulation that will outline the strategy of the country on biofuels development and the approach taken for the same. It will also deal with the fiscal and financial incentives provided by the government for this purpose.

Ethanol production capacity

The current installed overall alcohol capacity of 3000-mn liters and fuel ethanol capacity of 1500-mn liters is sufficient to cater to the demand in the country for a 5% blend until 2011-12. Therefore, given an assured supply of sugarcane the demand for ethanol can easily be met from the distiller's end.

Availability of biomass

Large quantities of biomass is available in the country, which could, theoretically, be converted to large amounts of ethanol once the technology has been completely developed and is commercially viable.

Some of the sources for biomass, which could be used, are rice straw, sugarcane bagasse, wheat straw, and other agricultural residues, wood residues such as saw dust, leftover branches and barks from logging. Another source that is widely available and inexpensive is animal waste.

13. SUGGESTIONS ON KEY CONCERNS

There is no doubt that ethanol remains one of the most lucrative alternative green fuels available today. An efficient implementation of India's biofuel program will go a long way in reducing India's growing expenditures on crude oil and other petroleum product imports and address environment concerns. It will also help in reducing India's carbon emissions, which are increasing by more than 3% per year, making India one of the top global contributors to carbon emissions.

Given that India is one of the world's largest producers of sugar and sugarcane, most of the ethanol produced in India is from molasses.

If the 5% blending mandate is successfully implemented all over the country, total ethanol demand would currently be approximately 2355-mn liters, which can be sufficiently met by the capacity from distillers. The direction that the industry will take is dependent upon a delicate balance between feedstock, technology and regulation. Also, it is given that prices of molasses will vary year on year. Therefore, distilleries attached to a sugar producer will have the lowest risk in terms of availability or cost of production issues. On the other hand, distilleries that either manufacture fuel ethanol by purchasing molasses from external sources or by purchasing and further distilling rectified spirit will be lesser protected and will have lower reliability of supply.

In 2006-07, sugarcane production was on the higher side and the production of sugar exceeded demand and the amount of molasses available would have been sufficient to meet this demand for ethanol as well.

However, if the crop fails, like it did three years back in 2003-04, the supply of ethanol will fall short of the demand and the mandate cannot be successfully met. Also, in years where the yield is low, it may not be commercially viable to blend ethanol with petrol. Therefore, from the feedstock perspective, the mandate for a 5% blend should be increasingly implemented in the country across a period of four to five years.

In the meantime, active measures must be taken for increasing efficiency in production of ethanol, making it more cost-effective; considerable resources should be spent in research and cultivated of alternate feedstock for ethanol, such as sweet sorghum.

The slow phasing in of a 5 per cent blending mandate will ensure the success of such a mandate with assured raw material availability and commercial viability.

Once this mandate has been successfully implemented and the technology for the production of lignocellulosic ethanol is commonly available and feedstock issues have been sorted out, the mandate could then increase the percentage of ethanol in blended petrol to 10 percent.

Therefore, we see that even though a mandate could secure demand, it might not be possible to secure sufficient feedstock (currently, the only feedstock being sugarcane) to supply this ethanol without the right technology being in place.

Since the capacity of ethanol distillation is sufficient to meet demand, it is safe to assume that the demand for ethanol over the next few years, with a planned phasing in of the blending mandate, can be met predominantly through available feedstock such as sugarcane, corn, maize etc. Sweet sorghum is also an option that must be actively considered. Active measures taken by manufacturers to secure such as alternative feedstock will ensure supply and availability of feedstock at commercial viable prices in order to meet the mandate. However, for the mandate to be successfully implemented across the country, it is imperative that there is no significant variation in taxes and duties within different states. Biofuels must be treated like a national program in order to ensure successful implementation.

Since the refining companies are justified in purchasing ethanol arriving at the mixing depots at a price not greater than that of petrol and the manufacturers also currently have high production costs, it is necessary to give sufficient duty and tax exemptions in order to increase the manufacturer's margins and make ethanol manufacture a lucrative business. This will also ensure supply of raw material at viable prices. The rising demand according to the mandate and its implemented nationwide will also make the issue of margins for the manufacturers less important.

Also, over the next 3-5 year period, when production of cellulosic ethanol becomes commercially viable and widely used, the cost of production is slated to decrease. Having said that, it is imperative, in the short term, to provide sufficient regulatory incentives to the manufacturers to ensure demand for ethanol arising from the mandate is met through local production.

Currently, there is a lot of research in the area of bioethanol with the objective of making it a sustainable, dependable and commercially viable alternative. With advancements in the area of lignocellulosic ethanol and enzymatic technologies, the efficiency of this fuel is sure to improve.

The concerns on energy balance can also be addressed with a closed-loop ethanol plant model where the energy for distillation comes from fermented manure, produced from cattle, which have been fed the by-products from the distillation. The leftover manure is then used to fertilize the soil used to grow the grain. Such a process is expected to have a much lower fossil fuel requirement.

Therefore, it can be stated with considerable optimism that regardless of the current opinion on carbon neutrality of ethanol, its carbon footprint is set to decrease, helping to reduce global emission.

14. CONCLUSION

India already has a well developed ethanol industry in place as a result of the country's sugar production. There is also sufficient capacity for the production of fuel ethanol.

Therefore, the success of ethanol as a biofuel in the country will depend mainly upon two factors: availability and operational issues. While availability arise due to cyclic nature of sugarcane production, which will impact the cost of production of ethanol as well, operational issues need to be sorted out by the government in terms of clear policy, regulations and infrastructure for petrol-ethanol blending and logistics.

The Indian biodiesel industry on the other hand is not as developed as the ethanol industry and is still at a nascent stage with no large scale production as yet. However, some plants are expected to be completed shortly and large scale production of biodiesel from India may begin in the near future.

Biodiesel manufacturers need to be able to secure feedstock, as price and availability of feedstock are critical parameters in this industry. Since the government does not have a clear policy in this area and plantations of Jatropha are still being developed, some certainly currently exists in the market. However, these issues can be addressed by cooperation between Government and industry.

In the long run, the concept of biorefinery could be the ideal business model to ensure maximum efficiency, utilization of resources, waste management, and will be key to higher profitability.

A biorefinery integrates biomass conversion processes and equipment to produce a host of chemicals, fuels and power from biomass sources. The downstream activities could be diverse. For example, 40-50% of biomass consists of cellulose and other components such as lignin (15-20%) and hemi cellulose (20-30%).

The biomass that is fractionated to these components could be then further utilized. The cellulose can be converted to glucose and further to ethanol, xylitol, sorbitol, mannitol, lactic acid, glycolic acid, etc. Hemicelluloses, which could be processed to pentose sugars, can be converted to ethanol, xylose and xylitol. Lignin could be used for energy generation, as a biofuel additive or as an asphalt binder.

The utility of the biorefinery concept can be studied through two routes: Sugar based and thermo chemical. In the sugar platform, lignocelluloses or starchy biomass could be converted to fermentable sugars, which upon microbial fermentation could be converted only to bioethanol, but also to proteins, chemicals or biopolymers and energy. Through the thermo chemical platform, biomass could be gasified (syngas) using thermo chemical reaction to generate fuels and byproducts.

The wastes generated from food production and food processing such as wheat straw or waste oil could be utilized in the biorefinery for a host of profitable products.

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 art technology such as, molecular sieve technology for making anhydrous alcohol.
- Integration of distillery with sugar plant to have multiple choice of making sugar, or direct sugarcane to ethanol.

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, corn, 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.

15. RECOMMENDATIONS ON ETHANOL

- The country must move towards the use of ethanol as substitute for motor spirit. Though it is technically feasible to design and run automobiles on 100% ethanol, for the reason of its limited availability and compatibility with vehicles presently in use, blending of ethanol with motor spirit needs to make a very modest beginning to be raised to 10%, as capacity to produce anhydrous ethanol is built up.

- Ethanol may be manufactured using molasses as the raw material. The industry should be encouraged to supplement the production of alcohol from molasses by producing alcohol from sugarcane juice directly in areas where sugarcane is surplus. For this purpose restrictions on movement of molasses and putting up ethanol manufacturing plants may be removed.

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

- 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.

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

To reduce cost of production of ethanol, the following measures may be considered:

- Provision of incentives for new economic sized distilleries incorporating state of art technology such as, molecular sieve technology for making anhydrous alcohol.

- Integration of distillery with sugar plant to have multiple choice of making sugar, or direct sugarcane to ethanol.

- Economics of ethanol production from other feedstocks such as sugar beet, corn, potatoes, grain, straw etc should be studied. R&D should be carried out to develop technologies which are competitive in cost of production of ethanol from molasses.

16. REFERENCES

1. http://www.sciencedirect.com
2. http://www.google.co.in
3. http://www.e85.org
4. http://www.planningcommission.com
5. http://www.ethanolfacts.com
6. http://en.wikipedia.org/wiki/Ethanol
7. http://www.journeytoforever.org/ethanol.html
8. http://www.ethanolindia.net
9. http://www.caprockbiofuels.com/products.html
10. http://www.ieindia.org/pdf/86/hc16802.pdf
11. http://www.transportation.anl.gov/pdfs/TA/347.pdf
12. http://www.transportation.anl.gov/pdfs/TA/375.pdf
13. http://www.renewingindia.org/etheth.html
14. http://www.drivingethanol.org
15. http://www.eere.energy.gov/afdc/fuels/**ethanol**.html
16. http://www.autobloggreen.com/category/**ethanol**
17. M L Mathur and R P Sharma. 'Internal Combustion Engine (7th Edition)'. *Dhanpat Rai Pub/ications (P) Ltd,* New Delhi, 2001.
18. Wang, M., C. Saricks, and D. Santini, 1999b, *Effects of Fuel Ethanol Use on Fuel- Cycle Energy and Greenhouse Gas Emissions*, ANL/ESD-38, Center for Transportation Research, Argonne National Laboratory, Argonne, IL, Jan.
19. Wang, M.Q., C. Saricks, and M. Wu, 1997, *Fuel-Cycle Fossil Energy Use and Greenhouse Gas Emissions of Fuel Ethanol Produced from U.S. Midwest Corn*, prepared for Illinois Department of Commerce and Community Affairs, Center for Transportation Research, Argonne National Laboratory, Argonne, IL, Dec.
20. Wang, M.Q., 1996, *Development and Use of the GREET Model to Estimate Fuel - Cycle Energy Use and Emissions of Various Transportation Technologies and Fuels*, Center for Transportation Research, Argonne National Laboratory, ANL/ESD-31, March.
21. Weinblatt, H., T.S. Reddy, and A. Turhollow, 1982, *Energy and Precious Fuels Requirements of Fuel Alcohol Production*, prepared for U.S. Department of Energy, Washington, D.C., Dec.
22. Pimentel, D., 2003, "Ethanol Fuels: Energy Balance, Economics, and environmental Impacts Are Negative," *Natural Resources Research*, Vol. 12: 127-134.

23. S P Sriram and M B Reda 'A Performance Study of Iso-butanol, Methanol and Ethanol-gasoline Blends using a Single Cylinder Engine.' *West Virginia University,* SAE paper no- 932953, 1993, P 576.

24. S Beyerlein, J Steciak, D Mcilroy and D Blackketter. 'Catalytically Assisted Combustion of Aquanol in Demonstration Vehicles.' *University of Idaho,* USA, 2001, P 14.

25. F J Ferfecki and S C Sorenson. 'Performance of Ethanol Blends in Gasoline Engines.' *Transactions of the ASAE,* vol 26, no 1, 1983, P 38.

26. Office of Coal, Nuclear, Electric and Alternate Fuels (1994) *Alternatives to Transportation Fuels - An Overview, Energy Information Administration.*

27. Klasson, K.T., Elmore, B.B., Vega, J.L., Ackerson, M.D., Clausen, E.C. and Gaddy, J.L. (1990) Biological Production of Liquid and Gaseous Fuels from Synthesis Gas. *Applied Biochemistry and Bioengineering,* 24/25, 857-873.

28. Energy and Greenhouse Gas Balance of Biofuels for Europe - an Update (2002) *Concawe Report No. 2/02.*

29. Gover, M.P., Collings, S.A., Hitchcock, G.S., Moon, D.P. and Wilkins, G.T. (1996) *Alternative Road Transport Fuels – A Preliminary Life-cycle study for the UK,* ETSU R92, London, HMSO.

30. Levy, R.H.(1993) Les biocarburants. *Report to the French Government Based on Figures from the Commission consultative pour la production des carburants de substitution.*

31. Richards, I.R. (2000) Energy balances in the growth of oilseed rape for biodiesel and of wheat for bioethanol. *Report for the British Association of Bio Fuels and Oils (BABFO),* Ipswich, Levington Agriculture Ltd.

32. EU (1994) Application of biologically derived products as fuels or additives in combustion engines. *Publication No. EUR 15647 EN,* Directorate-General XII Science, Research and Development.

33. http://www.usda.gov/wps/portal/usdahome

34. Pimentel, D. (2001) The Limits of biomass utilization. In: *The Encyclopedia of Physical Science and Technology.* Academic Press., NY.

35. Searle, G.R. (1995) Octane Quality and Knock. In: *Motor Gasoline,* College of Petroleum and Energy Studies, Oxford, Royal Society of Chemistry publication.

36. CRC (1993) *Handbook of Chemistry and Physics.* 74th ed., CRC Press, Boca Raton, Fla.

37. Bechtold, R.L. (1997) Alternative Fuels Handbook. *SAE Press*, ISBN 0-7680-0052-1.

38. Mueller Associates, Inc. Status of Alcohol Fuels Utilization Technology for Highway Transportation: a 1986 Perspective, Spark-Ignition Engines (1985) *Report N°ORNL/Sub/85-22007/4*, National Technical Information Service,Springfield, Va.

39. Alternative Fuel in the Automotive Market (1995) *Concawe Report 2/95*.

40. Hammel-Smith, C., Fang J., Powders, M. and Aabakken J. (2002) Issues Associated with the Use of Higher Ethanol Blends (E17-E24). *NREL Technical Report NREL/TP-510-32206*.

41. Nersasian, A. (1980) The Vol. Increase of Fuel Handling Rubbers in Gasoline/Alcohol Blends. *SAE Paper No. 800789.*

42. Dunn, J.R. and Pfisterer, H.A. (1980) Resistance of NBR Based Fuel Hose Tube to Fuel-Alcohol Blends. *SAE Paper No. 800856*.

43. http://www.amesim.com