

BIO - ETHANOL

A study of energy and emissions

Report prepared for

THE SWEDISH ETHANOL DEVELOPMENT FOUNDATION (SSEU)

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BIO - ETHANOL

CONTENTS		Page
1	Abstract	1
2	Background - objectives	2
3	Production paths to ethanol	3
3.1	Lignocellulose - a significant base of raw materials	3
3.2	Technical development	4
3.3	Byproducts - important economic factors	4
3.4	Choice of raw materials - prerequisites	4
3.5	Conversion - sources of information	5
3.6	Conversion plant alternatives - prerequisites	6
4	Summarising the whole chain: a discussion	8
4.1	High amplification	8
4.2	Yields of ethanol	8
4.3	Grain - amplification of up to 8	8
4.4	Greater amplification with wood	9
4.5	Biofuels within the system	10
	Tables 1-2, Figures 1-3	11
5	Gaseous emissions in the chain	16
5.1	Greenhouse gases	16
5.2	Acidification and over-fertilisation	17
5.3	The formation of ozon	18
5.4	Risks for cancer	18
6	Use in engines	19
	Figures 4-6	
Appendix	"Low-level blending and bio-ethers"	

Bio - Ethanol

1 ABSTRACT

- Bio-alcohols represent a long-term potential to the transport sector as it moves towards an eco-cycle society, and towards fulfilling objectives to reduce the effects of greenhouse gases, acidification and health-related risks.
- An immediate change can be wrought by promoting ethers as components of gasoline, by introducing flexible-fuel vehicles (FFV), and by continuing to develop the use of ethers as motor fuels for heavy-duty diesel engines in suitable fleets.
- Analysis of the whole chain for the production of ethanol from grain (wheat) and lignocellulose (wood) shows that for each added unit of fossil energy, 4 - 14 times as much bio-energy is obtained for use as motor fuels, fodder and fuels outside the system as a replacement for fossil-based products. In the wheat-based chain, the figure is between 4 and 8, where the higher value represents small-scale, local applications. In the wood-based chain, the number is 9 - 14, where the lower value represents intensive cultivation of Salix, and the higher value represents extensive forestry and conversion according to the CASH process.
- A prerequisite is that biofuels be used consistently as fuels and motor fuels throughout the entire chain. Generally, this praxis is not followed in today's ethanol conversion plants. The reduction of carbon dioxide emissions from fossil sources is at least 80% when bio-bases are used instead of fossil bases.
- Yields of ethanol (in units of energy) for external use are relatively low: 23 - 33% from the grain base, and roughly 19% from the wood base. Byproducts make up 50% or more of the total energy yields.
- In addition to reduced carbon dioxide emissions from fossil sources, measurements show a considerable reduction of nitrogen oxide emissions (up to 40% from ethanol), and of particles, PAC and other cancer-related gases. However, additional measurements should be made to better assess effects on the environment.

2 BACKGROUND - OBJECTIVES

2.1 Carbon dioxide emissions must be reduced

Emissions to the air, ground and water have marked or detrimental environmental and health-related effects, which must be reduced or eliminated to fulfil the criteria for an eco-cycle society. In principle, no systematic contamination of the biosphere can be allowed without eventual consequences for mankind. In practice, however, we talk of more stringent limits, or critical loads; i.e., not releasing more than "nature and mankind can tolerate." We have begun to see these kinds of definitions for acid rain, and limiting or guiding values for air quality (WHO, national). At the climate convention (Rio, 1992), political agreements were reached regarding measures against the increase of greenhouse gases (fossil-related carbon dioxide, methane, dinitrogen oxide, ozone-forming gases) in the atmosphere, to counter feared impacts on the climate. Initially, carbon dioxide emissions from fossil sources are to be stabilised at the 1990 level through the year 2000; thereafter, emissions must be reduced. However, researchers indicate that we must reduce emissions by as much as 70 - 80% if the climate is to remain unaffected by human activities. Moreover, to attain acceptable levels of influence on health and the environment, emissions of other substances must be reduced by similar amounts.

2.2 Increasing share of emissions from the transport sector

In Sweden, it is estimated that the transport sector answers for nearly 40% of all carbon dioxide emissions. Corresponding world figures are approximately 20% and rising. Thus, corrective measures must be taken within the transport sector if our long-term objectives are to be fulfilled. This is particularly true of emissions that effect health and the environment. Naturally, energy efficiency, which is an ongoing - albeit slow - procedure, can lead to reduced specific energy usage for both goods and passenger traffic (with effects on all types of emissions). If energy efficiency is to be emphasised to any extent, however, then it will mean accepting a whole new automobile culture.

2.3 Bio-alcohols, a long-term answer

Biomass-based motor fuels are a potentially better adapted to existing systems, and give desired effects more promptly. Indeed, **bio-alcohols** represent an immediate, embraceable point of departure for alternative sources of motor fuels.

However, to accurately judge the effects of bio-based fuels, two points must be considered:

(a) The entire chain - from raw materials to end use (cradle to grave) - to understand the total consumption of fossil energy resources, and to judge whether an eco-cycle has been obtained.

(b) Other effects of emissions from bio-based fuels on health (cancer, respiratory diseases, allergies) and the environment (acidification, over-fertilisation). Today, for example, we know that the pollutants below have these kinds of effects.

<u>Greenhouse effect</u>	<u>Acidification and Over-fertilisation</u>	<u>Health-related effects</u>
Carbon dioxide	Sulphur oxides	Ozone
Dinitrogen oxide	Nitrogen oxides	Nitrogen dioxide
Methane	Ammonia	Aldehydes
Ozone (formed indirectly from organic compounds and nitrogen oxides)		Benzene
		Butadiene
		Ethene, propene
		PAC

In the section below, we will discuss in greater detail the use of energy throughout the entire chain. Moreover, we will discuss the influence that the production and use of bio-ethanol have on health and the environment.

3 PRODUCTION PATHS TO ETHANOL

3.1 Lignocellulose - a significant base of raw materials

Today, most ethanol is produced biochemically through fermentation of sugars. Smaller amounts of ethanol are produced through synthesis via ethylene, which generally has its origin in crude fossil petroleum. However, ethanol can also be produced thermochemically, from biomasses via gasification to synthesis gas, and synthesis via methanol-methylacetate, selectively, arriving at ethanol. However, since thermochemical production yields less and costs more, it is not practical to continue this process beyond methanol. **Thus, only the biochemical production ethanol is of interest, even for technical ethanol.**

Possible yields of ethanol are determined by the content of fermentable sugars in the raw materials. Currently, the production of ethanol is based almost entirely on sugar cane (Brazil) and grain (corn), and only

the lignocellulose-based ethanol is the one that is obtained as a byproduct from the production of sulphite pulp. This production, however, is dying out, and in Sweden, only one plant remains (Domsjö). The work to improve process methods continues for all raw materials, but the most extensive work focuses on the use of lignocellulose, since its base of raw materials comprises greater useful acreage and gives higher volumes.

3.2 Technical development

To improve the conventional technique, continuous studies are made of both the saccharification of starch, and fermentation to ethanol using membrane reactors or reactors with immobilised yeast - which give high concentrations of yeast and thereby high productivity. Continuous fermentation with high concentrations of yeast through separation and recycling is applied today in Alfa Laval's *Biostill process*. The search for micro-organisms, yeast, or bacteria species that can tolerate high concentrations of ethanol must prevail to reduce the amounts of energy that are used when distilling to remove water.

A supply of high-content sugar concentrates reduces the need to remove water; thus pre-concentration by evaporation or through methods using membranes is being studied. Pre-concentration of ethanol - possibly through integrating the fermentation and distillation stages - and other distillation methods such as the membrane method (pervaporation) and extraction are also being studied to optimise conversion plants with respect to energy usage and costs.

3.3 Byproducts - important economic factors

When grains are used as raw materials, the conversion of byproducts (fodder and food products) are important to the economic outcome.

The optimum size of plants has been studied. In an Australian study, the optimally sized plant was found to produce between 150,000 - 250,000 m³ ethanol per year from sugar cane or sorghum, depending on how efficient the materials were transported, and what requirements were set for capital gains.

3.4 Choice of raw materials - prerequisites

Two types of raw materials have been selected for this study: (a) grain, in the form of **autumn wheat**, and (b) lignocellulose, in the form of **Salix** short-rotation forests from agriculture, and **tree residues** (chips and shavings of various kinds) from forestry.

3.4.1 Grain

Assuming previous figures can be verified, energy-quality wheat is preferred over food-quality wheat when producing motor ethanols, because its yields of dry substance (10%) and starch content are greater. Thus, energy-quality wheat should yield greater amounts of ethanol. Information about agricultural investments for conversion plants, fertiliser, machinery, motor fuels and outcome were obtained from the Federation of Swedish Farmers (LRF, Dahlgren), the Swedish University of Agricultural Sciences (SLU; Sonesson), and the agricultural consultant in Sörmland (County Government Board; O. Hammar). One group of data, however, has been altered: the energy content of biomass materials was not reported, but rather the fossil energy used to produce them.

3.4.2 Small-scale - local ethanol conversion plants

As an alternative to large central conversion plants that produce ethanol, dried protein fodder and carbon dioxide, studies are also being made of local conversion plants whose only externally marketable products are ethanol and the consumption of wet fodder within the region where the wheat (including straw fuel) was produced.

Studies are also being made to find alternatives to artificial fertilisers (NPK, etc.), including the addition of manure from stables and wet manure (which can include digested sludge from biogas plants at sewage treatment plants).

3.4.3 Salix - tree residues

To raise fast-growing Salix on converted farmland, a model calling for six harvests during a twenty-five year period is used. Information about the production of Salix was taken from the same sources as above. To make a comparison, data from the production of tree residues from forestry are analysed and the characteristic qualities of the two categories of raw materials are collected. Information about forestry materials are taken from the SSEU demonstration conversion plant project.

3.5 Conversion - sources of information

To make a conversion, data was borrowed from SSEU's preliminary projects (Dahlgren, LRF, and J. Lindstedt AB), Chematur Engineering and the Lund Institute of Technology, who based conversion plants on wheat and tree residues; supplementary data was added from two earlier foreign studies.

The wheat-based conversion plant, based on experiences won from the operation of a demonstration conversion plant in Lidköping, produces

byproducts - limited in this case to fodder protein, since this plant aims to produce the maximum amount of motor fuels possible. The fodder is delivered as a dried product or in a wet form to nearby consumers. The latter presumes the existence of small conversion plants with their own local areas of supply and consumption.

In the lignocellulose-based plant projects, the first step of conversion (hydrolysis to fermentable sugar) is made with diluted acid (CASH) or concentrated acid (CHAP). Residue products of non-fermentable material consists of solid residue, enriched on the lignin and organic substance dissolved in water. Coniferous wood has a higher content of C6-sugar than deciduous wood (particularly true of Salix) and gives somewhat higher yields of ethanol (2-3%). Getting the greatest possible yield will necessitate developing the fermentation of C5-sugars from hemicellulose, as well. A determining factor for yields is the content of bark, since bark contains considerably less cellulose.

3.6 Conversion plant alternatives - prerequisites

3.6.1 Wheat: large conversion plants

Autumn wheat yields 4.59 tons of kernels dry substance (at 18 MJ/kg) per hectare each year, and 0.85 tons straw of extractable dry substance (at 17.4 MJ/kg). The wheat is transported 20 kilometres from the fields where it is grown to a central collection terminal. From there it is transported 150 kilometres, by truck, to a conversion plant whose production capacity is approximately 200 m³ ethanol per day (with 5 mass-% water). The plant uses straw in its own central power/heating plant to produce an independent supply of electricity and steam. Solid residue and spent mash are evaporated/dried to produce protein fodder. Additional amounts of straw are taken from neighbouring excesses of food-quality wheat acreage (transport of the straw and its portion of energy during cultivation has been taken into account).

Ethanol is used as the diesel engine fuel throughout all phases of the system. In a comparative alternative, diesel oil would have been used throughout all phases of the system, and the plant's process fuel would have been a fossil fuel.

3.6.2 Wheat: local conversion plants

A local ethanol conversion plant has a 40 km supply radius, and a production capacity of 20 m³ of ethanol per day. (Chematur's calculation gives a slightly higher yield of ethanol than was requisite in the previous example; in this study, the same yield has been used in both cases.) Solid residue and spent mash were deposited in the same area

as the wet fodder. Extractable straw was used for fuel in the plant's own boiler to produce steam. Excess amounts of straw are sold for fuel. All necessary electricity is purchased (assumed to be produced from bio-products). Instead of NPK-artificial fertilisers, wet manure and manure from stables are used during cultivation as prime sources of phosphorus, potassium and nitrogen. The cultivation method has been modified somewhat to reduce the use of machines and energy. Grain is dried at the farm using a boiler fuelled with biomass instead of oil. Ethanol is used as a diesel engine fuel throughout all phases of the system.

3.6.3 Salix - CASH

The raw materials used in this system comprise fast-growing Salix, which yields 230 tons dry substance (at 18.6 MJ/kg) per hectare over a 25 year period (6 harvests). The transport distance to the refinery is 150 kilometres. The CASH process should convert at least 100,000 tons dry substance per year. The plant generates its own electricity and steam using biogas from a waste water treatment plant and from lignin fuel in its own power/steam plant. Excesses of dried lignin-enriched residue products are sold as solid fuel. Ethanol is used as a diesel engine fuel throughout all phases of the system.

3.6.4 Tree residues - CASH

The raw materials used in this system comprise tree residues, primarily sawdust and chips (i.e., virtually bark-free materials), from forestry and forest industries based on coniferous wood. The average transport distance to the plant is 150 kilometres. The CASH process should convert at least 100,000 tons dry substance (at 19.2 MJ/kg) per year. The refinery generates its own electricity and steam using biogas from a waste water treatment plant and from lignin fuel in its own power/steam plant. Excesses of dried lignin-enriched residue products are sold as solid fuel. Ethanol is used as a diesel engine fuel throughout all phases of the system.

4 SUMMARISING THE WHOLE CHAIN: A DISCUSSION

Calculations have been made based on the conditions described above. The results are summarised in *Tables 1 and 2*, and are illustrated in *Figures 1, 2 and 3*.

4.1 High amplification

The contribution of fossil-based energy to the manufacture of machines and artificial fertiliser (thereby excluding motor fuel, which is presumed to come from ethanol produced from the system) gives an amplification **during the cultivation** (including transport to the conversion plant) to gains (in terms of energy) of roughly 7 - 35 times as much biomass. This quotient is lowest for intensive cultivation of grain, and highest for extensive forestry. In the local system - using wet manure - the quotient is higher (nearly 12) than in a system that only uses fossil-based artificial fertiliser (nearly 7), but the former has more limited applications. If fossil fuels had been used, the quotient would have dropped from 7 to 4. The cultivation quotient for *Salix*, which requires much less artificial fertiliser and machine energy (and motor fuels), is approximately 22.

4.2 Yields of ethanol

The cultivated biomasses are the raw materials used in self-sufficient energy-specific **conversion** plants to produce ethanol for use as a motor fuel. However, large amounts of byproducts (fodder protein, solid fuel) are also produced. The total net yield (see *Table 2*) of marketable products, less the use of motor fuels (ethanol), electricity and steam (generated from the combustion of straw, biogas and lignin) within the system, is 42 - 60% (calculated using the low heat values of the dry substance from raw materials). The yield of ethanol is highest in grain bases (23 - 33%; more starch than in cellulose materials), and highest of all in local production, since the fodder product is not dried and smaller quantities of motor fuel are consumed.

4.3 Grain - amplification of up to 8

The quotient between net marketable products and added fossil energy in the whole grain-based system gives an amplification (see *Figure 1*) of approximately 4 - 8, where the highest value represents the local case, which also includes a slight excess of straw as a fuel product. In cases where fossil fuels are used for transport or in the conversion plant, amplification sinks (see *Figure 2*) from 4 to slightly more than 1 (approximately 1.25 if the excess straw is counted as marketable fuel), i.e., not much better than motor fuels and fuels based on fossil

petroleum, which always has an amplification less than 1.

It is doubtful, when viewed with an eye to energy, whether the fodder product should be included as we have done here (as a product of energy). Instead, it would be more correct to credit the system for the fossil energy that was used for the protein fodder product that the new product replaces (soybean meal). This has been done in other analyses (Life of Fuels). However, in this case, the above-named quotient was hardly affected by the calculation. Similarly, no analysis has yet been made of how the use of energy is distributed amongst the various products. An analysis of this kind (Life of Fuels) could be interesting in another context.

4.4 Greater amplification with wood

In the wood-based cases, a net value of approximately 19% (ethanol) was obtained from input energy to the dry substance of the raw materials (ethanol), and a total of 42 - 43% was obtained when excess lignin fuels were counted. It makes no difference whether electricity and steam are produced by an outside co-generation plant, or in one's own plant, since efficiency is assumed to be nearly identical in either case. However, amplification is higher (9 - 14) than when using grain, owing to lower contributions of fossil energy in the whole system. The figures cited above apply to the CASH process at its current level of development, and can assuredly be improved somewhat through continued development.

4.4.1 CHAP - paper refuse

Comparisons with other hydrolysis processes using the same raw materials have been made (LTH). Hydrolysis using **concentrated acid** (CHAP) is estimated to give 35 - 40% greater yields of ethanol than CASH, but the process gives no solid-fuel byproducts for sale. These are consumed when drying the raw materials prior to conversion, and afterwards, when recovering the acid. Thus, the CHAP process is predominantly suitable to already dried, cellulose-rich raw materials (paper refuse). **Enzymatic** hydrolysis is judged to give approximately 30% greater yields of ethanol than CASH, but less lignin, which, together with its slightly larger internal needs for electricity, produces a somewhat lower total yield.

4.4.2 Untreated raw materials - process fuels

In each case, product yields would be better - in terms of energy - if the process fuel (for steam and electricity) used a portion of the raw materials directly instead of for already processed lignin fuel.

4.5 Biofuels within the system

The yields may seem low, but they are characteristic of the elaborate conversion that is required of today's technology, using a carbon-rich bio-based raw material to arrive at a hydrogen-rich motor fuel. However, it is hardly fair to compare these figures with the production of motor fuels from ready-made, semi-finished crude oils found in nature. If carbon dioxide is brought into the comparison, however, the judgement of well-designed conversion plants will rule swiftly in favour of bio-based raw materials, even when biomass (or its products) replace a share of the process fuel in a oil refinery.

The condition that will justify the bio-based plant demands that biofuels be used within the system. Otherwise, with respect to carbon dioxide, nothing is gained, a point that is often brought up (by Taschner, Amoco, Volvo, etc.), and that is typical of the majority of current ethanol production. This fundamental fact is often left out of the debate. However, without this condition, compared to fossil fuels from oil, equally large emissions of carbon dioxide, and possibly even larger total emissions of greenhouse gases are obtained.

Table 1. ENERGY BALANCES (cultivation, harvest, transport)

Case	WHEAT Large	WHEAT Local	Salix CASH	Tree residue CASH
	--- GJ/hectare, yr. ---			GJ/10 ton DS
Cultivation, harvest				
Seed/cuttings	0.8*	0.8*	0.04	--
Transport, diesel oil	(9.34)	(6.77)	(1.89)	(5.19)
NPK, etc.	7.18	2.88	3.02	1.3
NPK transport, diesel oil	(0.25)	(0.13)	(0.08)	(0.04)
NPK, machines	0.24	0.1	0.08	0.04
Harvest machines, transport	--	--	0.03	--
Machine energy	2.85	2.82	0.22	0.25
Drying, diesel oil	(1.56)	0.08*	--	--
Drying, electricity	0.01*	0.01*	--	--
Transport:				
20 km to terminal	(0.74)	--	(1.86)	--
40 km to plant	--	(1.0)	--	--
Machine energy	0.6	0.6	0.6	--
Transport wet fodder	--	(1.84)	--	--
Transport:				
150 km to lg. plant	(1.75)	--	(4.06)	(4.67)
Machine energy	1.75	--	4.06	4
Total excl. diesel oil:	13.44	7.30	8.04	5.58
Total incl diesel oil:	(27.08)	(17.03)	(15.73)	(14.58)
PRODUCTION:				
GJ in dry substance	97.4	97.4	171	192
+ excess straw	25.3	--	--	--
* Represents fossil fuels input during the production of biomass.				

Table 2. ENERGY BALANCES DURING CONVERSION

	WHEAT Large	WHEAT Local	Salix CASH	Tree residue CASH
	--- GJ/hectare, yr. ---			GJ/10 ton DS
CONVERSION:				
Steam needed	27.8	9.8	41.4	45
Electricity	3.3	3.4	9.9	10.8
Intermediates:				
Ethanol, 96 vol-%	40.0	40.0	39.8	44.6
Lignin	--	--	86	93.5
Biogas (methane)	--	--	25	27.2
MARKETABLE PRODUCTS:				
Ethanol, 96 vol-%	28.5	31.7	33.3	36.2
Protein fodder	27.3	23.5	--	--
Lignin fuel	--	--	40.2	43.7
Excess straw	--	3.9	--	--
YIELD of marketable products during conversion (in %*):				
Ethanol	23.2	32.5	19.5	18.9
Fodder/lignin	22.2	24.1	23.5	22.8
Straw	--	4	--	--
Total:	45.4	60.4	43.0	41.7
* Calculated on energy content of input dry substance from biomass				

Wheat

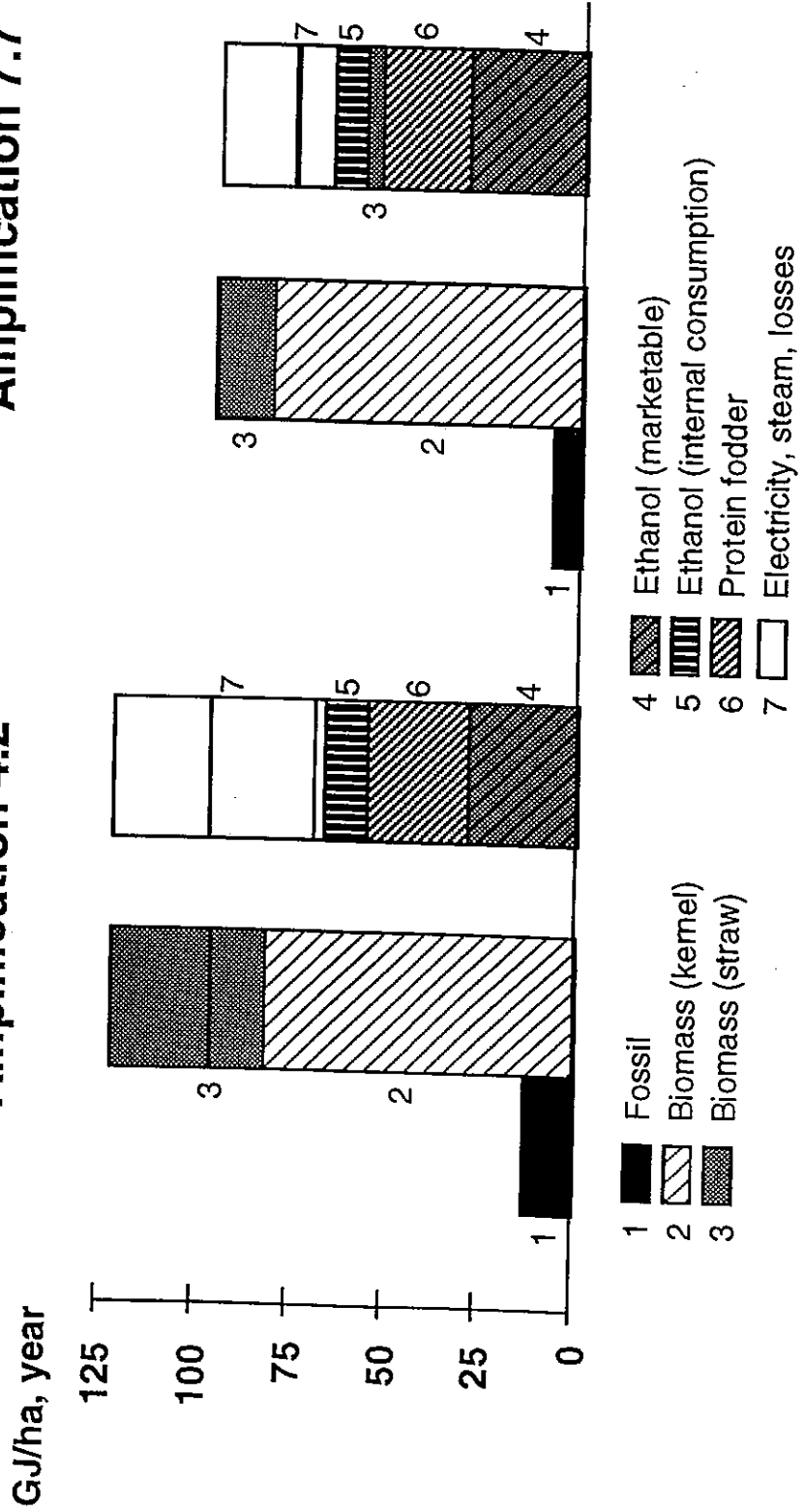
"Large"

Amplification 4.2

Wheat

"Local"

Amplification 7.7



Wheat "Large"

Diesel Oil & Fossil Process Fuels

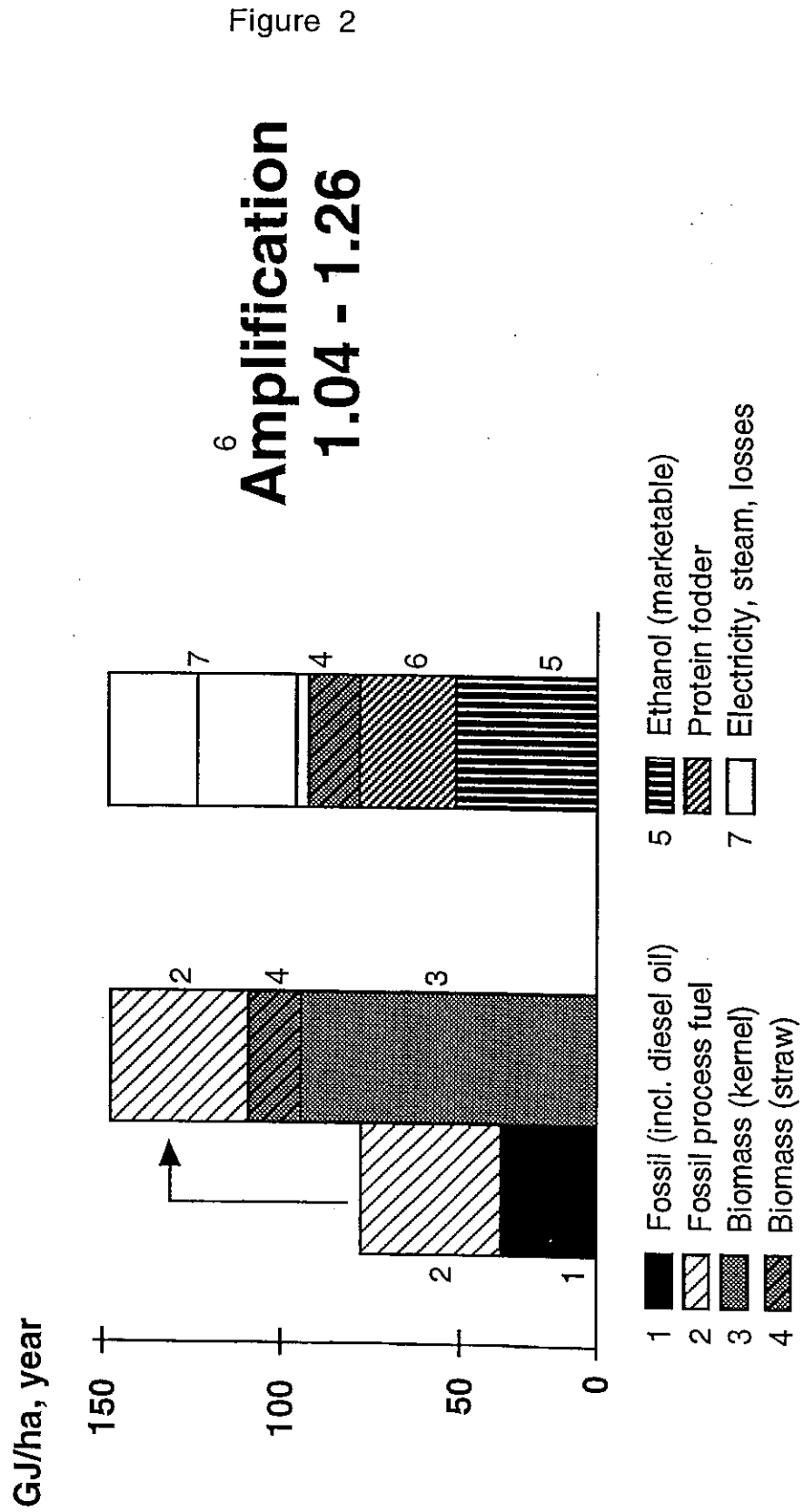
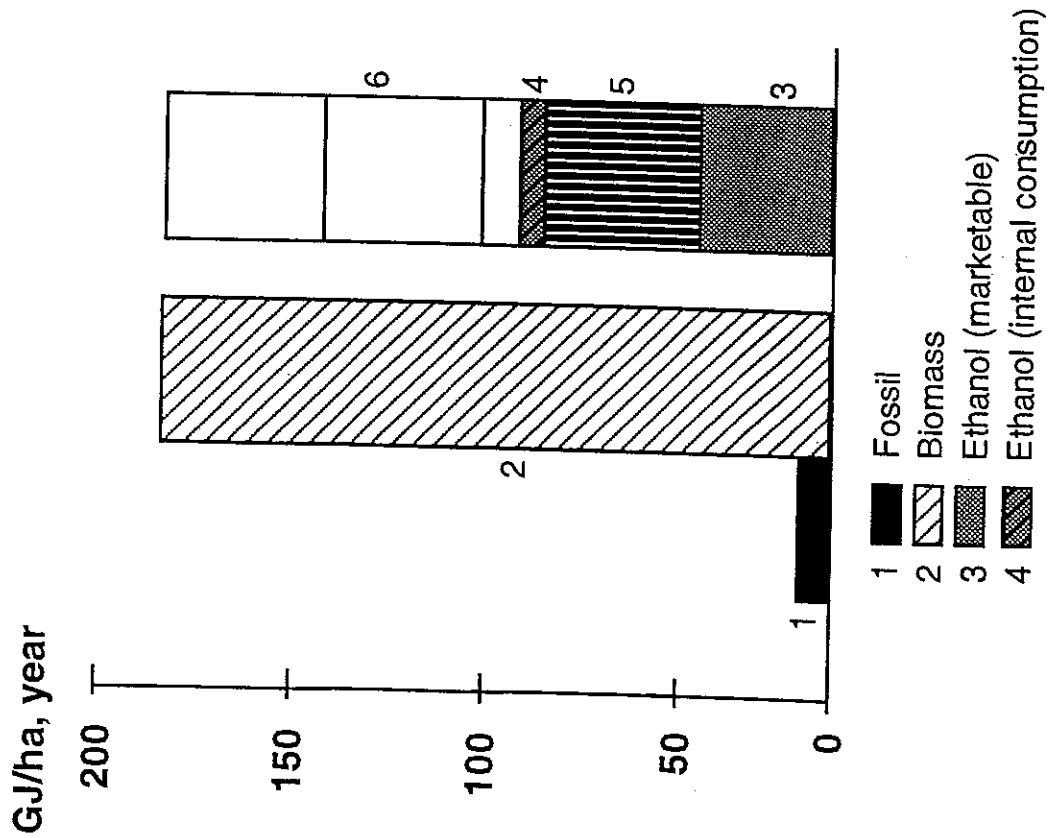


Figure 2

SALIX - CASH

Amplification 9.2



TREE RESIDUES - CASH

Amplification 14.3

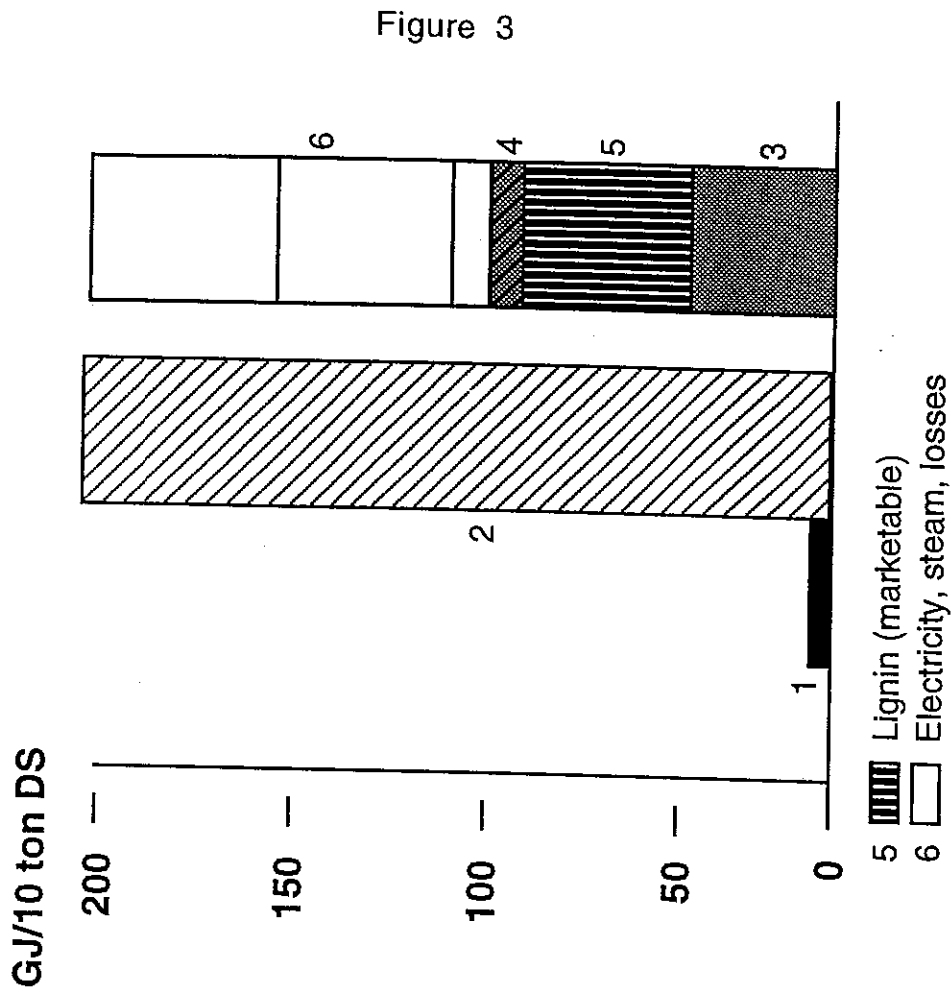


Figure 3

5 GASEOUS EMISSIONS IN THE CHAIN

Energy relationships represent an important part of the whole system, but equally vital to today's discussion are the effects that emissions of various compounds have on health, environment, and possibly even the climate. For a complete picture, we must consider emissions from the use of the motor fuels **and** the byproducts that are produced.

5.1 Greenhouse gases

5.1.1 CARBON DIOXIDE

The relative emissions of fossil-based carbon dioxide closely follow the inputs of the middle-distillate fossil fuels (diesel oil) in the systems. Thus, properly designed biomass systems can give dramatic reductions. Compared to the use of fossil-based fuels, the case for *Wheat: large-scale*, above, shows nearly an 80% reduction of carbon dioxide whenever biomass is used consistently within the system. In cases using wood, in which fossil process fuels have been considered, the percent reduction should be even greater.

Other greenhouse gases currently associated with motor fuels include methane, dinitrogen oxide and ozone.

5.1.2 METHANE

Although emissions of methane are low from engines operating on diesel oil, engines operating on ethanol have even lower emission levels. In the big picture, even emissions from the production phase - which may be somewhat higher during intensive cultivation of farmland due to microbiological activity in the soil - contribute small amounts of greenhouse gases. The handling of wet manure gives methane emissions (and ammonia); these however, are not new emissions resulting from an ethanol conversion plant, but are derived from already existing sources. Biogas plants for waste water from wood-based sources can give increased emissions of methane if they are not gas-tight. Each of these relationships should be studied more closely in order to quantify them.

5.1.3 DINITROGEN OXIDE

Emissions of dinitrogen oxide from engines operating on diesel are very low (approximately 1 promille of the nitrogen dioxide emissions), and less than from gasoline engines. It seems to be unclear whether emissions are higher when catalysts are used (this is the case in gasoline-based operations), but it seems unlikely for oxidising catalysts. Neither is it known whether ethanol operations will produce higher emissions of dinitrogen oxide. It is known, however, that

dinitrogen oxide is discharged from nitrogen-rich soil (particularly wetlands), and this occurs in a greater scale during intensive cultivation of crops. The release should also be influenced by the downfall of nitrogen oxides. Thus, reduced emissions from alcohol-driven engines imply a counter effect. Although the named relationships should be investigated more closely, in order that they may be quantified, the contribution to the total volume of greenhouse gases must be considered very low.

Ozone in the atmosphere nearest to the earth is also a greenhouse gas. Changes in the potential for forming ozone are discussed below.

5.1.4 Burning lignin fuel

Emissions from burning the byproduct lignin fuel are very dependent of the type of boiler used, since stringent requirements are placed on these when using solid fuels. Poor burning conditions in small boilers are known to produce high emissions of smog-forming substances, including even methane. Some boiler types, such as fluid-bed boilers, are known to discharge increased emissions of dinitrogen oxide. Today, not enough information is available to assess these kinds of emissions, and studies should be made in order to determine their contributions.

5.2 Acidification and over-fertilisation

5.2.1 Lower NO_x emissions

Combustion in a diesel engine gives higher nitrogen oxide emissions than combustion in a boiler; when proper methods are observed, emissions should not exceed 100 mg/MJ, and in larger plants they should be less than 50 mg/MJ. The best diesel engine operating on ethanol - a bus used in a city driving cycle - gives approximately 350 mg/MJ. Nevertheless, the ethanol engine gives nearly 40% less emissions than diesel oil operations (the reduction is slightly less in otto-engines when compared to gasoline). In automobiles with otto-engines and catalytic exhaust gas systems, the level of emissions for environmental class-2 automobiles is below 75 mg/MJ, and when ethanol is used (FFV) nitrogen oxide emissions can be as much as 20 - 30% lower than from gasoline operations.

5.2.2 Lower sulphur emissions

Because ethanol fuel is nearly sulphur-free, sulphur oxide emissions from ethanol are very low. The difference between environmental class-1 diesel oils is not especially great, but considerably better than today's gasolines, whose sulphur levels reach 200 ppm. Emissions in the production chain and during combustion of lignin fuels should also be considered, however. Although the proportion of sulphur in

wood-based biomass is normally relatively low, emissions are nevertheless at a level of 500 ppm (equivalent to 1000 ppm in oil), which level is high enough to warrant taking measures to retain the sulphur in the ash (to a large extent, this occurs naturally), and to further reduce the emissions of sulphur, which otherwise could reach levels as high as 25 mg/MJ. The level of sulphur in straw can be high.

5.3 The formation of ozone

Reactions between oxygen, nitrogen oxides and organic compounds form ozone in the atmosphere. An important factor is the reactivity of the organic compounds, which is highest for gaseous olefins and aldehydes. A comparison of emissions from diesel oil engines, gasoline engines and ethanol engines shows (the comparative materials are tenuous) that diesel operations contribute as much as catalyst-equipped gasoline-driven automobiles, since the emissions of hydrocarbons were dominated by olefins and aldehydes; ethanol gave only slightly marginal differences due to relatively large emissions of ethene and acetaldehyde. Nevertheless, the lower nitrogen oxide emissions are a positive factor, when the formation of ozone is determined by the level of nitrogen oxides in the air. This assessment was made by comparing gasoline with measurements from flexible-fuelled vehicles using an E85 motor fuel.

Emissions of specific organic materials from combustion are not yet defined, but they should be low under optimum conditions in boilers, or when compared to combustion in engines. More important to the formation of ozone are the probable emissions of nitrogen oxides from combustion in furnaces. Additional studies are required.

5.3 Risks for cancer

5.4.1 Low PAC emissions

Long-term (lifetime) exposure to air that is polluted with certain compounds can cause cancer. These compounds include benzene, 1,3-butadiene, formaldehyde and acetaldehyde (considered air toxins by American legislation); in Sweden, ethene and propene have also been added to this list. The substances have different degrees of potency and are weighted accordingly. In addition to these are PAC (polycyclic aromatic compounds) - more particularly, nitrated PACs. The potential risk for cancer from nitrogen oxides, which could be significant, is still unknown.

Previously, diesel oil operations gave the highest emissions of the above-named compounds, and in particular, PAC, which are generally associated with particles. However, these emissions can, and have been, reduced dramatically with modern environmental class diesel oils

and oxidation catalysts.

According to studies made of SL's ethanol buses (in Stockholm), PAC emissions from ethanol operations using diesel engines are as low as the modern diesel oil buses named above, and the biological activity (Ames's test) also appeared to be low. However, the test information was incomplete and additional studies should be made.

The combined toxicity of the gaseous substances cannot be reported in this study, due to incomplete information. They are, however, estimated to be slightly lower due to reduced emissions of benzene and formaldehyde, in spite of increased emissions of (lighter-weighted) acetaldehyde.

5.4.2 E85 - better than gasoline

Comparisons with gasoline driven vehicles - made from measurements on FFV vehicles - showed that the combined risk was reduced by more than one-half when E85 was used instead of gasoline.

6 USE IN ENGINES

Ethanol can be used in several ways in engines:

- As a direct low-level blending in gasoline, or indirectly as ether for existing vehicles
- As a mixed fuel for high blending in gasoline in vehicles that use lambda-sond control
- As an alcohol motor fuel in FFVs
- As a motor fuel in diesel engines

6.1 Low-level blending

Low-level blending represents an immediately accessible possibility for existing vehicles, within the limits set by driveability. The indirect method, via ethers, is preferred by motor fuels and motor vehicles manufacturers, due to the practical problems of formulating fuels and water-related problems in the systems during distribution.

Low-level blending in gasoline is summarised more completely in the appendix. Some results are illustrated in *Figure 4*. Additional information can be found in "*R 1994:5, Oxygenater i motorbensin*" (Ecotraffic, October 1993), published by Nutek (in Swedish).

6.2 Mixed fuels

Mixed fuels with higher mixtures of ethanols represent a niche fuel for fleets that have their own refuelling stations. These are not expected to be implemented for general use within the foreseeable future. More detailed data about emissions from their use is not available.

6.3 Ethanol in FFVs

Ethanol has begun to be used as an alcohol fuel in flexible fuel vehicles. Equipped with fuel sensors, FFVs can operate using gasoline alone, or any reasonable mixture of gasoline and ethanol up to at least E85. Aside from the very large market potential of this alternative as a bio-alcohol, preliminary test results indicate that emissions of nitrogen oxides are 20 - 30% lower, and emissions of cancer-related compounds (air toxins) are also lower (by one-half). Some of these results are illustrated in Figure 5.

The status of FFVs is treated in greater detail by a report entitled "Introduktion av FFV" (*Introduction of Fuel-Flexible Vehicles*), prepared by Ecotrafic R&D for KFB in March 1994 (in Swedish).

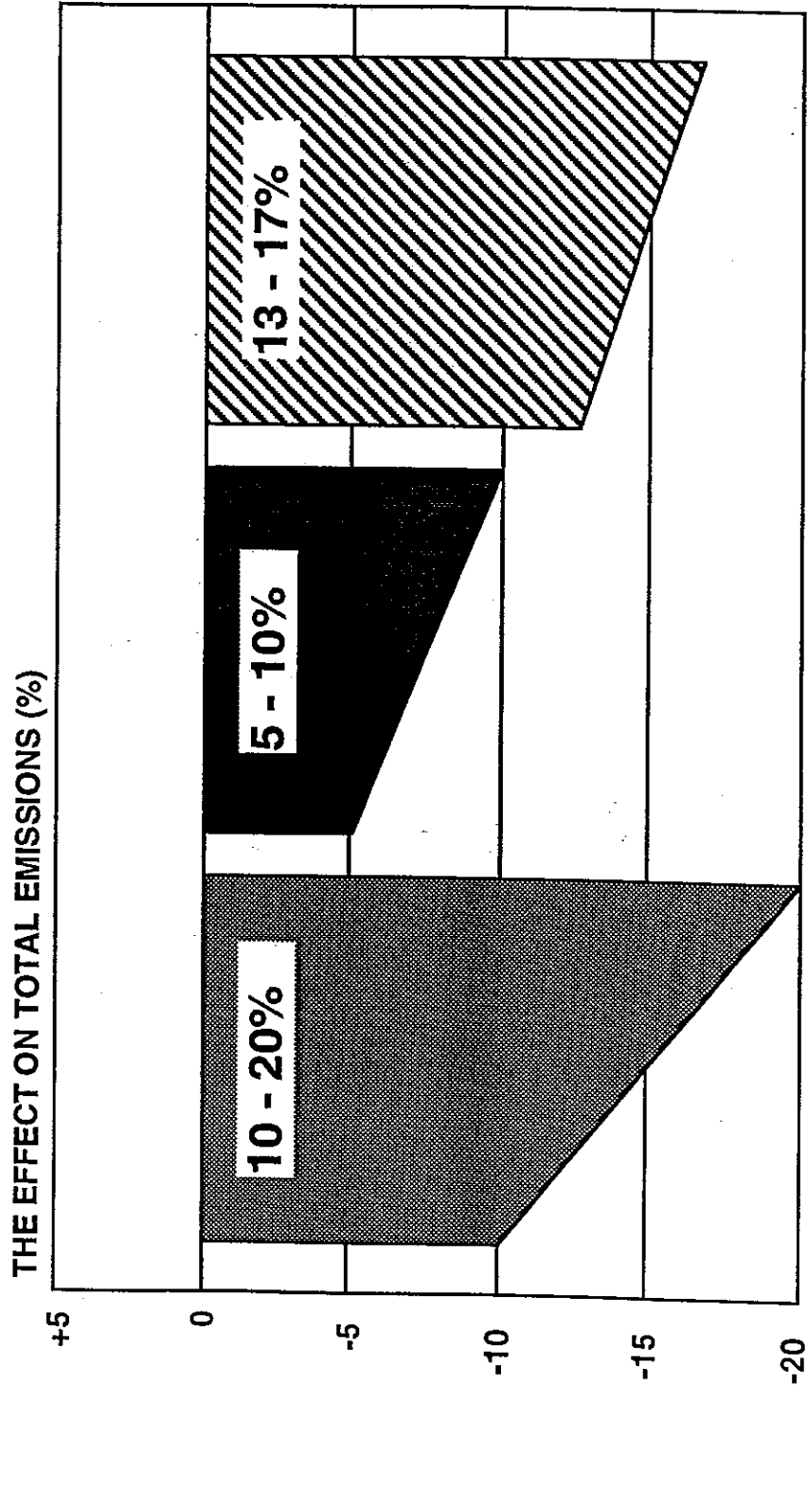
6.4 Alcohols in diesel engines

The use of ethanol as a diesel engine fuel has been treated thoroughly in reports by SL on the operation of ethanol buses in Stockholm. Immutible results show a 40% reduction of nitrogen oxide and low emissions of particles (low even for future requirements) and PAC. Lower emissions of other gaseous, cancer-related compounds were indicated, but could not be confirmed due to a lack of adequate information. Some results are illustrated in Figure 6.

More information about alcohols as diesel engine fuels can be obtained from the KFB report, entitled, "1994:1, *Fossila och biobaserade MOTORALKOHOLER*" (Ecotrafic R&D, October 1993; in Swedish).

THE EFFECT OF CITY FUEL ON ENVIRONMENTAL EMISSIONS

(Compared with ordinary gasoline)



Source: Neste

- CARBON MONOXIDE
- UNBURNED HYDROCARBONS
- EVAPORATED EMISSIONS IN THE ENTIRE DISTRIBUTION CHAIN

Figure 4

EMISSIONS - FFV (in FTP) E85 COMPARED WITH GASOLINE

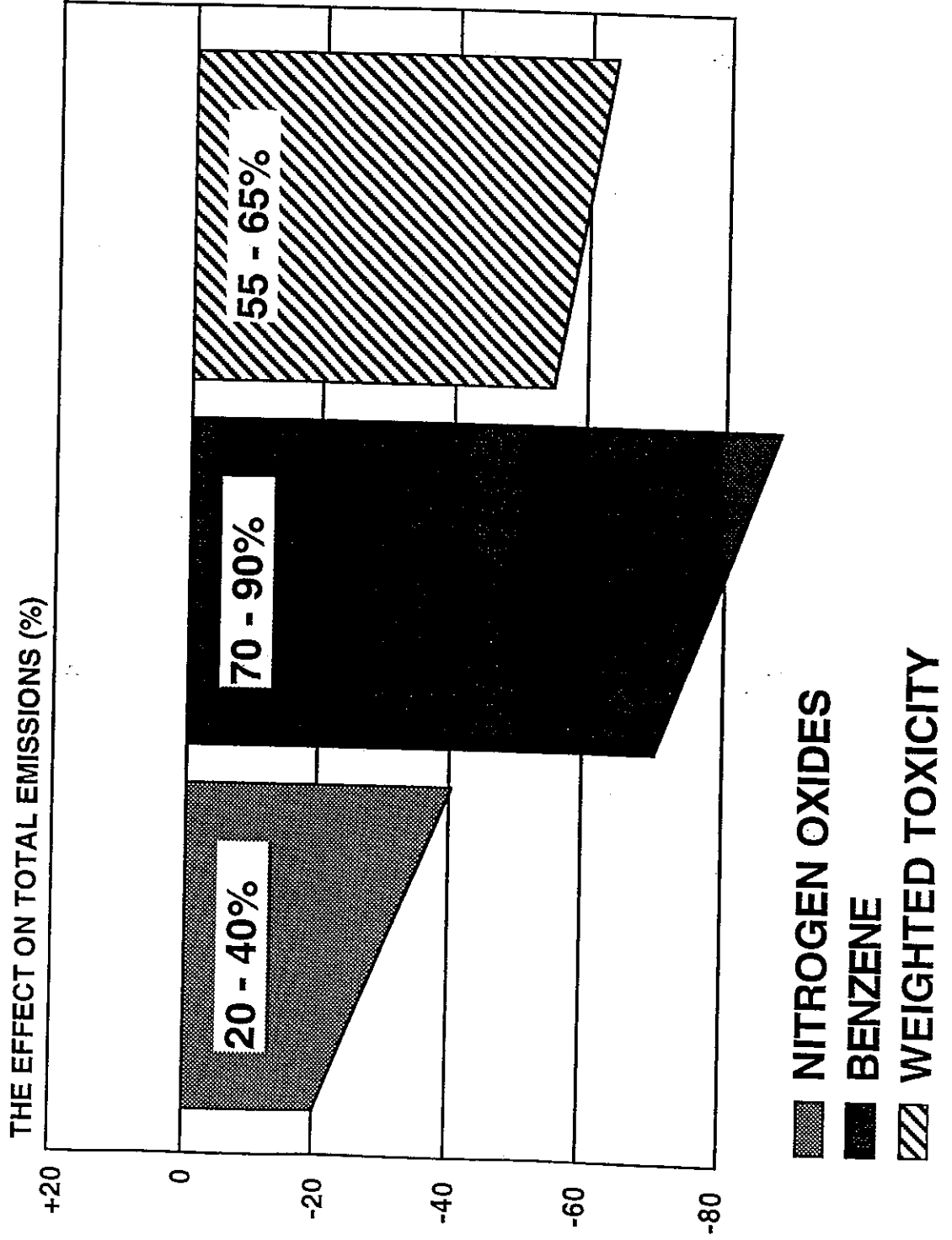


Figure 5

EMISSIONS - BUS (in the bus cycle) ETHANOL WITH A CATALYST VS. DIESEL OIL WITH A CATALYST

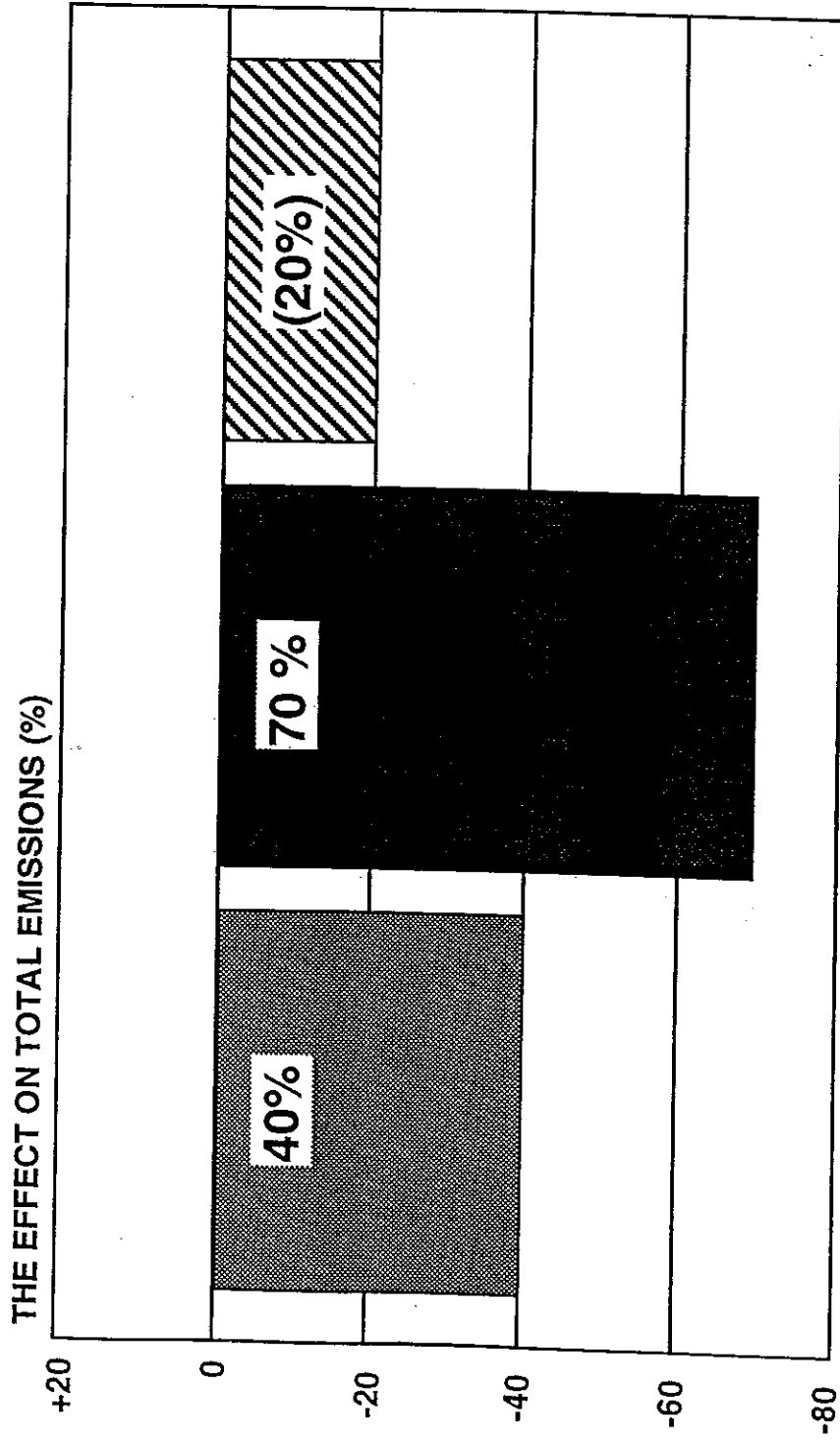


Figure 6

- NITROGEN OXIDES
- PARTICLES
- ▨ WEIGHTED TOXICITY

Low-level blending and bio-ethers

Presentation at the conference

"Bioalkoholer - Drivmedel från förnybara råvaror"

(Bio-alcohols - Motor fuels from renewable resources)

Arranged by SVEBIO, etc., Göteborg, 16 March 1994

Presented by: Bengt Sävbark, Ecotraffic R&D AB

OXYGENATES - *compounds with chemically bound oxygen, normally an aggregate term for alcohols and ethers.*

ALCOHOLS AS COMPONENTS OF GASOLINE

Low-level blending - a definition

Oxygenates, and alcohols in particular, have a lower average energy content than gasoline, and cannot therefore be blended in unlimited amounts in gasoline for automobiles designed to run on gasoline without encountering driveability problems. These arise due to the applications used in many fuel systems. It is known that modern automobiles with regulated lambda-sond systems can tolerate fairly high blends, corresponding to 15 - 20% ethanol.

However, for general market use, the blend must be limited so that the fuel can be used by all automobiles. Thus, the limit of alcohol content is usually set at levels corresponding to 2 - 2.5 mass-% oxygen (5.5 - 7 vol-% ethanol). **This is the definition of low-level blending.**

For this reason, upper limits of 5 vol-% for ethanol and 3 vol-% for methanol were implemented early on. The Swedish gasoline standard enforces this latter limit, plus a maximum 2 mass-% oxygen content.

Current EC directives include these individual upper limits for ethanol and methanol, and stipulate that gasoline with up to 2.5 mass-% oxygen may be marketed freely. Higher contents are allowable given national approval, but oxygen contents exceeding 3.7 mass-% must always be stated on the fuel pump.

Characteristics of the blends

Important characteristics of fuels for manufacturing, handling and using fuels include the level of octane, viscosity, density, energy content and stability. Alcohols and ethers distinguish themselves on many accounts from hydrocarbons. However, the effects are

relatively minor when talking about low-level blends.

The **octane level** is high for current alcohols, and in particular for blended levels.

Low-level blending - unchanged good driveability

Low-level blends are intended for use in existing vehicle populations, and given the maximum limits of 2 - 2.5 mass-% oxygen content and an unchanged volatility specification, blends can be used without motorists ever noticing a difference. Likewise, by limiting the alcohol content, material problems will not arise in the automobile's fuel system, which at an earlier point in time was a real worry for many older models of vehicles.

Newer vehicles are constructed using materials that better tolerate higher alcohol concentrations, and modern automobiles with regulating lambda-sond systems are capable of using high concentrations of alcohols without developing runnability problems of any kind.

Low-level blending can comprise blends of different alcohols or blends with other oxygenates such as ethers.

Possible combinations of oxygenates

Content in the blend	Example								
	1	2	3	4	5	6	7	8	9
Methanol, vol-%	3	2	-	-	2	1.5	-	-	-
Ethanol, "	-	2	5.5	5	3	-	3.5	-	-
Butanol, "	2	1	-	1	-	1.5	-	-	-
MTBE, "	-	-	-	-	-	5	4	11	-
ETBE, "	-	-	-	-	-	-	-	-	13
Oxygen, mass-%	2	2	2	2	2	2	2	2	2

Startability, vapour-lock, consumption

Alcohol blends have actually eased the problem of cold-engine starts, and they tend to reduce or eliminate the risk for knocking (higher road octane levels).

However, driving under very hot conditions can give rise to driveability problems (vapour-lock when restarting after stopping); this is particularly true if the fuel has not been formulated after the above-mentioned vapour pressure limitations or using proper measurement methods.

The fuel consumption observed for the given limits of oxygen content were practically unchanged, implying an improved thermal efficiency (made possible by the alcohol's better burning characteristics in the lean range).

Storage in depots. Fuel is commonly stored in unlined underground caverns on top of movable beds of water. However, this is not currently possible with gasoline that contains alcohol. By contrast, above-ground storage in cisterns does not incur any problems once the system has been started, is kept dry, and rust-protective linings have been inspected and renovated. If the blend is to be made at the depot, then blending equipment and cisterns for both alcohol and the gasoline base will be required.

Blending at stations is not recommendable, owing to limited control.

Experience (OK Stockholm, 1983) shows that problems, such as water in the system or freezing during the winter, are reduced since the system is kept "dry" - this is because condensation is continually absorbed in the gasoline and water does not accumulate.

Gasoline tanks are normally shielded against corrosion (due to occurrences of water) by protective lining or cathode protection. The question is whether new cisterns for alcohol-gasoline blends will require this type of protection (this needs to be verified). Experience also shows that cathode protection using sacrificial anodes of magnesium cannot be used. Thus, for existing tanks, the question is whether the shielded linings can tolerate gasoline blended with alcohol. This is judged to be the case for the level of alcohol specified by the standards for low-level blending.

When implementing low-level blends of gasoline, dilapidated tanks should be renovated.

The world - international availability and demand

Alcohols, methanol, ethanol and the ether MTBE have been international commodities for several decades, and are registered among international commodities exchanges. The majority of these alcohols are marketed to the chemical process industry.

Today, oxygenates, alcohols and ethers are already used in gasoline for several reasons:

- They act as high-octane components in place of unhealthy lead-additives
- They act as extenders, to reduce the one-sided dependence on oil
- They act as agents for reducing health/environmentally damaging emissions

Ethers - primarily MTBE, but others such as TAME and ETBE - already represent a major product, and their use is expected to expand rapidly in programmes for reformulated gasoline. Natural gas based MTBE has proved to be cost efficient, and ethers are accepted within the oil industry, since they can be handled in the distribution chain without significant problems or added costs compared to alcohols. One exception, however, is storage on beds of water in underground caverns, which has been avoided up to now.

The automobile industry also accepts blends of ether in gasoline for the existing vehicle population.

Refineries and the petrochemical industry can produce large quantities of different types

of ethers by using other olefins than iso-butene, which is used for MTBE.

The alcohol currently used to produce ethers is methanol, derived from fossil natural gas.

However, given the right price, alcohols derived from biomass could be used just as easily. Within a few years it will be possible to produce ETBE (in Sweden) from bio-ethanol (which already exists in the market in small volumes), given the same economic tax incentives that are used for ethanol. These controls worked well to market ethanol from SSEU's project to produce ethanol from lignocellulose. Further down the road, the issue remains undecided as to which bio-alcohol, methanol and/or ethanol should be produced in large volumes.

Bio-origins can be accurately identified using the carbon-14 method.

The use of ethers as components of gasoline reduces emissions of carbon monoxide and hydrocarbons, reduces the potential formation of ozone, and the net discharge of certain poisonous compounds. These gains are what lie behind new American legislation (including a mandatory blending of oxygenates) whose goals stipulate a reduction the above-named emissions by 15 - 25% without increasing discharges of NOx.

Ether oxygenates are also preferred over alcohol oxygenates because they do not increase the volatility of gasoline. From a technical point of view, ETBE has an advantage over MTBE due to its lower volatility, lower water solubility, higher octane content, and a larger contribution as a bio-based compound. MTBE on the other hand, is preferred for its lower ozone-forming potential.

Based on data and several years of experience with MTBE, ethers are not judged to imply any health-related risks to mankind. However, the basis for this judgement is not thoroughly grounded, and should be followed up.

Today, oxygenated gasoline is marketed in two countries on the grounds that its use will benefit health and the environment. In Finland, roughly 80% of all gasoline contains 11% MTBE (fossil; ~ 2 weight-% oxygen). In France *Total* and *Elf Aquitaine* have begun selling oxygenated gasoline, including bio-ETBE. ETBE is used in gasoline in Italy, too.

Conclusions

- Ethers comprise high-quality components in gasoline.
- The use of ethers in gasoline will expand considerably - in part by helping to make gasoline more cost-effective to produce, and in part by meeting new reformulation and environmental class requirements.
- The use of ethers (maximum 2.5 weight-% oxygen) in gasoline reduces net emissions that are damaging to health and the environment without increasing NOx.
- Ethers are used internationally and will become standardised through developments in the USA and within the EC.
- The access to raw materials for ethers based on fossil and biomass sources is not limited.
- MTBE based on natural gas from fossil sources is cost effective, and will be the dominating ether at the international level through the year 2000. Later, it can be phased out and replaced by bio-based sources.
- ETBE is technically superior to MTBE, and will be used if economic tax incentives eliminate its added cost.
- Ethanol for use in ETBE can speed the domestic production of ethanol in planned test plants using the CASH process.
- It is expected that ETBE will begin to be produced in Sweden within 2 - 4 years if the economic tax incentives used for gasoline blends are also applied to ethanol in ethers.
- Long-term economic tax incentives and lasting decisions are a must if industry is to invest in the production of ETBE in Sweden.
- When ETBE is used, carbon dioxide emissions from gasoline-driven traffic in a natural eco-cycle may be reduced by as much as 7%.

OXYGENATES

