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Bioethanol: role and production technologies

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1. Introduction

Bioethanol (CH_3CH_2OH) is a liquid biofuel which can be produced from several different biomass feedstocks and conversion technologies. Its main physical and chemical characteristics, compared to diesel and gasoline fuels, are given in the Table 8.1.

Table 8.1. Main physical and chemical properties of bioethanol (Source: DG XII 1994; Blondy 2005; Mc Cormick et al. 2001).

	Diesel	**Ethanol**	**Gasoline**
Low Heating Value - LHV (MJ/kg)	42.7	26.9	43.7
Low Heating Value - LHV (MJ/l)	36.4	21.0	32.0
Viscosity (cSt)	2.5	-	-
Density (kg/m^3) @ 15°C	830 - 880	790	700 - 780
Cetane number	> 45	below 8	-
Octane number (MON)	-	96 - 106	79 - 98
Stoichiometric ratio	14.5	9	15.1
Vapour pressure @ 38°C (psi)	0.04	2.5	7-9
Flash point (°C)	55-65	13	-40
Boiling temperature (°C)	170-340	78	33-213
Vaporization heat (kJ/kg)	-	842	300
Auto-ignition temperature (°C)	230-315	366	300-371
Flammability limits (°C)	64-150	13-42	(-40)-(-18)
Flammability limits (% vol)	0.6-5.6	3.3-19.0	1.4-7.6

P. Ranalli (ed.), Improvement of Crop Plants for Industrial End Uses, 209–251.

Bioethanol can be used as chemical in industrial applications, as fuel for energy generation, or as food. It can be produced by synthesis or by fermentation processes, and be or not denatured. Ethanol can be used neat or blended with gasoline or diesel fuels. It is also used for the production of ETBE (Ethyl Tertiary Butyl Ether), an oxygenated fuel obtained by mixing ethanol and isobutylene and reacting them with heat over a catalyst. ETBE promotes clean gasoline combustion, thus improving air quality.

2. Bioethanol market

Biomass currently supply 4 % of EU energy needs from biomass (Biomass Action Plan, 2005). The increased use of biomass is expected to generate a wide range of benefits and advantages, such as a greater diversification of energy supply and reduction of energy imports, reduction of greenhouse gas emissions, and creation of new permanent jobs, especially in the rural areas.

Bioethanol is playing a very important role in the liquid fuel market: bioethanol worldwide production was greater than 18 Mt/y in 2003, sig-

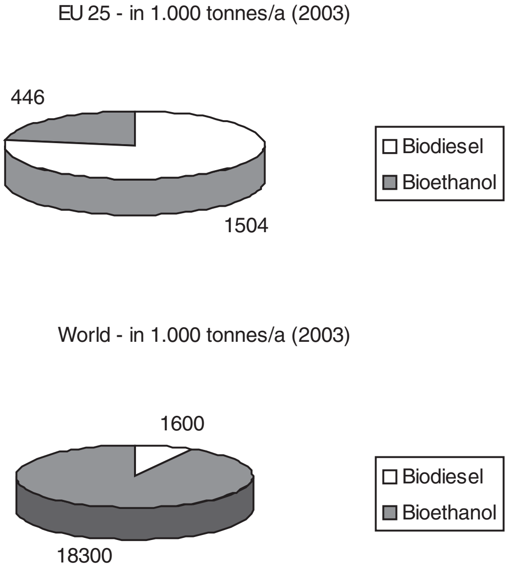


Fig. 8.1. EU-25 and World bioethanol production (from Biofuel Barometer, June 2004).

nificantly higher than biodiesel (approximately 1.6 Mt/y worldwide production). The characteristics of the biofuel sector however are very different in USA or EU-25, where biodiesel production was more than three times higher than bioethanol. In energy terms, at world level bioethanol represented more then 89 % of the energy in biofuels in 2003 (considering both bioethanol and biodiesel), while it was below 18 % in EU-25.

Bioethanol accounted for 2.8 % of motor gasoline worldwide, while biodiesel reached only 0.2 % (1 % in EU).

The most important bioethanol production Countries in the world are Brazil and US/Canada, as shown in Figure 8.2.

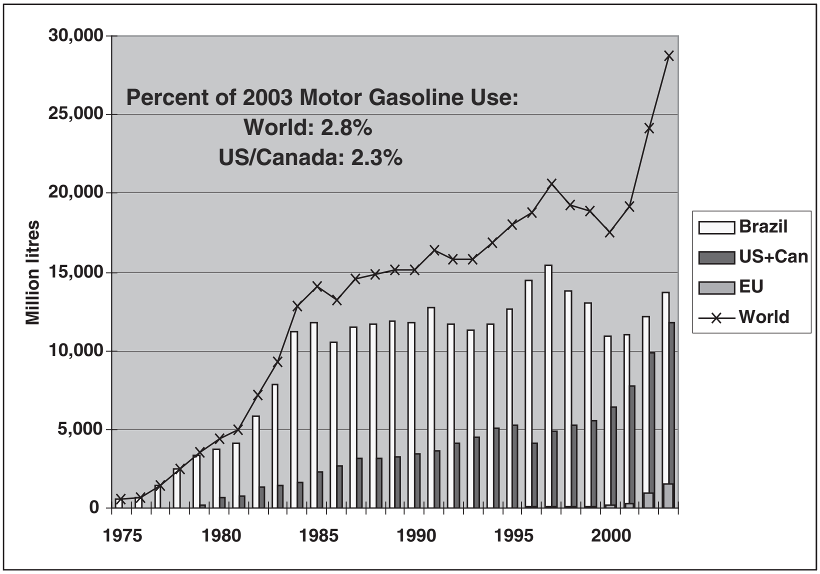


Fig. 8.2. World bioethanol production (Source: Fulton L. 2004; F.O. Licht).

Sugar cane is the main feedstock for bioethanol production in Brazil, while corn and sugar beet are the major resources in US and EU respectively.

The increased biofuel production in the EU (EU-25 considered only for 2004) is illustrated in Figure 8.3.

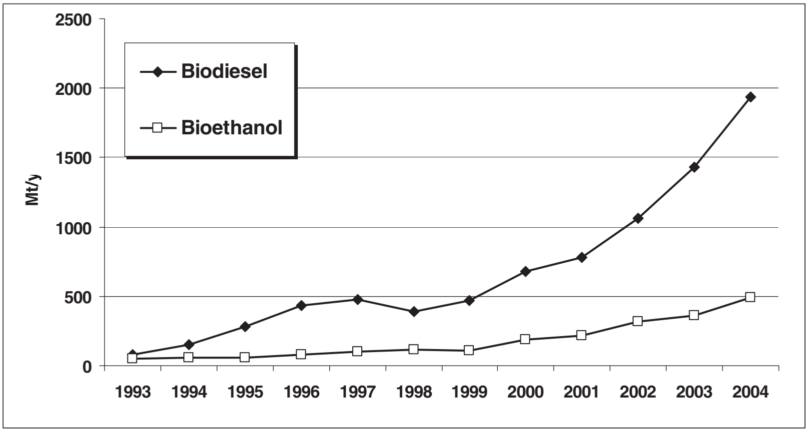


Fig 8.3. Bioethanol production in EU (from Eurobserv'ER, www.energies-renouvelables.org).

The distribution of bioethanol and ETBE production among the various EU Countries is reported in the next graph ("EC" means wine alcohol transformed into bioethanol as automotive fuel and marketed by the European Commission, in the framework of the common wine market management).

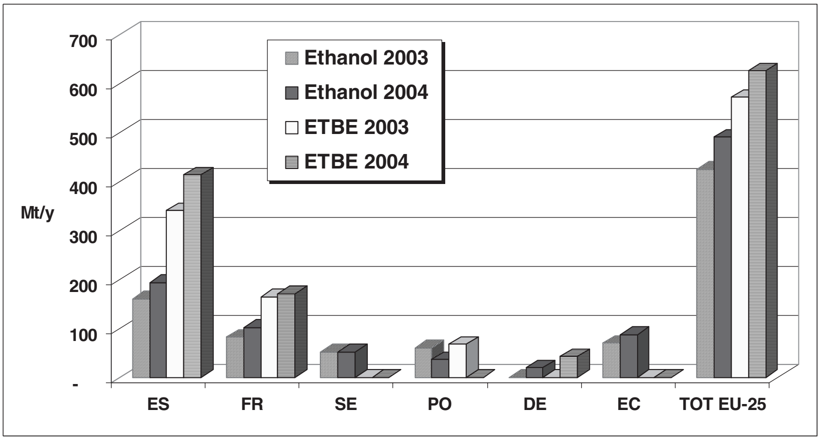


Fig. 8.4. Bioethanol and ETBE production (from Eurobserv'ER, www.energies-renouvelables.org).

In 2003, three EU Countries, ES, FR and PO, produced 96 % of EU bioethanol/ETBE: 5 EU Member States only were producing bioethanol/ETBE at that time.

In 2003, community legislation set ambitious targets for biofuels (Directive 2003/30/EC of 8 May 2003 on the promotion of the use of biofuels or other renewable fuels for transports, OJ L123 of 17 May 2003, page 42). This "Biofuel" Directive states that Member States must ensure by end of 2005 a 2% and by end 2010 a 5.75% minimum proportion of biofuels of

Table 8.2. Biofuel progress at National level (EU-25) towards Biofuel Directive (Source: Biomass Action Plan 2005).

Member State	Market share 2003	National indicative target for 2005	Targeted increase 2003-2005
AT	0.06%	2.5%	+2.44%
BE	0%	2%	+2%
CY	0%	1%	+1%
CZ	1.12%	3.7% (2006)	+ 1.72% (assuming linear path)
DK	0%	0%	+0%
EE	0%	2%	+2%
FI	0.1%	0.1%	+0%
FR	0.68%	2%	+1.32%
DE	1.18%	2%	+0.82%
GR	0%	0.7%	+0.7%
HU	0%	0.4-0.6%	+0.4-0.6%
IE	0%	0.06%	+0.06%
IT	0.5%	1%	+0,5%
LA	0.21%	2%	+1.79%
LI	0% (assumed)	2%	+2%
LU	0% (assumed)	not yet reported, assume 0%	not yet reported
MT	0.02%	0.3%	+0.28%
NL	0.03%	2% (2006)	0% (promotional measures will come into force from January 2006)
PL	0.49%	0.5%	+0.01%
PT	0%	2%	+2%
SK	0.14%	2%	+1.86%
SI	0% (assumed)	0.65%	+0.65%
ES	0.76%	2%	+1.24%
SV	1.32%	3%	+1.68%
UK	0.03%	0.3%	+0.27%
EU25	0.6%	1.4%	+0.8%

all gasoline and diesel fuels sold on their market. Biofuels can be made available as pure (neat) fuels, blended in mineral oil derivatives or liquids derived from biofuels such as ETBE.

A recent communication and assessment from the European Commission (Biomass Action Plan, 2005) concluded that the 2005 reference value will not be achieved: assuming that all Member States are able to meet the targets they have set, only a share of 1.4 % will be reached.

About 90 % of biofuel consumption is covered by domestic raw material, 10 % by imports. Approximately 1.8 million hectares (out of 97 million hectares in EU-25) were used for biofuel production in 2005. The observed trend shifted towards low blends and away from high blends or pure fuels, that were the main part in 2001. A report on Directives' implementation will be elaborated by the Commission in 2006.

However, various authors are expecting a fast growth of bioethanol in the EU, thanks to improved lignocellulosic-to-ethanol processes, currently at demonstration stage.

More recent market estimations for bioethanol in 2010 give the figures reported in the following table**.**

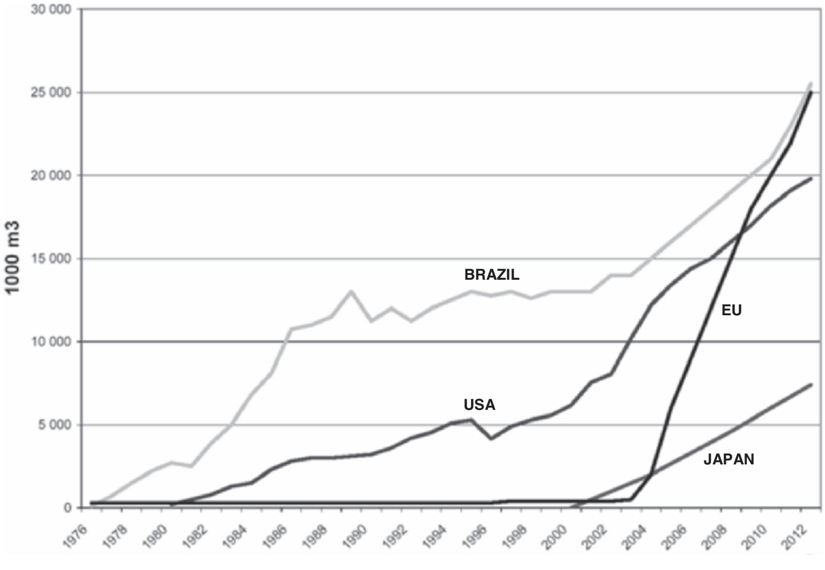


Fig 8.5. Future trends in bioethanol markets (source: Luiz Otavio Laydner, CFA Banco Pactual, Brazil).

Table 8.3. Bioethanol market estimations at 2010 (Piacente and Wolter 2005).

Country/region	Billion liters
Brazil	21
USA	18-20
Europe (EU)	9-14
Japan	6
South Korea	1.9
China	4.8
Eastern Europe	1-2
Canada	1-2
Total	**60-75**

As regards supporting measures to biofuels in the EU, two main instruments are adopted by Member States for promoting the use of liquid biofuels for transports:

- Tax exemption
- Biofuel obligation

Tax exemption can be implemented under the Article 16 of the Directive 2003/96/EC of 27/10/2003 restructuring the Community framework for the taxation of energy products and electricity (OJ L 283 of 31.10.2003 page 51), which allows Member States to apply exemption or reduced rate of taxation to biofuels and other products produced from biomass. Several EU Countries, such as Germany, France, Italy, Sweden, United Kingdom, received state aid approval to biofuel tax exemption or reduction measures. This approach, however, requires that tax reductions or exemptions are modified in line with changes in the price of raw materials, in order to avoid overcompensation. This represents a first risk of such measure: other possible problems due to adoption of tax exemption measures are related to investor uncertainty (the Energy Taxation Directive limits the duration of tax exemptions to 6 years only), and the adoption of quota-based approaches, that create risks of non-transparency, arbitrary allocation, and increased market concentration (Biomass Action Plan 2005).

Biofuels obligations instead require that fuel supply companies incorporate a given percentage of biofuels in the fuel they place on the national market. It is a simpler and effective way to promote the introduction of higher amounts of biofuels, as the problem of oil dependence is addressed to the sector where it is originated. Moreover, these measures are not subject to time limits and establish sound and stable frameworks, which are basic requirements for investors.

A further technical barrier to biofuels is represented by the Directive 98/70/EC of 13 October 1998 relating to the quality of petrol and diesel fuels (OJ L 350, 28.12.1998), as amended by Directive 2003/17/EC of 3 March 2003 (OJ L 76, 22.3.2003). By limiting the vapour pressure of petrol, limits are established on ethanol, ether and other oxygenates content. The Commission is reviewing the fuel quality directive.

3. Production technologies

Bioethanol can be produced from (i) sugar or starch crops (as sugar cane, sugar beet, corn and wheat), and from (ii) lignocellulosic biomass. While production technologies are well known and developed for microbiological fermentation of sugar and starch crops, bioethanol from lignocellulosic via acid/enzymatic hydrolysis or thermochemical processes is not yet fully developed at industrial scale (Hamelink et al. 2005).

Table 8.4. Typical bioethanol yields from different feedstocks (Schieder 2005).

Crop	Expected bioethanol yield (lt/ha/y)
Grain	1,800 – 2,500
Corn	up to 3,800
Sugar cane	up to 5,600
Sugar beet	up to 7,000
Lignocellulosic biomass	up to 9,000

The production of bioethanol from lignocellulosic biomass represents a very promising alternative able to significantly increase feedstock availability and to reduce feedstock costs, but requires the industrialization of innovative processes and technologies currently at pilot/demonstration stage. Various conversion processes can be employed to produce bioethanol from lignocellulosic biomass.

Bioethanol from sugar/starch crops through traditional production technologies is included in the group of “1st Generation Biofuels” (together with Pure Plant Oil and Biodiesel obtained from Vegetable Oil estherification), while bioethanol from lignocellulosic biomass is considered as a “2nd Generation Biofuel”.

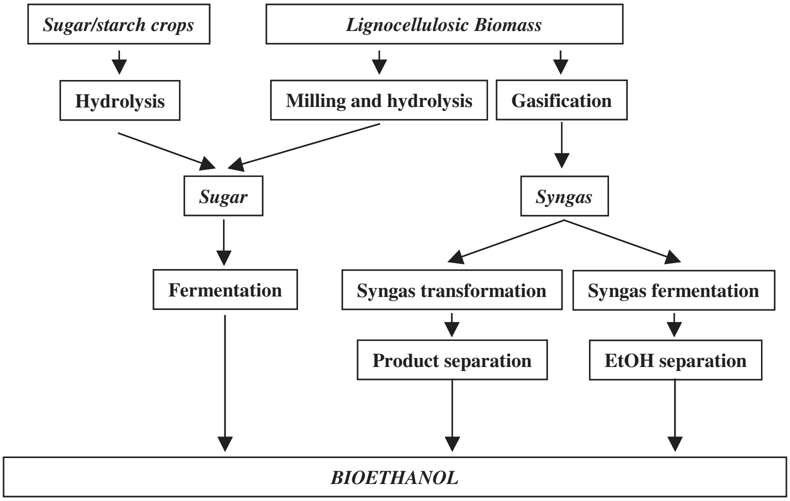


Fig. 8.6. Main pathways for bioethanol production (modified from Hamelinck et al. 2005; Spath and Dayton 2003).

3.1 Bioethanol from sugar or starch crops

Bioethanol production processes from sugar or starch crops are the most traditional and developed pathways. Fermentation is performed by microorganisms (yeasts, bacteria, fungi) in the absence of oxygen according to the following main reactions:

$$C_6H_{12}O_6 \rightarrow 2\,C_2H_5OH + 2\,CO_2$$

The theoretical maximum yield of ethanol is 0.5111 kg of bioethanol and 0.4889 kg of CO_2 per kg of sugar. *Saccharomices cerevisiae* is the typical yeast for hexose sugars fermentation.

The fermentation of 5-carbon sugars (pentoses, such as arabinose and xylose) derived from lignocellulosic biomass is also possible (see next chapters), but not with ordinary strains of yeasts, such as *Saccharomices c.*

$$3\,C_5H_{10}O_5 \rightarrow 5\,C_2H_5OH + 5\,CO_2$$

3.1.1 Bioethanol from sugar cane and sugar beet

Sugar Cane. Sugar cane is initially milled to extract sugars, which amount corresponds to 12-17 % (90% saccharose and 10 % glucose): the extraction efficiency is around 95 %. The remaining solid product is the bagasse which consists of lignocellulosic material.

After extraction, which is different according to the type of distillery (producing ethanol only, or ethanol and sugar), the sugar content has to be adjusted to 14-18% to achieve optimum fermentation efficiency of yeast, the most common being *Saccharomyces c.*, at temperatures around 33-35 °C and cell density of 8-17 % v/v (Zimbardi et al. 2002). Fermentation is interrupted at ethanol concentration of approximately 10 %: then, the broth is sent to the distillation and rectification phase, which product is an azeotropic solution of 95 % v/v ethanol. Further concentration to absolute ethanol (high grade or anhydrous ethanol) is finally achieved by molecular sieves or distillation using benzene or cyclohexane (azeotropic distillation).

The co-product of the distillation phase is the “vinasse”, which amount is 10-15 time the ethanol production, and that is sent to the cane fields for fertilisation and irrigation purposes.

The solid lignocellulosic residue, the bagasse, can be used for cogeneration (simultaneous generation of electricity and heat), so to provide the process with the necessary energy input. This also results in a further reduction of greenhouse gas emission, as the bagasse is biomass, i.e. a renewable fuel.

Sugar Beet. Sugar beet is also a typical feedstock for bioethanol production. Differently from sugar cane, which is first crushed and squeezed to mechanically extract the juice, the sugar beet slices are initially treated by contact with water or beet juice at 70-80°C. Temperature is a critical parameter for the diffusion process as it has to break down the proteins in the cell walls. The juice is fermented by yeast (as *Saccharomyces c.*) or bacteria: the use of bacteria is however still at batch level. The pulp, once drained, is used as animal feed or sold to the chemical or pharmaceutical industry (substrate for the production of citric acid and its esters).

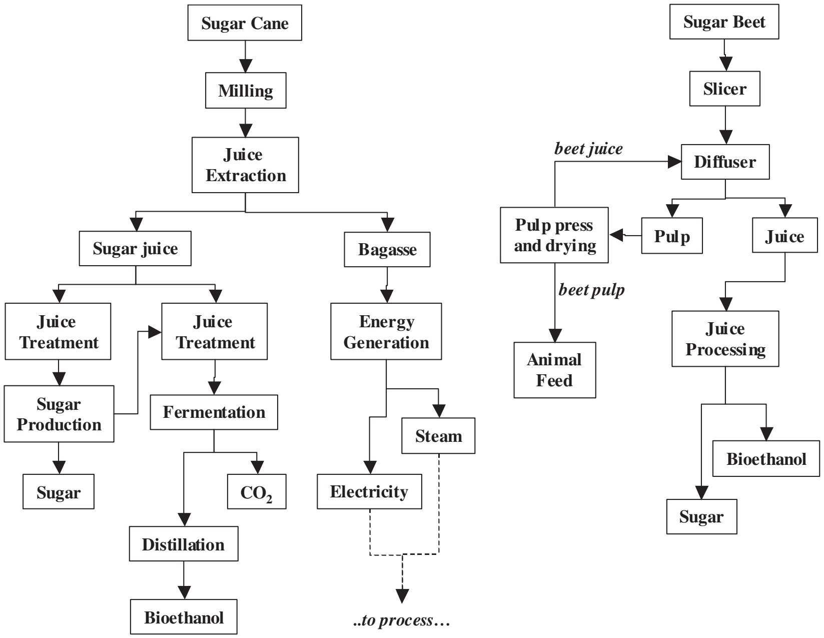


Fig. 8.7. Main processes for bioethanol production from sugar cane and sugar beet (Zimbardi et al. 2002).

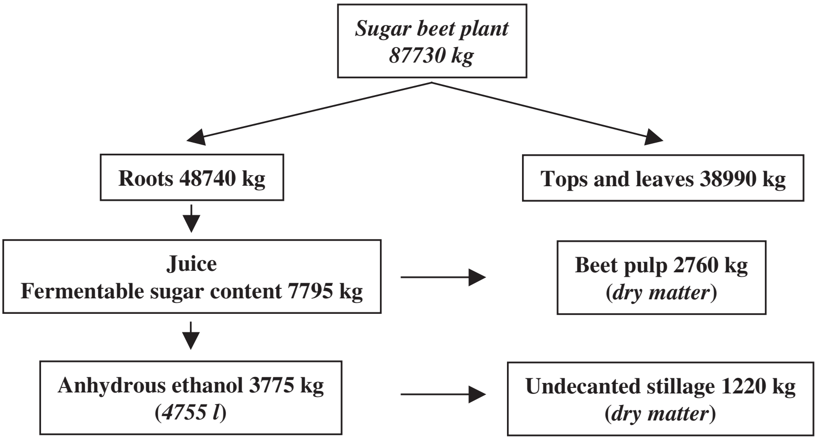


Fig. 8.8. Mass balance of sugar beet to ethanol (source: DGXII 1994).

3.1.2 Bioethanol from starch crops

Starch crops (as corn, wheat, barley, oat, etc) are also other typical feedstocks for bioethanol production through traditional technologies. Starch is a polymer constituted by glucose molecules (monomers) C-O bonded together in different stereoisomerisms (α or β bonds).

The most used milling processes in starch-to-bioethanol production plants are (i) wet milling or (ii) dry milling (Zimbardi et al. 2002).

- In the wet process (DGXII 1994), after backing and saccharification, a glucose solution is obtained (starch process)
- In the dry process, a rude home grinding of the grains is carried out, followed by a backing-liquefaction in hot water.

Wet milling. The traditional wet milling process starts with softening the grains (steeping) in a 0.1-0.2 % SO_2 water solution at 50°C for 1-2 days. The softened grains are then milled: oil, protein and starch-rich are separated, while the concentrated (50 % v/v) steep water becomes Corn Steep Liquor and the remaining liquid is used for adjusting the pH (4-4.5) of the saccharification process, supply nutrients to the fermentation process, and make the fermentation broth sufficiently diluted to make it compatible with the yeasts.

The gelatinised starch fraction, after addition of NaOH at 70°C (so that pH becomes 5.5-6.2), is liquefied (DGXII, 1994) by adding the α-amylase enzyme (stabilised by adding $CaCl_2$). Dextrins are produced during this phase. Maltose is a disaccharide composed by linking two glucose molecules (monosaccharides): it is the typical product of starch digestion. Other disaccharides are sucrose (glucose + fructose: it is the common table sugar) and lactose (glucose + galactose: the main sugar in milk). Glucose, galactose and fructose are 3 structural isomer sugars.

Starch hydrolysis (liquefaction)

$$\underset{\textit{starch}}{2\,n\,C_6H_{12}O_{11}} + \underset{\textit{water}}{n\,H_2O} \xrightarrow[(\alpha\text{-amylase})]{} \underset{\textit{maltose}}{n\,C_{12}H_{22}O_{11}}$$

Dextrins are then converted into glucose by the glucoamylase enzyme (saccharification).

$$\underset{\textit{maltose}}{C_{12}H_{22}O_{11}} + \underset{\textit{water}}{H_2O} \xrightarrow[(\text{glucoamylase})]{} \underset{\textit{glucose}}{2\,C_6H_{12}O_6}$$

$$\underset{\textit{saccharose}}{C_{12}H_{22}O_{11}} + \underset{\textit{water}}{H_2O} \xrightarrow[(\text{invertase})]{} \underset{\textit{glucose}}{C_6H_{12}O_6} + \underset{\textit{fructose}}{C_6H_{12}O_6}$$

Finally, fermentation (i.e. conversion of monosaccharides into ethanol and CO_2) is carried out by yeast (again, the most used is *Saccharomyces c.*) at lower temperature (~29-35°C). Bioethanol and CO_2 can then be recovered for various applications (for the food industry, for dry ice making, etc).

$$\underset{\textit{glucose, fructose}}{C_6H_{12}O_6} \rightarrow \underset{\textit{bioethanol}}{2\,C_2H_5OH} + \underset{\textit{carbon dioxide}}{2\,CO_2}$$

450 g of yeasts must be added per 1000 l of mash, corresponding to about 5-10 mill.cells per ml (DG XII, 1994). The sugar concentration should be 16-24 % to achieve a bioethanol production 8-12 %, with a pH of 4.5 – 5. Theoretical yields are 0.568 kg EtOH / kg starch, and 0.538 kg EtOH / kg saccharose.

Fermentation can be performed as a batch or a continuous process, depending on the plant. Above 8-10 % v/v concentration yeasts cannot survive anymore: the liquor is then distilled to 95 % v/v concentration. Distillation is performed in column: it is a very energy-demanding part of the entire process. Recently (Grassi et al. 2005), low-cost crystal hydrated compounds have been proposed to achieve a significant reduction of energy demand for bioethanol separation.

Depending on plant type, before distillation yeasts can be recovered by centrifugation.

Anhydrous ethanol (absolute ethanol, 99 % v/v) can finally be obtained through dehydratation by molecular sieves or other similar processes.

In case gluten is not recovered (Modified Wet Milling process), the “stillage” which remains after fermentation (10-15 times the ethanol volume) is used to produced Distillers’ Dried Grain (DDG) and Distillers’ Dried Soluble (DDS), that have a market as animal feed thanks to their nutritional value (proteins, fibre, fats).

Dry milling. Grains are here directly milled, without pre-treatment: after water addition and heating, the slurry is then hydrolysed, fermented and distilled as in the wet milling process. While wet milling assure the production of purer starch and higher value co-products, dry milling offer some advantages such as lower power demand, lower investment costs, and higher bioethanol production.

A summary of the processes described above is reported in the next tables for the corn-to-ethanol process.

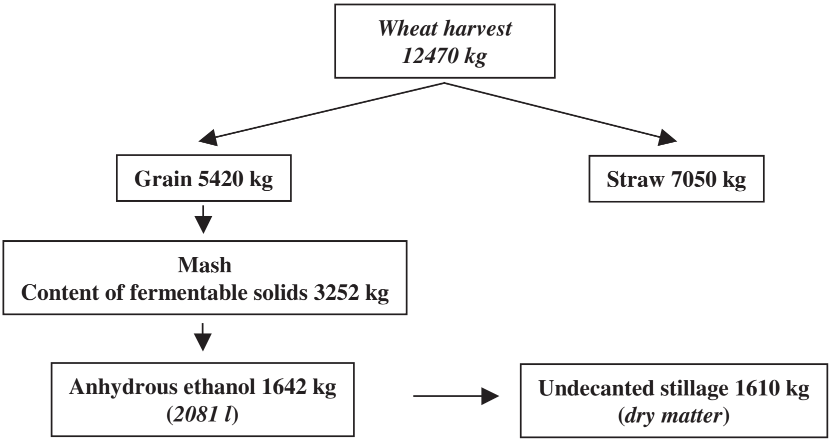


Fig. 8.9. Mass balance of wheat to ethanol (source: DGXII 1994).

Table 8.5. Main products from wet and dry milling corn-to-ethanol processes.

	Wet Milling Processes	Dry Milling Process	Applications
Bioethanol	Yes	Yes	Fuel, chemical
CO_2	Yes, but not always recovered	Yes, but not always recovered	Food industry, dry ice
Corn Oil	Yes	No	Human consumption
Gluten Feed	Yes	No	Animal feed (protein content: ~20 % wt dry basis)
Gluten Meal	Yes	No	Animal feed (protein content: ~60 % wt dry basis)
Corn Steep Liquor (CSL)	Yes	No	Animal feed (protein content: ~50 % wt dry basis)
DDG-DDS (DDGS)	No	Yes	Animal feed

3.2 Bioethanol from lignocellulosic biomass

Lignocellulosic biomass today represents the most interesting and promising feedstock for bioethanol production. It is abundant and widely available (either from woody or herbaceous crops, various kind of wastes, etc).

The main constituents of lignocellulosic biomass are cellulose, hemicellulose, lignin, extractives and ash (Van Loo and Koppejan 2002; Bryden 1998, Zimbardi et al. 2002).

- Cellulose $(C_6H_{10}O_5)_n$ is a high molecular weight linear polymer, consisting of chains of bonded glucose monomers $(C_6H_{12}O_6)$. Fibers walls mainly consist of cellulose, which accounts for 30-60 % of wood (lignocellulosic) dry weight. It is a rigid, ordered compact polymer, and resistant to chemical attack.
- Hemicellulose is a short branched polymer similar to cellulose, but built from several sugars that encase cellulose fibres. It consists of short, highly branched, chains of sugars. It contains five-carbon sugars (usually D-xylose and L-arabinose) and six-carbon sugars (D-galactose, D-glucose and D-mannose) and uronic acid. It corresponds to 10-40 % of wood dry weight. Part of hemicellulose is composed by 5-carbon sugar (as xylose and arabinose), the remaining by 6-carbon sugars (glucose, mannose, galactose). The amount of 6-carbon sugars is higher in softwood, while hardwood contains more 5-carbon (xylose) sugars. Hemicellulose is amorphous and relatively easy to hydrolyze to its constituent sugars.
- Lignin is a three-dimensional non-sugar polymer which strength the wood fibers. It accounts for 10-30 % of wood (lignocellulosic) dry weight.
- Extractives are non structural components (terpenes, fats and waxes, phenolics) that give the biomass a wide range of properties as taste, odor, color, etc. They can be "extracted" by using solvents such as water, benzene or alcohol. Their amount is up to 5-10 % dry-weight.
- Ashes are inorganic salts contained in biomass.

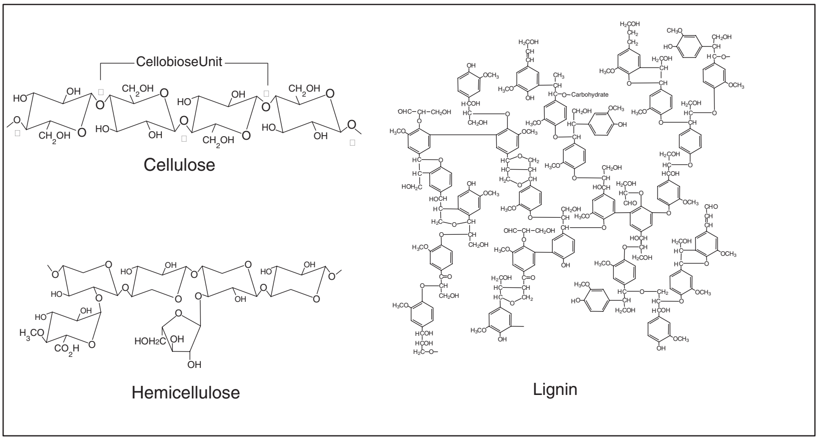


Fig. 8.10. Cellulose, hemicellulose and hypothesized lignin chemical structure (reprinted from Zimbardi et al. 2002).

Table 8.5. Composition of various types of biomasses (source: Sun and Cheng 2002).

Lignocellulosic materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwoods stems	40–55	24–40	18–25
Softwood stems	45–50	25–35	25–35
Nut shells	25–30	25–30	30–40
Corn cobs	45	35	15
Grasses	25–40	35–50	10–30
Paper	85–99	0	0–15
Wheat straw	30	50	15
Sorted refuse	60	20	20
Leaves	15–20	80–85	0
Cotton seed hairs	80–95	5–20	0
Newspaper	40–55	25–40	18–30
Waste papers from chemical pulps	60–70	10–0	5–10
Primary wastewater solids	8–15	Not available	24–29
Coastal Bermuda grass	25	35.7	6.4
Switch grass	45	31.4	12.0

Table 8.6. Typical lignocellulosic biomass composition (source: Hamelinck et al. 2005).

Feedstock	**Hard wood**			**Softwood**	**Grass**
	Black locust	**Hybrid Poplar**	**Eucalyptus**	**Pine**	**Switchgrass**
Cellulose	41.61	44.70	49.50	44.55	31.98
Glucan 6C	*41.61*	*44.70*	*49.50*	*44.55*	*31.98*
Hemicellulose	17.66	18.55	13.07	21.90	25.19
Xylan 5C	*13.86*	*14.56*	*10.73*	*6.30*	*21.09*
Arabinan 5C	*0.94*	*0.82*	*0.31*	*1.60*	*2.84*
Galactan 6C	*0.93*	*0.97*	*0.76*	*2.56*	*0.95*
Mannan 6C	*1.92*	*2.20*	*1.27*	*11.43*	*0.30*
Lignin	26.70	26.44	27.71	27.67	18.13
Ash	2.15	1.71	1.26	0.32	5.95
Acids	4.57	1.48	4.19	2.67	1.21
Extractives	7.31	7.12	4.27	2.88	17.54
Heating value (GJ_{HHV}/t_{DM})	19.5	19.6	19.5	19.6	18.6

Various demonstration projects are currently ongoing on ethanol production from lignocellulosic biomass (Biomass Action Plan, 2005). A first 4 million liters plant was realised and operated by Iogen in Ottawa (Canada), followed by a 150,000 liters facility in Sweden by ETEK. A third 5 million liter unit is under construction in Spain by Abengoa (Zimbardi *et al*. 2002).

3.2.1 Hydrolysis

The hydrolysis process consists of breaking the carbohydrates that constitute the biomass into monomeric sugars, which can then be fermented by microorganisms to produce bioethanol. Two main hydrolysis methods are used:

- Chemical hydrolysis: it can be carried out as (i) Concentrated Acid Hydrolysis or (ii) Dilute Acid Hydrolysis
- Enzimatic hydrolysis

Concentrated Acid Hydrolysis. The process (Zimbardi et al. 2002) starts with hemicellulose hydrolysis in a heated 10 % sulphuric acid solution (two hours) and lignin removal. 5-carbon and 6-carbon solubilised sugars are then separated from the solid residue, which mainly consists of cellulose and lignin, and sent, after neutralization, to the fermentation unit.

After hemicellulose hydrolysis and lignin recovery, a second stage of cellulose hydrolysis is therefore performed: cellulose is converted to sugars according to the following reaction (Hamelinck et al. 2005): $(C_6H_{10}O_5)n + nH_2O \rightarrow nC_6H_{12}O_6$.

The solid residue is mixed with a 30 % acid solution, which is then further concentrated up to 70 % by heating. The crystalline structure of the cellulose is here broken. Suspension in hot water into a hydrolytic tank is afterwards implemented, in which 10 % acid concentration media is realised, and heating at 100°C for two hours is carried out.

The solution, which contains 10 % acid and 10 % glucose after the cellulose has been completely hydrolysed, is neutralised by adding Calcium hydroxide $Ca(OH)_2$: the hydrated gypsum ($CaSO_4$ $2H_2O$) which is formed precipitates and is removed, and sugars are finally conveyed to the fermentation plant. The use of the filtered gypsum is an important aspect of the process, especially as regards its economical performances: it could be used in agriculture (as a soil conditioner) or represent a waste to be disposed of. Gypsum production range from 0.02 kg/kg feedstock to 0.6-0.9 kg/kg feedstock, depending on the acid recycling strategy.

The efficiency of this process ranges from 90-96 % for hemicellulose to xylose (5-carbon sugar) to 79-90 % for cellulose to glucose (6-carbon), depending on feedstock type. The process therefore guarantees very high total yields, in the order of 90 %.

Variations of this process have also been developed by various Companies, such as Arkenol.

The separation of the acid for recycling is a critical aspect to improve the process economics.

Lignin is a solid residue of the process, which remains available for various uses, as heat and power generation.

Dilute Acid Hydrolysis. This process dates back to 1800 (first commercial plant in 1898). The dilute acid hydrolysis process first hydrolyses the hemicellulose in mild process conditions (typical process parameters: 0.5-0.7 % H_2SO_4 at 160-190°C) to recover the 5-carbon sugars. The reaction has to be controlled under mild conditions in order to avoid sugar degradation: this not only reduces yields but also causes the formation of inhibitors of the fermentation process (furfurals and other by-products).

Cellulose in the remaining solids is then hydrolysed in a 0.4-2 % H_2SO_4 solution at 200-215°C. As in concentrated acid hydrolysis, solid residues (lignin and residual cellulose) can be used for heat and power generation, while the sugar-rich liquid is sent to fermentation. Ethanol yield (Zimbardi et al. 2002; Hamelinck 2005) is in the range of 74 to 89 % of the theoretical value (89 % for mannose, 82 % for galactose, and only 50 % for glucose).

The reactor design is of particular importance in dilute acid hydrolysis processes, in order to reduce sugar degradation (and so the formation of yeast inhibitors, as furfural), maximise sugar yields and improve the economics of the process.

Enzymatic Hydrolysis. Enzymatic processes, in which selected cellulase enzymes break the polymeric chain of the cellulose and hemicellulose leaving the monomeric sugars available for fermentation, perform a higher hydrolysis yields than chemical processes. However, a barrier for these processes is represented by enzyme costs, that accounts for approximately 40 % of total costs (Zimbardi et al. 2002).

As only 20 % of the biomass pore volume can be reached by the large cellulase enzymes molecules, biomass pre-treatment becomes an essential step in enzymatic hydrolysis processes. In fact, biomass pre-treatment is of primary importance to improve cellulose hydrolysis and therefore increase sugar yields, which are above 90 % with pre-treatment while remain below 20% without pre-treatment. Pre-treatment aims at increasing the surface accessible to enzymes by destroying the cell structure, breaking the ligninhemicellulose shealth around cellulose and reducing the cellulose polymerisation and crystallinity.

Biomass (Hamelinck et al. 2005) has first to be cleaned (if necessary) and sized (from few centimetres to 1-3 mm).

A cost-efficient pre-treatment stage is a key to the success of the cellulose-to-ethanol process, and a significant R&D effort is today devoted to this area (Ballerini and Monot 2005). Pre-treatment has to be optimised so to increase the yield of cellulose hydrolysis by reducing residence time (i.e. reduced capital costs) as well as enzyme consumption (i.e. reduced operating costs). Moreover, mass losses should be minimised in terms of non fermentable products and fermentation inhibitors.

A list of possible biomass pre-treatment techniques is summarised in the following table.

Table 8.7. Biomass pre-treatments for enzymatic hydrolysis processes (Zimbardi et al. 2002; Hamelinck et al. 2005; Ballerini and Monot 2005).

Biomass pre-treatment				
Method	***Type of process***	***Examples***	***Xylose yield***	***Downstream enzymatic effect (%)***
Physical	Mechanical	Milling Grinding	-	-
	Non mechanical	Irradiation High pressure steaming Liquid Hot Water	- - 88-98 %	- - > 90%
Chemical	Alkali	Dilute NaOH	60-75 %	55
	Oxidative	Oxidative treatment in alcaline peroxide medium	60-75%	50%
	Dilute acid	Dilute sulphuric acid	75-90 %	<85
Physical or Combined Physical-Chemical	Steam explosion (uncatalysed) Steam explosion (catalysed)		45-65 %	90
	Ammonia Fiber Explosion (AFEX) Carbon Dioxide Explosion		-	50-90 (2 steps) 75 (2 steps)
Biological	Enzymes produced by fungi (lab scale)		-	-

Table 8.8. Examples of pre-treatment processes for hydrolysis (Ballerini and Monot 2005).

Physico-chemical	Steam explosion	Iotech, Abengoa, BCI, Sun Opta, CIEMAT, ENEA
	Steam explosion in acid conditions	ASCAF (IFP), Iogen, Un.Lund, ENEA
	Hydrothermal process	Elsam/Sicco
	Wet oxidation	Risoe, Biocentrum-DTU
Chemical	Dilute acid	NREL, ETEK

Energy demand for biomass comminution is indicated in the tale below.

Table 8.9. Energy requirement for mechanical comminution (reprinted from: Cadoche and Lòpez 1989).

Lignocellulosic materials	Final size (mm)	Energy consumption (kWh/ton)	
		Knife mill	Hammer mill
Hardwood	1.60	1.30	130
	2.54	80	120
	3.2	50	115
	6.35	25	95
Straw	1.60	7.5	42
	2.54	6.4	29
Corn stover	1.60	NA[a]	14
	3.20	20	9.6
	6.35	15	NA[a]
	9.5	3.2	NA[a]

[a] NA - not available

Among these processes, steam explosion is probably the most used pretreatment technique, which can be either uncatalysed (if steam only is used) or catalysed (if chemicals are used). Steam explosion (Zimbardi et al. 2002) consists of feeding a high-pressure reactor with chopped biomass and saturated water steam: biomass is then expelled through a valve. During this process, which can be operated in a batch or continuous mode, the biomass is “exploded” and its main constituents (cellulose, hemicellulose and lignin) separated by the sudden decompression to atmospheric pressure. Steaming times are of the order of seconds/minutes, while typical process parameters are 1.5-4 MPa and 180-230°C. The performances of the steam explosion process depend on the severity of the operating conditions, i.e. temperature and pressure: however, an excessive increase in these parameters promotes the formation of inhibitors of fermentation. Reported xylose-sugars yields are in the range of 45 % - 65 % (Hamelinck et al. 2005). Acid catalysts (as SO_2, which oxidizes at H_2SO_4) can be used for improving the steam explosion process and increase the overall yield. Steam explosion can be carried out in batch or continuous plants.

Examples of steam explosion plants exist in EU and USA.

Table 8.10. Selected steam explosion plants in EU and USA.

Owner	Location	Capacity	Type	Status
CIEMAT	Spain	200 kg/h	Batch	Existing
Lund University	Sweden	Lab scale	Batch	Existing
ENEA	Italy	300 kg/h		Existing
Stake techn.	Virginia, USA	Lab scale	Bach	Existing
ASCAF	France	2-4 t/h	Continuous	Existing
Abengoa	Babilafuente (Salamanca) Spain	70 t/d	Continuous, Sun-Opta techn.	Contract signed

Liquid Hot Water (LHW) is a further interesting pre-treatment technique for biomass-to-ethanol hydrolysis processes (Hamelinck et al. 2005): it uses compressed hot water, above saturation point, which hydrolyse the hemicellulose and perform a high xylose recovery (88-98 %) without acid or chemical catalyst. LHW is still at laboratory scale.

The main advantages offered by enzymatic hydrolysis are related to the very mild process conditions, that give high yields, and the reduced capital and maintenance costs (reactor materials), as corrosion problems are reduced (Hamelinck et al. 2005).

Since intermediate products (cellobiose and glucose) act as inhibitors of cellulase activity, these have to be removed (by ultrafiltration or by simultaneous fermentation in the same reactor) or extra-enzymes have to be supplied to the reactor. Cellulase represents a significant cost of the enzymatic hydrolysis process, while the main consumable for dilute and concentrated acid hydrolysis is H_2SO_4.

Summarising and comparing (Hamelinck et al. 2005) the three main hydrolysis processes, i.e. dilute acid, concentrated acid, and enzymatic hydrolysis, it can be concluded that:

- the glucose yield vary significantly, from 50-70 % (dilute acid) to 90 % (concentrated acid) to 75 % (enzymatic). Enzymatic hydrolysis promise yields up to 95 % in the future.
- Operating temperatures and residence times are also very different: from 215°C and few minutes (3 min) of dilute acid, to 40°C and 2-6 h of concentrated acid, to 50°C and 1.5 days of enzymatic hydrolysis.

A considerable R&D effort is devoted to process integration. The following main options are today under investigation and development:

- Separate (or Sequential) Hydrolysis and Fermentation, SHF
- Simultaneous Saccharification and Fermentation, SSF
- Simultaneous Saccharification and Co-Fermentation, SSCF
- Consolidated Bio Processing, CBP

Separate (or Sequential) Hydrolysis and Fermentation, SHF. This technique first performs the hydrolysis step converting cellulose into C6 sugars, and then the fermentation step to produce bioethanol. While the positive aspect of this sequential approach is the ability to guarantee optimal process conditions for enzyme and microorganisms (pH, T, oxygen), two distinct reactors are needed, and the inhibition activity of glucose on microorganisms must be taken into account.

Simultaneous Saccharification and Fermentation, SSF. Saccharification and fermentation are carried out simultaneously in a single reactor, thus allowing for cost saving and reduction of inhibitors, increasing hydrolysis rate. Obviously, the optimisation of process conditions for both enzymens and microorganisms at the same time is the critical issue of this solution.

Simultaneous Saccharification and Co-Fermentation, SSCF. Continuous alcoholic co-fermentation of hexose and pentose sugars in a coimmobilized system configuration containing cultures of *S.cerevisiae* and *C.shehatae*.

Consolidated Bio Processing, CBP. All enzymes and bioethanol are produced in a single reactor by a single microorganisms community.

Process costs are expected to significantly decrease from SSF (10.5 €/GJ) to SSCF (9.8 €/GJ) to CPB (4.5 €/GJ). A detailed description of these processes is available in literature (as Hamelinck et al. 2005; Zimbardi et al. 2002; Zacchi 2005).

3.2.2 Thermochemical conversion processes

A different approach to bioethanol production from lignocellulosic biomass is represented by the thermochemical path, which consists of biomass gasification followed by catalysed reaction or fermentation. In fact, in both cases, the first stage of the process is the production of a low calorific value gas, which is then cleaned, and either catalytically synthesized to the final product or fermented.

Three main steps characterise of the first method (Caraballo 2005):

1. *biomass gasification*, in which syngas is produced (and cleaned) from solid biomass. Gasification is the thermochemical conversion of biomass at high temperature (~ 800°C), in the presence of an oxidising agent (as air, steam or oxygen), into a low calorific value raw gas, steam and tar.
2. *syngas transformation*, where gas composition is adjusted by catalytic synthesis processes
3. *separation of products*

Main advantage of the thermochemical processes is the capability to use the entire biomass as well as different feedstocks, but gas cleaning is still a major issue to make this solution sufficiently efficient and economically viable. The products of these processes are also called BTL (Biomass To Liquid) fuels, as liquid fuels are produced from solid (lignocellulosic) biomass.

The synthesis of ethanol and other alcohols from syngas is a very important part of the process. In particular, ethanol synthesis is carried out similarly to Fisher Tropsch or methanol production, but with lower results and therefore overall efficiency. In order to increase bioethanol yield, more R&D effort has to be directed to the catalyst field.

Table 8.11. Main reactions for ethanol and higher alcohol synthesis (Caraballo 2005).

Methanol synthesis	$CO + 2\ H_2 \rightarrow CH_3OH$
Water shift reaction	$CO + H_2O \rightarrow CO_2 + H_2$
Ethanol synthesis	$2\ CO + 4\ H_2 \rightarrow C_2H_5OH + H_2O$
Higher alcohol synthesis	$n\ CO + 2n\ H_2 \rightarrow C_nH_{(2n+1)}OH + (n-1)\ H_2O$
Olefins formation	$n\ CO + 2n\ H_2 \rightarrow C_nH_{2n}OH + n\ H_2O$
Paraffins formation	$n\ CO + 2\ (n+1)\ H_2 \rightarrow C_nH_{(2n+2)}OH + n\ H_2O$
Synthesis of other products	DME, methyl ester, acetic acid, etc
Product homologation	

The H_2/CO ratio has to be optimised to maximise the product yield (approximately 1 for ethanol synthesis), as well as process parameters such as pressure (typically > 50 bar), temperature (~ 240-350°C), and the type of catalyst.

Another possible option for bioethanol production via mixed thermochemical-biological path is represented by syngas fermentation (Spath and Dayton 2003). Similarly to the above reported BTL route, the initial stage is again biomass gasification: the CO and H_2 rich syngas is then fermented to bioethanol, which is recovered from the broth with processes similar to those typical of the corn industry, as distillation and adsorption. The cell mass can be recycled to the gasifier, while it is not approved as animal feed.

As for the previous case, a significant advantage offered by the adoption of a first gasification stage is that a wide range of low-cost biomass feedstocks can be used, thus increasing biofuel production potential and reducing feedstock costs.

The fermentation reactor can be a simple gas-sparged reactor (either batch or continuously operated), but other designs (as two-stage reactors) with better performances have been studied and proposed (Klasson et al. 1991). Weak aspects of the gas-sparged reactor are low volumetric productivity, low gas conversion and very diluted bioethanol production (up to 2% v/v).

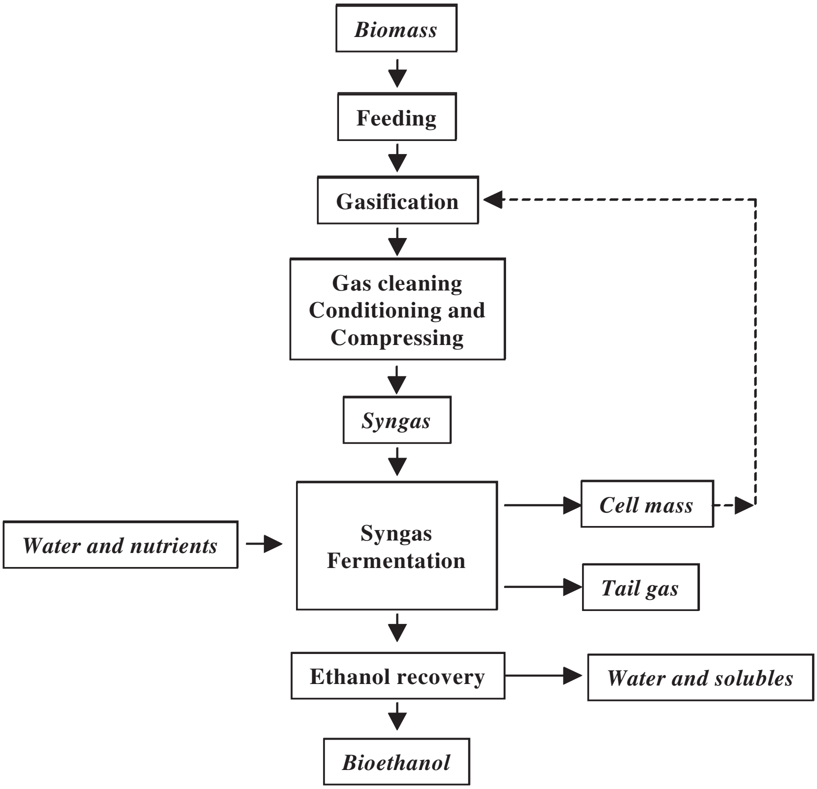


Fig 8.11. Bioethanol production via syngas fermentation (modified from Spath and Dayton 2003).

4. Bioethanol use as transport fuel

4.1 Ethanol/ETBE in spark ignition engines

Ethanol can be used in different ways as engine fuel. Non-food bioethanol is always denatured by adding a small amount of foreign materials which makes it unsuitable for human consumption. Blends of 5 % v/v (E5) anhydrous bioethanol in gasoline do not require any modification to standard engines or to the distribution infrastructures. Bioethanol is blended in gasoline up to 10 % v/v (E10) in USA and even up to 22 % v/v (E22) in Brazil, a major bioethanol producer. Brazil bioethanol use in cars dates back from 1975 for gasohol, blends of gasoline and anhydrous alcohol and 1979 for hydrated ethanol (neat ethanol cars) (Moreira 2005).

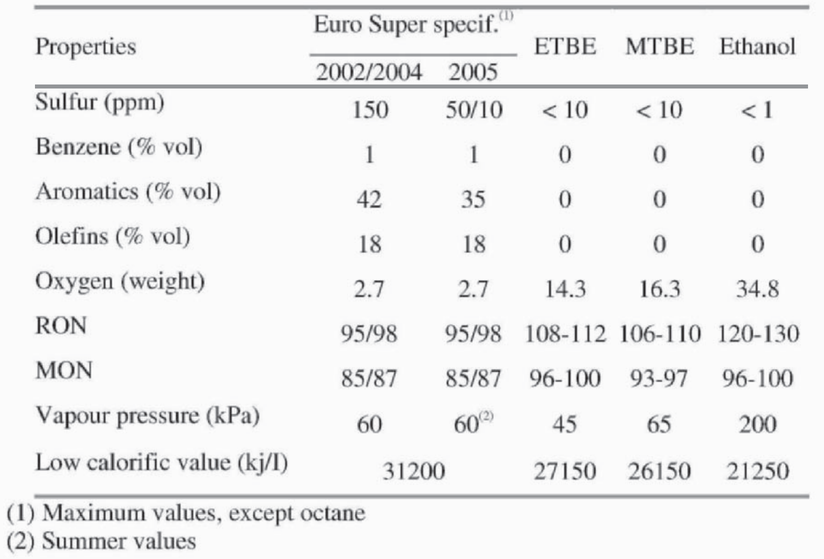
The use of higher blends of bioethanol in gasoline is also possible but the technology has to be adapted to meet the different physical-chemical characteristics of the biofuel. 85 % v/v (E85) is used in Flexible Fuel Vehicles: FFVs represent a main innovation in the car market, as these vehicles are able to recognise any blend from 0 % to 85 % and consequently adapt the main engine parameters. Neat hydrous ethanol can be used in dedicated E95 Internal Combustion Engine Vehicles (ICEV), or in Fuel cell vehicles with on-board reforming.

Table 8.12. Neat and blended bioethanol fuels and use in different Countries (Schieder 2005; Specht 2005).

Neat/blended biofuel	Description	Use	Countries
ETBE	<15 % v/v blend in gasoline	All gasoline engines	Spain, Italy, Germany, France
E5	5 % v/v ethanol in gasoline		Any country
E10 (Gasohol)	10 % v/v ethanol in gasoline	All gasoline engines in USA	Sweden, Canada, USA, Brazil
E22	22 % v/v ethanol in gasoline	All gasoline engines in Brazil	Brazil
E85	85 % v/v ethanol in gasoline	Flexible Fuel Vehicles (FFV)	Brazil, USA, Sweden
E95	95 % v/v ethanol in gasoline	Dedicated engines	Sweden, Brazil
E100	100 % ethanol		
EtOH in Diesel (Diesehol) + Additive	< 15 % v/v ethanol in diesel	Almost standard diesel engine	Sweden, USA

The ethanol’s low volatility limits the ignition capacity of bioethanol at low temperature (cold start): so, without blending with gasoline, the issue of wintertime start must be carefully addressed by engine manufacturers. Ethanol is also used for ETBE $CH_3CH_2OC(CH_3)_3$ production. ETBE (Ethyl-Tertiary-Butyl-Ether) is an oxygenated additive for gasoline made from ethanol (47 %) and % isobutylene (53 %), which can be blended to gasoline up to 15 % vol (known as ETBE/15G). Properties of ETBE are summarised and compared to both MTBE and ethanol in the next table.

Table 8.13. ETBE properties (Source: Blondy 2005).



Properties	Euro Super specif.[(1)]		ETBE	MTBE	Ethanol
	2002/2004	2005			
Sulfur (ppm)	150	50/10	< 10	< 10	< 1
Benzene (% vol)	1	1	0	0	0
Aromatics (% vol)	42	35	0	0	0
Olefins (% vol)	18	18	0	0	0
Oxygen (weight)	2.7	2.7	14.3	16.3	34.8
RON	95/98	95/98	108-112	106-110	120-130
MON	85/87	85/87	96-100	93-97	96-100
Vapour pressure (kPa)	60	60[(2)]	45	65	200
Low calorific value (kj/l)	31200		27150	26150	21250

(1) Maximum values, except octane
(2) Summer values

ETBE has a low volatility and a low aromatic content, thus reducing Volatile Organic Compound emissions. Its high octane number makes this oxygenated additive particularly suitable for high efficiency engines, in which the compression ratio is higher. ETBE is totally compatible with existing cars and infrastructures.

4.2 Ethanol in compression ignition (diesel) engines

4.2.1 Ethanol in Diesel (Diesehol)

Bioethanol in diesel oil (up to 15 % v/v) and almost neat ethanol fuel (i.e bioethanol with 10 % w/w additives) in diesel engines are also under investigation and used in some Countries, especially in Sweden.

The introduction of bioethanol in diesel oil seems a promising and effective mean to improve the environmental performances of the engine, especially in terms of smoke emission reduction: it is studied since the 1970's (South Africa). However, the properties of bioethanol are critical to its use in diesel: in particular, the reduction in the fuel cetane number (bioethanol cetane number is ~8, while typical values for diesel oil are around 48), the increased ignition delay, and the stability of the ethanol-diesel mixture (which can separate at temperature below room temperature) require the use of additives. The changes in other important fuel characteristics, as viscosity, lubricity and heating value, must also be properly addressed, together with the variation in Flash Point and Vapour Pressure.

Bioethanol can be added to diesel oil at different levels (Mc Cormick et al. 2001; Satgé de Caro 2001):

- Emulsions in the range of 5-15 % v/v of ethanol are technically possible (by adding a limited amount of organic polyfunctional additives) and economically interesting.
- 20-40 % v/v emulsions are possible, but the amount of additive needed per litre is considerable.
- The use of almost neat (90 %) ethanol in diesel is also technically possible (see next chapter).

Other possible means for using bioethanol in diesel engines are fumigation and dual injection (Chiaramonti and Tondi 2004), not discussed here because of minor interest for future applications.

Further than increasing the cetane number (which decreases linearly with ethanol content) and improving lubricity, emulsifiers are needed to stabilise the emulsion, to make the emulsion tolerant towards water and to increase material compatibility. They must be used also in case of very low amount (5 % v/v) of ethanol in diesel. Biodiesel is a good emulsifier for bioethanol in diesel fuels.

As regards the performances of engines with e-diesel (ethanol-diesel blends, up to 15 % v/v), recent experimental work (Dominguez et al. 2005) on off-road (2-cylinder, air cooled, mechanical direct injection) and light-duty

(4-cylinder, water cooled, supercharged, common rail) engines gave the following main results:

- Mechanical direct injection engines are sensitive to bioethanol addition (increased injection delay), while electronically (common rail) controlled ones are rather indifferent to bioethanol addition.
- A modest power output loss (5 % at 15 % v/v) was observed, due to the lower heating value of bioethanol compared to gasoline, as well as an increase in the brake specific fuel consumption
- Smoke opacity was lowered at higher bioethanol blends, while no clear conclusions were achieved as regards NOx and particulates. At low loads, instead, increase in HC and CO emissions was observed.

Transport, handling, storage and safety of diesel-ethanol mixtures are a major issue compared to diesel oil. In fact, the flammability limit of e-diesel is very close to pure ethanol, which is ~50°C lower than pure diesel and ~30°C lower than pure gasoline. Specific measures, norms and standards for ethanol-diesel blends have to be developed and applied in transportation and storage, since these e-diesel blends must be handled as gasoline and not as diesel oil.

4.2.2 Neat ethanol in diesel engines

Use of neat ethanol in diesel has been developed and widely tested in Sweden.

Sekab has developed and is commercialising a special bioethanol-based fuel for the use in large urban buses (ETAMAX-D). Specifications for ETAMAX-D are given in the table below (www.sekab.se; Wästljung 2005).

Table 8.14. ETAMAX-D main physical-chemical characteristics (from www.sekab.se).

Appearance		Clear, without particles	ASTM D 2090
PH		min 5.2, max 9.0	AMSE 1131
Water	% w/w	max 6.2	SS-ISO 760
Density (D 20/4)	g/ml	0.82 - 0.84	SS-ISP 758
Fuel Composition			
Ethanol 95 %	% w/w	90.2	
Ignition improver	% w/w	7.0	
MTBE	% w/w	2.3	
Isobutanol	% w/w	0.5	
Corrosive inhibitor	ppm	90	
Colour		Red	

MTBE (Methyl Tert-Butyl Ether) and iso-butanol are used as denaturants, ignition improver is Beraid 3540. Corrosion inhibitor is up to 125 ppm. SCANIA has been testing ethanol in diesel buses since 1985 in Sweden: today, 434 buses have been sold to 13 cities in Sweden. The main adaptation of city-bus engines are the following:

- Increase in compression ratio (24:1 / 18:1)
- Enlargement of nozzles (to allow for a larger fuel flow)
- Modification of the injection timing
- Installation of larger fuel tanks and increase in fuel pump flow
- Change of gaskets and filters

Stockholm (Ljung 2005) today has the largest EU bus fleet (253 buses in 2004, 132 new buses expected to run in 2005-2006) running with bioethanol: all inner city buses are fed with ethanol.

The environmental benefits associated with the use of neat bioethanol in diesel engines are considerable. NOx are reduced at 56 % of those typical of EURO 2 diesel engines, CO to 3.2-1 % of Euro 2 standard as well as HC (8-13 % of Euro 2 standard).

Table 8.15. Material compatibility with ethanol and ethanol-blended fuels (from Renewable Fuel Association 2002).

RECOMMENDED	NOT RECOMMENDED
metals	
Aluminium	Zinc-galvanized (ethanol only)
Carbon steel	
Stainless steel	
Bronze	
Elastomers	
Buna-N (hoses & gaskets) (1)	Buna-N (seals only) (1)
Fluorel (1)	Neoprene
Fluorosilicone (2)	Urethane rubber
Neoprene (hoses & gaskets)	
Polysulfide rubber	
Natural rubber (ethanol only)	
Viton (1)	
Polymers	
Acetal	Polyuretane (2)
Nylon (2)	Alcohol-based pipe dope (recently applied)
Polypropylene	
Teflon (1)	
Fiberglass reinforced plastic (2)	

(1) Registered trademark; (2) The manufacturer of the specific material should be consulted

The present status of ethanol engines is able to meet the Euro 4 standard (Wästljung 2005). CO emissions are 1.5 g/kWh, hydrocarbon 0.46 g/kWh, NOx 3.5 g/kWh, and particulates 0.02 g/kWh.

4.4 Material compatibility

When using bioethanol in engines, a particular attention has to be given to verify that engine and storage tank materials are compatible with this corrosive fuel. In fact, materials for tanks, pumps, sealants, filters, and other components have to be selected according to their characteristics: specifications on material compatibility with bioethanol are available.

Long-term tests (2000 hours) have been conducted on non-automotive engines to verify material compatibility with 10 and 20 % ethanol in gasoline (Orbital 2003). Metal, brass and polymeric materials were investigated. Corrosion of several metallic parts normally exposed to fuel was reported: care has to be given to those parts where the oxides could dislodge and become trapped between moving parts, thus accelerating component wear-out. All brass components showed to be tarnished, indicating that oxidation was occurring: this can affect fuel metering and control in carburetors. Finally, some polymeric components (as fuel line connectors, delivery hoses, bulbs, etc) were also significantly affected by the contact with ethanol: this cannot be accepted, as it can cause fuel leakage.

A number of guidebooks and information documents are available as regards handling, storing and dispensing ethanol fuels (Renewable Fuel Association 2002; Center for Transportation Research 2000).

4.4 Industries and biofuels

The growing interest in biofuels production and use is stimulating discussions among biofuel producers and end-user, namely car industries and oil Companies. They have recently expressed their point of view on biofuels and, in particular, on bioethanol.

Volkswagen AG (Seyfried 2005) seems in favour of 5 % v/v bioethanol blending (which should be possible to increase up to 10 % v/v without major efforts, while lower EtOH blending should be avoided). In addition, according to VW, E15-E20 blending in GDI (Gasoline Direct Injection) engines still need some R&D work, and significantly higher blending (as E85, in FFVs) presents higher risks of phase separation, require dedicated infrastructures for fuel distribution, and could be problematic as far as concerns cold start behaviour.

Abengoa is implementing a large project on bioethanol, in Spain.

Other industrial actors, as some EU oil Companies (e.g. Total, Blondy 2005), seems instead more interested in BtL (Biomass to Liquid) fuels (as Sunfuel), rather than on bioethanol.

5. Economics

Bioethanol production costs have been estimated and assessed by various authors, among which Hamelinck (2003 currency). A summary of Hamelinck's figures is given in the following table.

Table 8.16. Bioethanol production costs from different feedstocks and technologies (Hamelinck et al. 2005).

Feedstock type	Bioethanol cost	Country
Sugar cane	10-12 €/GJ$_{HHV}$	Brazil
Sugar/starch crops	16.2-23 €/GJ$_{LHV}$	USA, Europe
Lignocellulosic biom.	34-45 €/GJ$_{HHV}$	Europe
Lignocellulosic biom.	15-19 €/GJ$_{HHV}$	USA

Hamelinck also reports forecasts by various authors about future projected bioethanol costs, that range from 4.5-10 €/GJ$_{HHV}$, to 6-8 €/GJ$_{HHV}$, to 10-11 €/GJ$_{HHV}$.

Traditional bioethanol production in Brazil is today competitive with gasoline. The main reasons for bioethanol success in the Brazilian context (Moreira 2005) relies in the following three main factors:

- The external debt, which is decreased thanks to the savings generated by ethanol production and use
- The available land: 18 % increase of total harvested area in the period 1988-2004
- The low cost for manpower

These production costs have however been reached after a long development work of the entire chain, which lasted more than 20 years, as reported by Goldemberg.

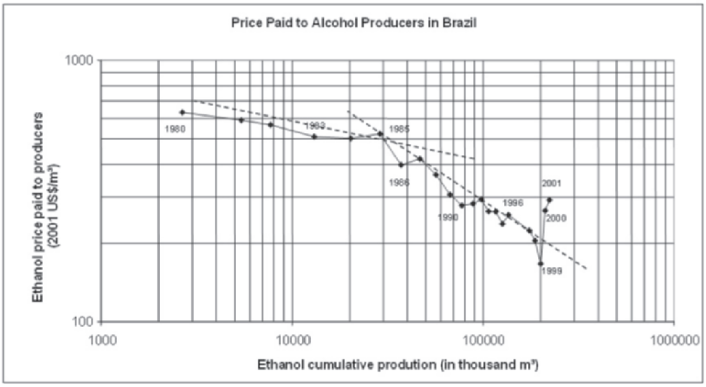


Fig. 8.12. Ethanol learning curve, Brazil (source: Goldemberg. Avail.at: http://www.treckin.com/seminarwssd/goldemberg.ppt)

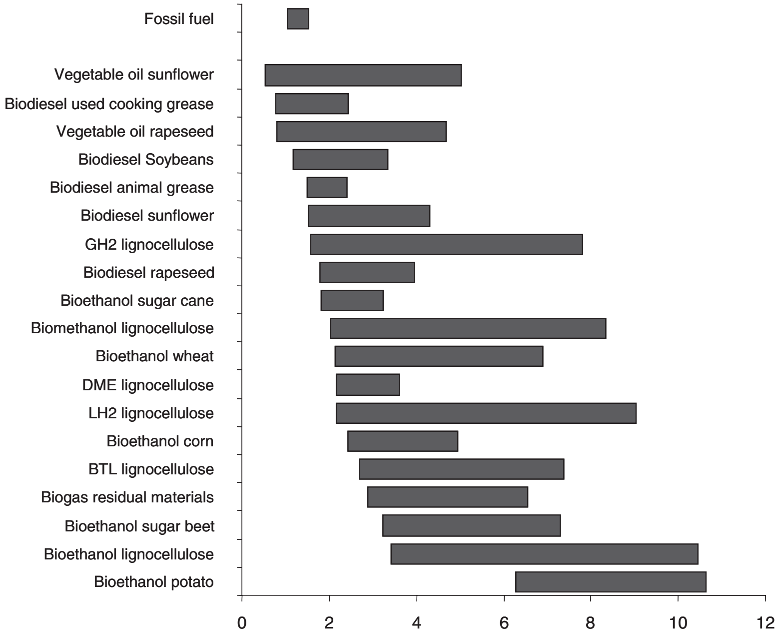


Fig. 8.13. Biofuel supply costs in €/100 km. (Source: IFEU).

IFEU also analysed various biofuels and related supply cost estimations. Main results are summarised in the following figure.

6. Environmental aspects and sustainable production in EU

The environmental aspects of bioethanol production and use is a major and very complex issue to be analysed, as it involves a proper understanding of the whole chain and the availability of a large amount of information. LCA or “well-to-wheels” studies must then be developed in order to achieve reasonable estimations. Deep investigations on GHG (Greenhouse gas) emission reduction, energy input/output ratio etc., have been carried out by various authors, and a considerable discussion is on going on these issues. Reviews are on this subject available in literature (e.g. IEA 2004).

The analysis of GHG emissions and energy balance of bioethanol must be carried out distinguishing between:

- Ethanol from grains
- Ethanol from sugar beets
- Ethanol from sugar cane
- Ethanol from lignocellulosic feedstocks

Ethanol from grains. A summary by the International Energy Agency (IEA) of the results of a large number of studies is reported in the following table.

As reported above, almost all studies except the one by Pimentel (2001) conclude that a GHG emission reduction in the range 20-40 % can be expected. The review of net-energy studies on bioethanol developed by the US Dept. for Agriculture (Shapouri et al. 2002) indicates that the key issues for these analysis are:

- Corn yield per hectare.
- Ethanol conversion efficiency and energy requirements.
- Energy embedded in the fertiliser used to grow corn.
- Assumptions regarding use of irrigation.
- The value, or “energy credit”, given for co-products produced along with ethanol (mainly animal feed).

These factors varies across the studies reviewed by Shapouri: in particular, Pimentel (2001) seems not to take into account the recent (last 10 years) improvements in crop yields and conversion efficiencies, and includes some factors (such as the energy embedded in farm equipment and the cement used in bioethanol plant construction) which however accounts only for a small part of the differences.

Table 8.17. Energy and GHG Impacts of Ethanol from grain: estimates from Corn- and Wheat-to-Ethanol Studies (reprinted from IEA 2004).

	Feedstock	**Ethanol production efficiency (litres/tonne feedstock)**	**Fuel process energy efficiency (energy in /out)**	**Well-to-wheels GHG emissions: compared to base (gasoline) vehicle (per km travelled)**	
				Fraction of base vehicle	Percent reduction
GM/ANL 2001	corn-a	372.8	0.50	n/a	n/a
GM/ANL 2001	corn-b	417.6	0.55	n/a	n/a
Pimentel 2001/91	corn	384.8	1.65	1.30	-30%[c]
Levelton 2000	corn	470.0	0.67	0.62	38%
Wang 2001a	corn-dry mill	387.7	0.54	0.68	32%
Wang 2001a	corn-wet mill	372.8	0.57	0.75	25%
Levy 1993	corn-a	367.1	0.85	0.67	33%
Levy 1993	corn-b	366.4	0.95	0.70	30%
Marland 1991	corn	372.8	0.78	0.79	21%
Levington 2000	wheat	348.9	0.90	0.71	29%
ETSU 1996	wheat	346.5	0.98	0.53	47%
European Commission 1994	wheat	385.4	1.03	0.81	19%
Levy 1993	wheat-a	349.0	0.81	0.68	32%
Levy 1993	wheat-b	348.8	0.81	0.65	35%

Note: Where a range of estimates is reported by a paper, "*a*"and "*b*" are shown in the feedstock column to reflect this. [c] Negative greenhouse gas reduction estimate connoted and increase. n/a: not available. Sources: Except for Levelton 2000, Wang 2001a and GM/ANL 2001, data presented here for these studies are taken from the comparison conducted by CONCAWE 2002.

IEA reports that recent evaluations estimate that one energy unit of bioethanol requires 0.6-0.8 fossil energy unit. It is important to remark that most of this energy is not petroleum-based: Shapouri estimates only 17 % from oil fuels, the rest from natural gas and coal, thus making only 0.12-0.15 energy units of petroleum-based fuels necessary to produce one unit of bioethanol from grains (or, alternatively, "one gasoline-equivalent litre of bioethanol displaces 0.85-0.88 liters of petroleum on a net energy basis"-IEA, 2004).

Ethanol from sugar beet. IEA indicates that GHG emission reduction could be up to 56 %, but also that (1) the same factors presented above for grains also apply to this feedstock, and that (2) more work is needed for a more detailed assessment which reduces the large variations in feedstock production and conversion efficiencies.

Ethanol from sugar cane. The use of fossil energy in bioethanol production from sugar cane is considerably lower than the previous cases, thanks to (1) the rather high yields of sugar cane under low fertilisation conditions and (2) the use of bagasse for power and heat to feed the bioethanol production process. The net energy balance (energy output/energy input) of bioethanol production have been widely studied over the last decades, and main findings report an energy gain between 0.56 and 0.84. Nevertheless, more recent work by Macedo et al. 2003, concluded that the net energy balance ranges between 8 and 10: it means that per each energy unit of bioethanol, only 0.1 unit of fossil energy are needed. These results are possible thanks to the significant improvement in sugar cane yields per hectare as well as in conversion processes, which have been achieved in the period 1985-2002.

As a consequence, well-to-wheel CO_2 emission reduction is estimated at 92 %, well above previous estimations by various authors (ranging between 35 % and 56 %).

Table 8.18. Energy balance of sugar-cane-to-ethanol in Brazil in 2002 (Reprinted from IEA 2004. Source: Macedo et al. 2003).

	Energy requirement (MJ/tonne of processed cane)	
	Average	**Best values**
Sugar cane production	**202**	**192**
Agricultural operations	38	38
cane transportation	43	36
Fertilisers	66	63
Lime, herbicides, etc	19	19
Seeds	6	6
Equipment	29	29
Ethanol production	**49**	**40**
Electricity	0	0
Chemicals and lubricants	6	6
Buildings	12	9
Equipment	31	24
Total energy input	**251**	**232**
Energy output	**2089**	**2367**
Ethanol	1921	2051
Bagasse surplus	169	316
Net energy balance (out/in)	**8.3**	**10.2**

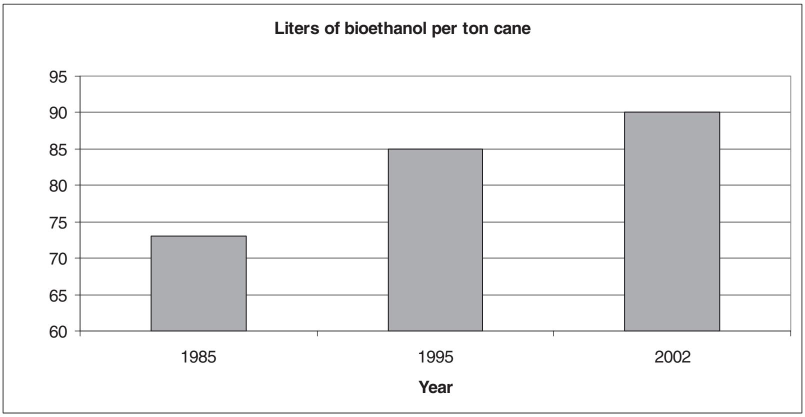


Fig. 8.14. Bioethanol production in Brazil (Source: Macedo et al. 2003).

Ethanol from sugar lignocellulosic biomass. The process efficiency as well as the well-to-wheel emission of bioethanol from lignocellulosic biomass has been evaluated by various authors: main differences are due to variations in end-use vehicle efficiency and assumptions on fertiliser needs. Average estimations are around 70-90 %.

Table 8.19. Energy and GHG Impacts of Ethanol from lignocellulosic: Estimates from Corn- and Wheat-to-Ethanol Studies (Reprinted from IEA 2004).

	Feedstock	**Ethanol production efficiency (litres/tonne feedstock)**	**Fuel process energy efficiency (energy in /out)**	**Well-to-wheels GHG emissions: compared to base (gasoline) vehicle (per km travelled)**	
				Fraction of base vehicle	Percent reduction
GM e*t al*. 2002	wood (poplar plantation)	n/a	1.20	0.49	51%
GM/ANL 2001	wood-*a*	288	1.30	n/a	n/a
GM/ANL 2001	wood-*b*	371	1.90	n/a	n/a
Wang 2001a	wood	288	1.52	-0.07	107%
GM/ANL 2001	grass-*a*	303	100	0.29	71%
GM/ANL 2001	grass-*b*	390	1.60	0.34	66%
Wang 2001a	grass	303	1.37	0.27	73%
Levelton 2000b	grass	310	1.28	0.29	71%
GM et a.l 2002	crop residue (straw)	N/a	n/a	0.18	82%

Table 8.19. Energy and GHG Impacts of Ethanol from lignocellulosic: Estimates from Corn- and Wheat-to-Ethanol Studies (Reprinted from IEA 2004).

	Feedstock	Ethanol production efficiency (litres/tonne feedstock)	Fuel process energy efficiency (energy in /out)	Well-to-wheels GHG emissions: compared to base (gasoline) vehicle (per km travelled)	
Levelton 2000b	corn residue (stover)	345	1.10	0.39	61%
Levelton 2000	hay	305	1.32	0.32	68%
Levelton 2000	wheat straw	303	1.12	0.43	57%

Note: Where a range of estimates is reported by a paper, "*a*" and "*b*" are shown in the feedstock column to reflect this.

n/a: not available

[a] Process energy includes both biomass and non-biomass energy sources.

Sources: GM *et al.* (2002), GM/ANL *et al.* (2001), Wang (2001a), and Levelton (2000b).

Considering non-GHG emissions, two types of emissions must be considered, i.e. exhaust and evaporative ones.

The use of bioethanol blended in gasoline at 5-7 % v/v is able to reduce CO emissions by 14-40 %, and Unburned Hydrocarbons (UHC) emissions are the same or lower (by 2-7 %) of gasoline-fuelled vehicles. Also particulate emissions benefit from bioethanol blends. Slightly increase or no change in NOx emissions are instead observed. Aldehyde emissions (chemical compounds associated with incomplete combustion of bioethanol) are reduced by the high efficiency of catalytic converters used in ethanol-cars.

Evaporative emissions relate to fuel evaporation and release in the atmosphere from vehicle fuel tank. Considering E85, it has fewer highly volatile components than gasoline, and therefore lower evaporative emissions. However, it also results into difficult ignition at low temperature (possible cold start problems for the engine).

As regards the EU region and its potential for environmentally sustainable biofuel production, the EEA (European Environmental Agency) recently carried out a wide analysis on bioenergy potential from agriculture, forest, and waste in 2010, 2020, 2030 (Wiesenthal 2005). Taking into account that the use of biomass must not generate additional pressure on farmland, forest biodiversity, and soil and water resources, and that all other environmental constraints must be respected, as regards energy crops the analysis achieved the conclusion reported in the following figure (see also EEA briefing 02-2005, ISSN 1830-2246).

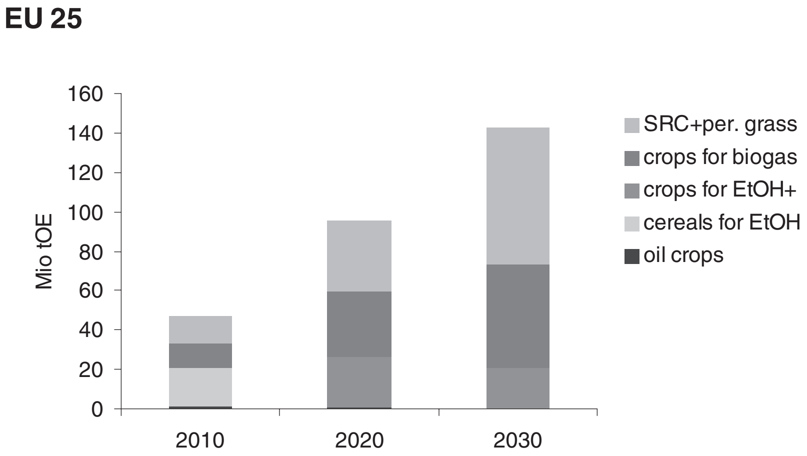


Fig. 8.15. Environmentally compatible bioenergy potential from agriculture by energy crops (Source: Eur. Envir. Agency – EEA, Wiesenthal 2005).

According to the EEA analysis, the potential offered by 1st generation biofuels seems limited in dimension: in particular, sugar beet and rapeseed oil do not look so favourable in the EU-25. However, as cereals generally have lower impact than sugar beet and better yield the rapeseed, in the short term traditional bioethanol from cereals seems more promising than biodiesel. In the medium-long term new technologies are expected to enter into the market (2nd generation biofuels), which are instead more promising from the environmental point of view, as they can use the whole crop (lignocellulosic material, including by-products from agriculture). Moreover, feedstock is less expensive that traditional oil/sugar crops.

Finally, the use of bioethanol-derived oxygenated additives, as ETBE and ethers, has a number of environmental advantages, such as reduction of carbon monoxide emissions, reduction in the aromatic content of gasoline and resulting toxics, reduction of olefin content of gasoline, reduction of volatile organic compounds emissions (precursors of ozone pollution), and reduction of carbon dioxide.

In the BIOFIT project ("Bioenergy for Europe: which ones best fit? – A comparative analysis for the community", available at www.ifeu.de) a comprehensive investigation based on ISO 14040-14043 standards (LCA analysis) has been carried out. Among various solid and liquid biofuels, ETBE from sugar beet has been evaluated and compared to MTBE (for France, Germany and The Netherlands). The use of ETBE offers advantages as regards greenhouse effect and reduction of fossil fuel use, while the impact in terms of acidification and eutrophication is not positive. The

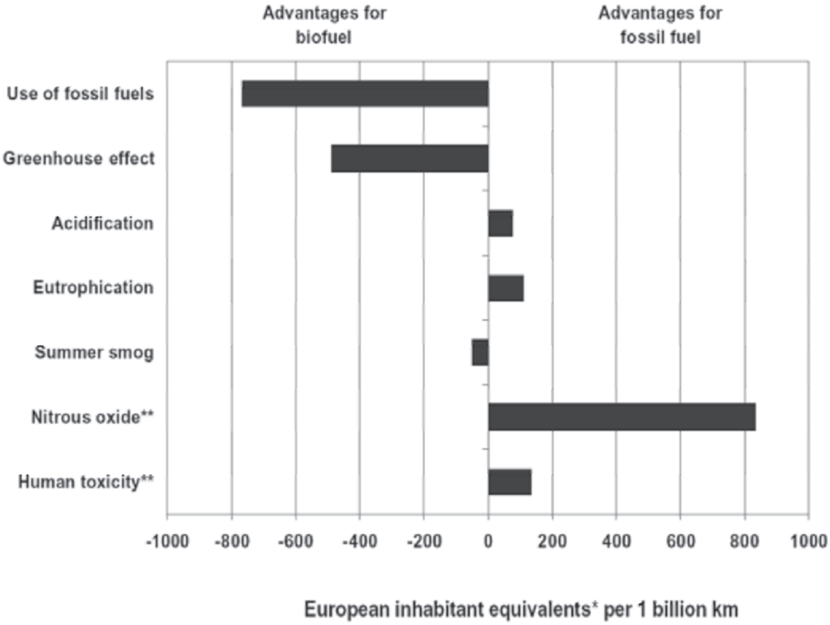


Fig. 8.16. ETBE from sugar beet versus MTBE (Source: IFEU, BIOFIT Final Report, available at www.ifeu.de)

effect on summer smog is instead almost equivalent. It has to be remarked that this study considered three EU Countries and sugar beet only.

7. Conclusions

Bioethanol is already the main actor worldwide in the biofuel sector, and its role is expected to steadily grow in the coming years. In fact, market estimations forecast a rapid increase in bioethanol production and use even in those regions of the world (such as Europe) where bioethanol is still lagging behind biodiesel. The development and industrialisation of hydrolysis technologies for bioethanol production from lignocellulosic biomass are expected to be the key issue for this development.

The potential for environmentally sustainable bioethanol production from lignocellulosic biomass is significantly greater than traditional production from sugar or starch crops. In addition, environmental benefits are higher as well.

The constant quality of bioethanol as transport fuel makes possible its use as neat or blended fuel in a wide range of engines, from spark to compression ignition ones.

Finally, the recent revision of the Common Agricultural Policy, together with the ambitious targets set by the European Commission in the framework of the Greenhouse Gas emission reduction measures, will boost the production and use of this biofuel in the next years in the EU.

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