1-Butanol as a 2nd Generation Biofuel for Compression Ignition- and Spark Ignition Engine Application

Diplomarbeit zur Erlangung des akademischen Grades Diplomingenieur an der Universität für Bodenkultur Wien

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Abstract

As a result of limited resources, concern about anthropogenic climate change and supply reliability, research is stressed on developing alternative, renewable fuels. The alcohol 1-butanol is seen as one potential substitute for conventional petrol and the common biofuel ethanol and can be produced along similar biotechnological pathways like ethanol. However, 1-butanol from lignocellulose already has partially been established in the past and lots of effort is put in research to re-establish and improve fermentation technologies for future 1-butanol production. This thesis evaluates conventional- and biotechnological production pathways of 1 butanol and examines combustion of 1 butanol in spark ignition- and compression ignition engines under consideration of technical-, ecological-, legal- and economical aspects.

Keywords: 1-butanol, ethanol, 2nd generation biofuels, fermentation, biofuel combustion, Well-to-Wheel analysis;

Directory

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List of Acronyms and Abbreviations

°C	Degree Celsius (to convert to °F: °F = °C x 1.8 + 32)
$\Delta_r H°$	Standard enthalpy change of reaction (101,325 kPa; 25 °C)
% (m/m)	Mass percent
% (v/v)	Volume percent
€	European Euro
ρ	Greek letter 'rho'; representing density
$	US Dollar
a	Anno (year)
ABE	Fermentative process with products mainly consisting of acetone, butanol, ethanol
ASTM	Former ‘American Society for Testing and Materials’; current ‘ASTM International’; a US standardisation organisation
ATP	Adenosine Triphosphate
BASF	Former ‘Badische Anilin- und Sodafabrik AG’; a chemical company
bbl	US Barrel (158,98 L)
BP	Former ‘British Petroleum’; a british energy company
BtL	Biomass-to-liquid
BuOH	Abbreviation for butanol (in this thesis: 1-butanol)
Bu85	1-butanol-petrol blend containing 85 % (v/v) 1-butanol
C	Atomic carbon
CCS	Carbon Capture and Storage
C_2F_6	Hexafluoroethane
CH_4	Methane
CHF_3	Trifluoromethane
$C_6H_{12}O_6$	Glucose (in this thesis: α-D-Glucose)
C_2H_5OH	Ethanol
C_4H_9OH	Butanol
CHP	Combined heat and power (‘Kraft-Wärme-Kopplung’ according to german convention)

CI engine	Compression Ignition engine (diesel engine)
CN	Cetane number (‘CZ-Cetanzahl’ according to german convention)
CNG	Compressed natural gas
CO	Carbon monoxide
CO_2	Carbon dioxide
CoA	Coenzyme A
CO_2eq	Carbon dioxide equivalent
CoA	Coenzyme A
CONCAWE	The oil companies’ European association for environment, health and safety in refining and distribution
COP	Conference of the Parties
CZ	Cetanzahl
DIN	German Institute for Standardisation (‘Deutsches Institut für Normung’)
DOW	Domestic organic waste (one of the two fractions of MSW); not to mistake for the ‘Dow Chemical Company’
DVPE	Dry vapour pressure equivalent
DWV	German hydrogen- and fuel cells association (‘Deutscher Wasserstoff- und Brennstoffzellen-Verband’)
E85	Ethanol-petrol blend containing 85% (v/v) ethanol
EC	Enzyme Commission number (Classification for enzymes)
EJ	Exajoule (10^{18} Joule)
EM	Embden-Meyerhof
EN	European standard (Europäische Norm)
EROEI	Energy Returned On Energy Invested
EtOH	Abbreviation for ethanol
EU	European Union
Euro 4 / -5	European Union vehicle emission standards
EUCAR	European Council for Automotive Research and Development
FAO	Food and Agriculture Organization of the United Nations
Fd	Ferredoxine
FT	Fischer-Tropsch process
G3P	Glyceraldehyde-3-phosphate

Gha	Giga-hectare (10^9 hectares)
GHG	Greenhouse Gas
GJ	Gigajoule (10^9 Joule)
GM	Genetically modified
GMO	Genetically modified organism
Gt	Gigaton (1 billion metric tons)
$GtCO_2eq$	Gigatons CO_2-equivalents
GWP	Global Warming Potential
H	Atomic hydrogen
H_2	Molecular hydrogen
$h\nu$	Indication for electromagnetic radiation from light; (h'nu')
ha	Hectare = 10.000 m^2 (2.471 acres)
HFC	Hydrofluorocarbon
HHV	Higher Heating Value (corresponding to H_s according to german convention)
hPa	Hectopascal (100 Pa)
ICE	Internal combustion engine
IPCC	Intergovernmental Panel on Climate Change
ISO	International Organisation for Standardisation
IUPAC	International Union of Pure and Applied Chemistry
JRC	Joint Research Centre of the European Commission
KDPG	2-keto-3-deoxy-6-phosphogluconate
kJ	Kilojoule (10^3 Joule)
kPa	Kilo Pascal (10^3 Pascal)
kWh	Kilowatt-hour
L	Litre (0,001 m^3)
LBST	Ludwig-Bölkow-Systemtechnik GmbH
LH_2	Liquid Hydrogen
LHV	Lower Heating Value (corresponding to H_i according to german convention)
LiAlH4	Lithium aluminium hydride
LiH	Lithium hydride

LPO	Low-pressure-oxo-process
MeOH	Abbreviation for methanol
MJ	Megajoule (10^6 Joule)
mm^2	Square millimetre
MPa	Mega Pascal (10^6 Pascal)
MSW	Municipal solid waste (divided into DOW - domestic organic waste and HRM - household recyclable material)
N	Atomic nitrogen
$NaBH_4$	Sodium borohydride
NaH	Sodium hydride
NBR	Nitrile butadiene rubber
N_2O	Dinitrogen monoxide (common name: laughing gas)
NO_x	Collecting term for the gaseous oxygen compounds of N (mainly N_2O, NO and NO_2 as N_2O_3, N_2O_4 and N_2O_5 are naturally not stable)
NOK	Normalkraftstoff
O	Atomic oxygen
O_2	Molecular oxygen
OECD	Organisation for Economic Co-operation and Development
Pa	Pascal (1×10^{-5} bar)
PFC	Perfluorocarbon
PM	Particulate matter
PP	Pentose phosphate
ppm	Parts per million
PTFE	Polytetrafluoroethylene (‘Teflon’)
PV-cell	Photovoltaic cell
RCH/RP	Ruhrchemie-Rhône-Poulenc
RON	Research Octane number
SF_6	Sulphur hexafluoride
SIDI engine	Spark Ignition Direct Injection engine (e.g. BMW engines with ‘High Precision Injection’); also referred to as DISI
SL	Storstockholms Lokaltrafik AB (Stockholm’s public transport company)
SO_x	Collecting term for the oxygen compounds of S (mainly SO_2 and SO_3)

SRF	Short rotation forestry
SULEV	Super Ultra Low Emission Vehicle
t	Metric tonne (10^3 kilogram)
ThlA	Thiolase A
TLV	Threshold limit value (corresponding to MAK – 'Maximale Arbeitsplatz-konzentration' according to german convention)
TMOT	Temperature of the engine (motor)
TTW	Tank-to-Wheel
TU	University for technical sciences
UCC	Union Carbide Corporation
UNFCCC	United Nations Framework Convention on Climate Change
USSR	Former Union of Soviet Socialist Republics
VES	Verkehrswirtschaftliche Energiestrategie
VOCs	Volatile organic compounds
WTO	World Trade Organization
WTT	Well-to-Tank
WTW	Well-to-Wheel
$Y_{P/S}$	Yield (product / substrate)

1 Methodology

Against the background of an increased awareness of a potentially man-made climate change and a descent in exploitable fossil resources, biofuels derived from renewable biomass are recently gaining importance. Whereas nowadays their market share worldwide amounts to roughly 1 % (v/v), the current dominating biofuels are biodiesel, a fatty acid methyl ester, and ethanol produced through fermentation of starch- or sugar containing biomass. Butanol, also a monovalent alcohol that is produced fermentatively will show several advantages over ethanol in both, production and combustion.

This thesis' aim is to provide an insight into the current state of research and state-of-the-art production methods for the 2nd generation biofuel candidate 1-butanol.

In giving an overview of the current methods for industrial production of 1-butanol, several sources of literature were collected and various companies were contacted to ensure that the processes presented within this thesis are up-to-date.

Research and development of future pathways in 1-butanol production are main chapters within this thesis and to achieve the objective of providing absolute up-to-date information on processes in development, interviews with researchers in the academia as well as engineers and researchers in industrial companies were performed.

Furthermore, evaluation and comparison of scientific papers in the field of butanol-fermentation was done to substantiate received information.

In an experimental part of the thesis, laboratory testing was done to gain insight in the suitability of 1-butanol as either a blending component or for pure use in spark-ignition- or diesel engines. Therefore, blends containing rising content of 1-butanol where mixed with conventional petrol and diesel respectively.

These blends were used for analysing density, vapour pressure, flash point, water absorption and boiling point curve; additionally, they were fed into a fuel analyser, that checks several physical-chemical properties and compares them to values of hundreds of fuels, stored in a database.

To provide insight into the efficiency and CO_2-neutrality of the biotechnological production process, a well-to-tank analysis was performed and to provide insight into the efficiency of the combustion process of 1-butanol, a tank-to-wheel analysis was also undertaken.

A final well-to-wheel analysis of the overall efficiency and CO_2-neutrality for 1-butanol was undertaken as well.

In addition to that, an assessment of the potential and technical feasibility of 1-butanol's usage as a motor fuel either neat or in petrol- and diesel blends is given.

If not otherwise stated, Otto-engine petrol produced according to the EN 228 within this thesis is referred to as ‘petrol’. Diesel produced according to the EN 590 is referred to as ‘diesel’.

For conversion of the U.S. Dollar into the European Euro the exchange rate of 1 € = 1.41 $, (which equates the average rate during preparation of this thesis) was taken, if not historic rates for statistic accuracy were taken. The average exchange rate for the year 2007 amounted to 1 € = 1.37 $.

2 Introduction

Mobility has been one main desire of mankind since ancient times and a key driver of development and personal progress. Surviving in changing conditions required man to move and adapt to new surroundings. Mobility in modern societies however, is no longer a qualification for personal survival, but for the welfare of the globalised world on the whole. Our societies' wealth is strongly based on the global trade and exchange of goods and personal well-being is heavily dependent on the possibility of individual mobility. Individual as well as commercial transportation for decades has relied on the inexhaustibility of fuels derived from fossil crude oil.

The recent proliferation of biofuel programmes can be attributed to a combination of several factors. The key drivers are shortly described in the following.

2.1 Key drivers to alternative fuels

Public awareness of alternative fuels rose significantly in the industrialised world through the so called 'oil crisis' in 1973 and 1979, and was initialised through man's realisation of negative impacts on the environment by the predominant use of fossil fuels in the 1980s.

Political awareness culminated in 1992, when 191 countries joined a treaty produced at the so called 'Earth summit' in Rio de Janeiro – the UNFCCC, United Nations Framework Convention on Climate Change that went into force in 1994.

The aim of the Convention was to gather and share information and policies on greenhouse gas (GHG) emissions and to concentrate international strategies and policies to address global warming.

The first legally binding action taken was the adoption of the Kyoto-protocol at the 3rd Conference of the Parties (COP 3) on 11th of December 1997.

After hard negotiations with the signing countries, the protocol entered into force on 16th of February 2005, the ninetieth day after at least 55 Parties to the Convention, accounting in total for at least 55 % of the total carbon dioxide emissions, ratified the protocol.

So far 175 parties have committed themselves to cut their emissions of six greenhouse gases by 5 % compared to 1990 in the commitment period 2008-2012.

The gases that contribute to the greenhouse gas effect and are affected by the Kyoto Protocol are [UNFCCC a; 2007]:

- Carbon dioxide (CO_2)
- Methane (CH_4)
- Dinitrogen monoxide (N_20)
- Hydrofluorocarbons (HFCs)
- Perfluorocarbons (PFCs)
- Sulphur hexafluoride (SF_6)

It might be interesting to note that the largest contributor to a natural greenhouse effect is water vapour. It is not directly linked with human activity, but could gain importance in the future, because it potentially forms a ‘positive feedback’ on climate change. As warm air can hold more moisture, a warmer global climate would lead to an increase in water vapour in the atmosphere and further contribute to an enhanced greenhouse effect.

Whereas CO_2 takes the centre stage in the discussion around climate change, it is not among the most harmful man-made substances affecting the global climate. How much a greenhouse gas is contributing to global warming is expressed by its ‘Global Warming Potential’ (GWP), where the radiative force of a gas and its lifetime in the atmosphere are considered for a given time period. The GWP scale is a relative scale referring to CO_2 with a GWP of 1.

Moreover the GWP data (on a 100 years period) is also used for emissions calculation of CO_2-equivalents using the following equation:

$$\text{GtCO}_2\text{eq} = \text{billion metric tons of the gas} \times \text{GWP of the gas}$$

The following table shows the GWP of the six gases affected by the Protocol.

Table 1: GWP for Kyoto Protocol affected GHG referred to CO_2; [IPCC a; 2007] [EPA; 2002]

Greenhouse gas	**Lifetime [years]**	**Global Warming Potential for a given time horizon**	
		20 years	100 years
Carbon dioxide [1] (CO_2)	50 - 200	1	1
Methane [2] (CH_4)	12	72	25
Dinitrogen monoxide (N_2O)	114	289	298
HFCs e.g. CHF_3	270	12.000	14.800
PFCs e.g. C_2F_6	10.000	8.630	12.200
Sulphur hexafluoride (SF_6)	3.200	16.300	22.800

It can be noticed, that methane shows 72 times the warming potential on a 20 years base, whereas on a long term basis of 100 years its warming potential is reduced down to 25 times compared to the potential of CO_2. This is due to the lifetime of the gas in the atmosphere – methane is a short-lived species.

Nevertheless, CO_2 is considered to be the most important greenhouse gas as its concentration in the atmosphere amounting to 380 ppm is significantly higher than methane with 1.8 ppm and dinitrogen monoxide with 0.319 ppm. [IPCC b; 2007]

Between 1970 and 2004 the worldwide CO_2 emissions from use of fossil fuels more than doubled (+ 107 %) to approximately 24 Gt CO_2. [IPCC c; 2007]

Subsequently the anthropogenic emissions of CO_2 are monitored with particular attention throughout the globe and lots of effort is made to cut emissions from carbon dioxide, whereas especially N_2O gains attention in recent discussion on emissions from agricultural activities.

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[1] No single lifetime can be defined for CO_2 because of the interaction in rates of uptake- and removal processes.

[2] GWP of CH_4 includes indirect effects from enhancement of ozone and stratospheric water vapour.

The following figure shows the worldwide contributors to anthropogenic emissions of CO_2 according to sectors.

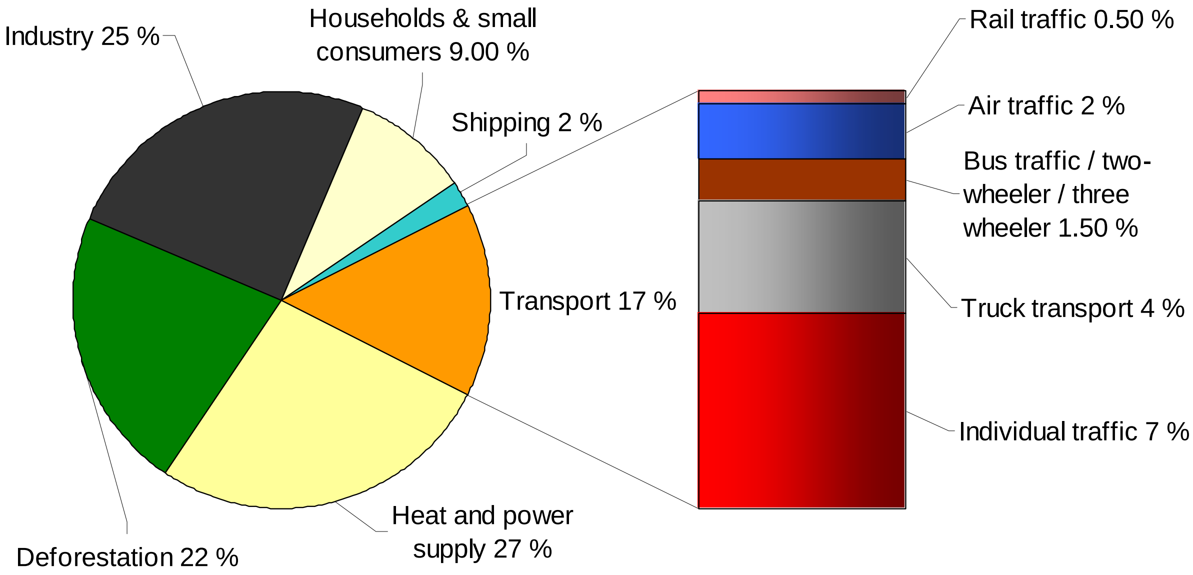


Figure 1: 2004 global anthropogenic CO_2 emissions arranged in sectors; [IPCC d; 2007]

For road bound traffic, which contributes by approximately 12 % to the anthropogenic CO_2 emissions, there is a chance to significantly increase automotive sustainability by blending conventional fuels with biofuels, thus increase overall car efficiency.

However it has to be mentioned that a significant reduction of CO_2, as well as of the other GHG, can only be achieved by the joint efforts of all causing sectors.

As world population increases and economies develop, the growing demand for energy since the industrial revolution is mainly being satisfied by products derived from crude oil.

This becomes clear in Figure 2, which shows the worldwide energy consumption between 1965 and 2006:

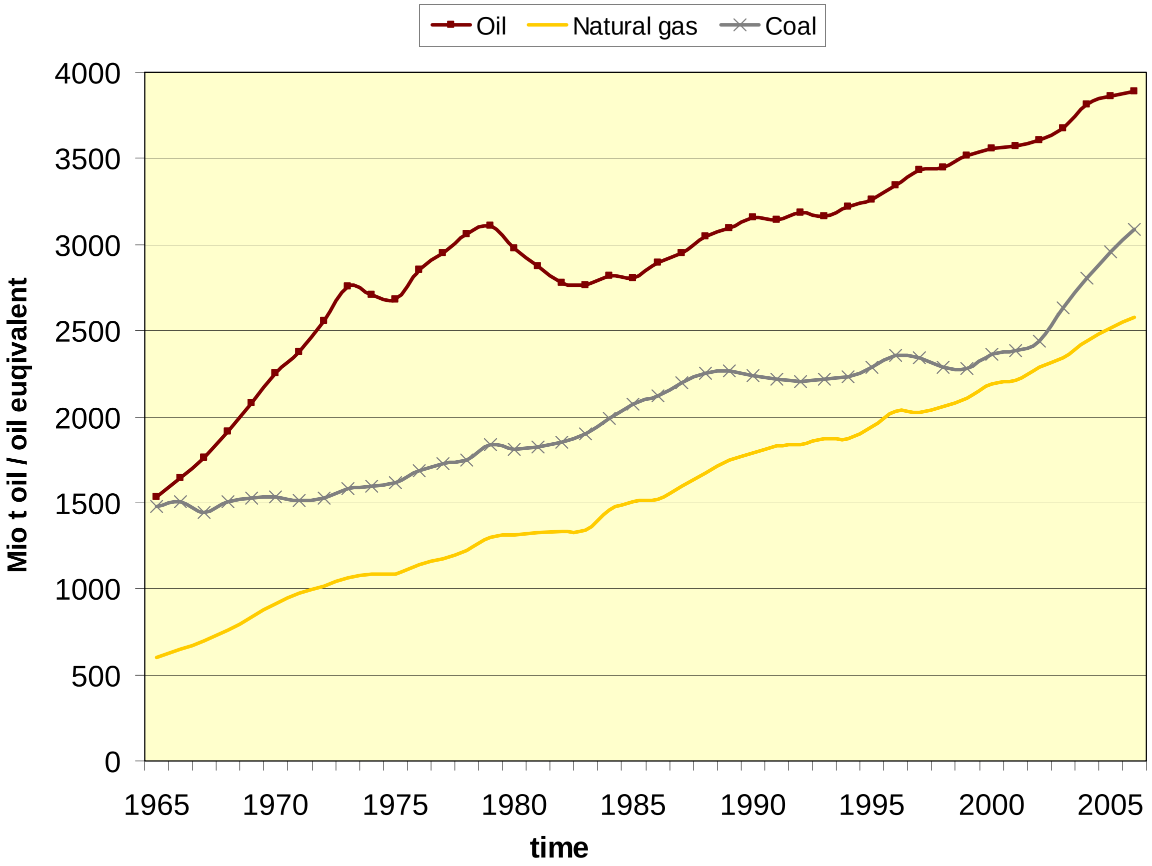


Figure 2: history of oil-, natural gas- and coal consumption between 1965 and 2006; [BP a; 2007]

A growing demand for energy in almost every industrial sector is projected with a worldwide annual growth in personal transport till 2050 of approximately 1.7 %. Road transportation of freight using heavy duty trucks will increase as well by 2.4 % annually up to 2050. [WBCSD a; 2004]

Blending fuels from petrochemical production with fuels of biotechnological production are seen as one near–term path of cutting growth of fossil fuels in automotive transportation.

Another fact that speaks for turning away from fossil fuels is the rising issue of dependency from countries which offer instable political conditions. An economic positive outcome of a more decentralised production of fuels would be the creation of value on a more regional basis.

This is especially of interest along the value chain of biofuels, as the cultivation of biomass could help less developed countries to establish an additional field of income (presuming a properly organised framework of trade).

2.2 Potential of biomass derived fuels

Energy derived from biomass (mostly in the form of wood) has been used on our globe for centuries. The industrial revolution, spreading out from the United Kingdom in the late 18th - and beginning of the 19th century has shifted the world from agricultural societies towards industrialised economies.

In the past decades application of biofuels declined to gain attraction again during recent years.

The benefits of biofuels are numerous, as they are being produced from renewable feedstock that can be grown by farmers, can have a positive local impact on economic value chains, may be produced in a sustainable manner and can be integrated relatively easily in the established infrastructure.

Moreover biofuels are seen as the only near-term substitute for petroleum fuels as they can be delivered through arranged logistics and can be combusted either blended or pure in conventional petrol and diesel engines without or with minor changes.

Yet propagation of biofuels causes drawbacks and challenges that have to be addressed (see Chapter 7 for details).

When judging the technical potential of biomass derived fuels it is important to differentiate between 1st generation biofuels and biofuels of the 2nd generation.

Feedstocks for **biofuels of the 1st generation** are harvested for their content of sugars (e.g. sugar beet, sugar cane), starch (e.g. corn, wheat) or oil (e.g. rape seed, soybean, jatropha) and can be converted into liquid fuels by means of conventional methods like transesterification for production of fatty acid methyl ester (FAME), commonly referred to as ‘Bio-Diesel’, or fermentation of sugars and starch for production of ethanol. The methods for producing biofuels of the 1st generation are well established and rolled out comparatively broadly in Europe and the American continent.

Feedstock for **biofuels of the 2nd generation** contains those crops and plants suitable for 1st generation-biofuels, plus any other cellulosic biomass. In contrast to 1st generation feedstock, not only sugars, starch or oil can be converted, but the whole lignocellulose containing biomass. Crop residues, tall grasses and wood are expected to significantly expand the quantities and types of feedstock available for production. Furthermore the growing competition for land between food crops and energy crops is expected to diminish, as greater amounts of biomass and residues from crop cultivation can be used for biofuel production.

When judging the efficiency of secondary energy ‘produced’ via biomass or comparing energy from biomass with energy obtained from wind power or solar energy, the efficiency of photosynthesis also shall be taken into consideration.

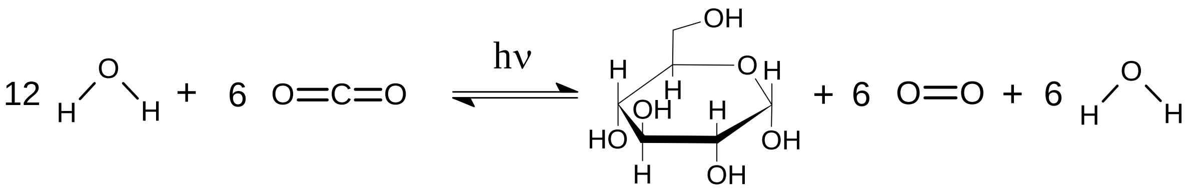
2.3 Photosynthesis efficiency assessment

Green plants are photoautotrophic organisms, meaning that they metabolise the carbon needed for energy and growth via inorganic CO_2 and the help of light and water.

Location of photosynthesis in the plant is the chloroplasts, specified compartments in the cells of the leaves, containing the pigment chlorophyll. One square millimetre (mm^2) of a green leave contains approximately 500,000 of these chloroplasts.

In these compartments of the cell, water and carbon dioxide react under influence of light to glucose and oxygen.

The brutto reaction of photosynthesis can be noted as follows (‘hν’ indicates electromagnetic radiation in form of light):



$$\mathbf{12\ H_20\ +\ 6\ CO_2 \longleftrightarrow C_6H_{12}O_6\ +\ 6\ O_2\ +\ 6\ H_20}$$

Figure 3: brutto reaction of the photosynthesis;

It should be noted that all the oxygen occurring in the reaction stems from water. This is considered by noting 12 molecules of water (instead of 6).

Supply of water and CO_2 as well as release of the products oxygen and water is managed by small pores on the underside of the leave’s surface.

Generally spoken the energy of solar insulation is converted into chemically bound energy of glucose, oxygen and water.

Glucose is often considered to not be a direct product of photosynthesis as the final product in the photosynthetic Calvin cycle is glyceraldehyde-3-phosphate (G3P). However, G3P is commonly metabolised further to starch and its transportable form glucose.

Photosynthesis is not a process of high efficiency, due to the occurrence of the following limitations:

- ~ 12 % of the annual insulation reaches the leaves
- ~ 50 % of the radiative spectrum is photosynthetically active (360 - 720 nm)
- ~ 85 % of that radiation is captured by the leaves
- ~ 21 % of which is photosynthetically converted into energy
- ~ 40 % are consumed by the plant (in photorespiration sustaining the plant)

This leads to an **efficiency of the photosynthesis** process in **C3-plants** of **approximately 5.4 %**.

Tropical **C4-plants** achieve through their differing metabolism (Hatch-Slack-pathway) slightly higher rates of photosynthesis efficiency of **roughly 6.7 %**. [Boyle a; 2004]

Besides theoretical conversion efficiency of solar energy, the overall yield of plants per hectare and year obviously depends on many factors as location, climate and weather, soil, nutrients and water supply.

According to an LBST (Ludwig-Bölkow-Systemtechnik GmbH) study (‘*Woher kommt die Energie für die Wasserstofferzeugung*’; 2006), the obtained energy in GJ fuel per hectare shows low values for biomass derived fuels compared to fuel (hydrogen) produced through electrolysis from photovoltaic (PV) current or wind power. The yields for hydrogen derived from wind power are estimated to amount to the double compared to hydrogen production from biomass (through short rotation forestry), while a production of hydrogen through PV-cells would lead to yields of approximately 650GJ per hectare and year. This is approximately 8 times the hydrogen yield obtained through conversion of short rotation forestry cultivation with approximately 80 GJ per hectare and year. [LBST a; 2006]

Yet, the economics are not being considered in the LBST-study. The drawbacks of higher conversion rates of solar insulation for PV-cells compared to photosynthetically produced biomass are significant higher prices for installation and maintenance. Biomass is plentiful (cellulose is the most abundant natural polysaccharide in the world) and comparatively cheap. Therefore biomass cultivation so far can be rated as an economic way of converting and storing energy.

3 Butanol – facts and figures

Generally speaking, alcohols can be described as derivates of water, where one hydrogen atom is displaced by an alkyl group, in case of 1-butanol by the butyl group CH_3-CH_2-CH_2-CH_2-.

1-butanol, CH_3-CH_2-CH_2-CH_2-OH (also referred to as *n*-butanol, butan-1-ol or butyl alcohol) can generally be produced along two different pathways. First is a petrochemical pathway which is well established for decades now, and second is a biotechnological pathway, that also was in use in former days but has been outstripped by the production on a fossil basis.

Butanol and other alcohols that are being produced along a biotechnological pathway are sometimes termed with the prefix '*Bio-*' to indicate a sustainable production process. It should be noted that 'Bio' among biofuels does not refer to any organic way of producing the feedstock, but the biological origin. Anyway, the chemical entity of course is unaffected by the method of production.

According to the International Union of Pure and Applied Chemistry (IUPAC) systematic definition saturated alcohols are being considered as derivates of alkanes, which leads to their IUPAC denotation of 'alcanols'.

Depending on the position of the hydroxyl group (-OH), the structure is numbered in such a way, that the hydroxyl group receives the lowest number starting from one end of the alkyl group.

According to that, 1-butanol, as one of the 4 isomers of C_4H_9OH (1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol), carries one hydroxyl group at its first position.

With the molecular formula CH_3-CH_2-CH_2-CH_2-OH, 1-butanol is also a primary alcohol, meaning that the carbon atom carrying the hydroxyl group is connected to one other carbon atom.

Figure 4 shows a space-filling model of 1-butanol, where carbon atoms are in grey, hydrogen atoms in white and the oxygen atom in red. For demonstration reasons, the length of bonds has been distended.

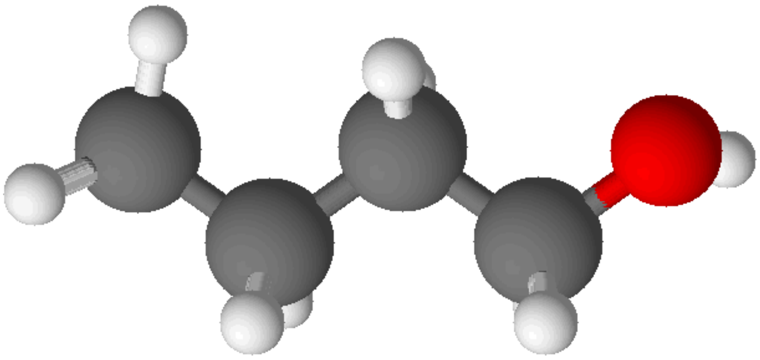


Figure 4: space filling model of 1-butanol;

The physical as well as chemical properties of the alcohols are determined significantly by the presence and position of the functional groups (alkyl- and hydroxyl groups).

Correspondingly, 1-butanol shows considerably different properties in comparison to other alcohols.

The following part gives an overview of 1-butanol's properties that would be of interest in automotive transportation.

3.1 Physical and chemical properties with fuel relevance

1-butanol is a combustible colourless liquid (at room temperature) with a very slight smell of banana and a **density** of 814 kg/m^3 (at 15 °C).

As a result of the presence of oxygen in the molecule's structure, 1-butanol is polar like all alcohols, which leads to intermolecular electrostatic forces. These hydrogen bonds allow the molecules to associate via the hydroxyl group and lead to an increase of the average boiling point by more than 100 °C compared to the corresponding alkane butane (- 0.5 °C). Accordingly, 1-butanol shows a **boiling point** of 117.7 °C.

But not only the boiling point is affected; also the **solubility in water** is determined by the hydrogen bonds. Since the hydroxyl group tends to interact with the positive partial charged hydrogen in the water molecule, it is called hydrophilic. However, the alkyl chain of the molecule is not capable of forming hydrogen bonds and therefore called hydrophobic. These two contrary forces lead to the difference in solubility of the alcohols as the hydrophobic forces increase, the bigger the alkyl chain is. This also becomes manifest in 1-butanols **hygroskopy**, which is by far lower than that of ethanol, for details see the Appendix section 'Results from laboratory testing' (available only in BMW-internal version).

One important reason why 1-butanol is seen to be advantageous over ethanol in the fuel delivery is that ethanol is miscible with water in any proportion, while 1-butanol is miscible with water in low amounts only (see Table 2 for details).

Another property that is dependant on the length of the alkyl chain and the potential to form hydrogen bonds is vapour pressure. As the alkyl chain increases, the vapour pressure decreases, because intermolecular forces between unpolar, hydrophobic alkyl chains – Van der Waals forces – rise. [Kosma a; 2001] The vapour pressure is a main factor when judging cold-start capability of a fuel. 1-butanol, with a **vapour pressure** of 0.67 kPa shows a rather low value, which could lead to cold-start problems in higher petrol blending rates under cold climate conditions. This issue does not apply for diesel blends, as diesel shows a vapour pressure in the magnitude of 1-butanol.

Combustibility, one main property for auto ignition demanded by diesel fuels, is detected by DIN 51773 and ISO 5165 and expressed through the cetane number (CN or german CZ). Combustibility of primary, monovalent alcohols rises with the number of C-atoms, whereas values in the dimension of diesel fuels are not obtained. 1-butanol has a cetane number of < 18, while Diesel shows cetane numbers of minimum 51. [Sperling a; 1988] [OMV a; 2007]

Another important factor among fuel requirements is **viscosity,** which plays a major role in the construction of fuel injection systems. The viscosity of 1-butanol lays in the magnitude of Diesel's viscosity and is lower than the viscosity of petrol. As a result, no major issues regarding injection nozzles and seal gaps ascribed to viscosity are anticipated.

Complete combustion of alcohols leads to gaseous products of CO_2 and H_2O, as Figure 5 illustrates.

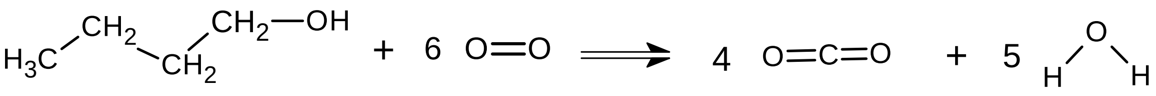


Figure 5: combustion reaction of 1-butanol (structure formula);

Per litre of 1-butanol combusted approximately 1933 g of CO_2 and 988 g H_2O vapour (referred to as water of combustion) occur. In comparison to the resulting amount of water from combustion for the same energy density, 1-butanol produces ~ 1.6 times more water than petrol. Within the scope of motor combustion it is not the masses or volumes of fuels that are relevant, but the energy density of the fuel.

Energy density or energy content usually is expressed by the calorific value. The Higher Heating Value (HHV, or H_s according to german convention), or gross calorific value is equal to the thermodynamic heat of combustion or reaction enthalpy and takes account of the enthalpy of evaporation of gaseous products, especially water, when all products show a temperature of 25 °C.

As this value is not very meaningful for combustion processes among fuels containing hydrogen, instead of the HHV, the **Lower Heating Value** (**LHV,** or **H_i** according to german convention), or net calorific value is commonly being used. The LHV usually is lower than the HHV as the enthalpy of evaporation is not being considered, because it usually cannot be obtained in combustion processes. For calculation of the HHV water is assumed to be present in liquid state at 25 °C, while in calculations of the LHV water is assumed to leave the observed system in gaseous state.

The energy content of a molecule is dependent on its compositions of elements. The higher the oxygen proportion in a molecule, the lower the LHV; due to that reason longer chained monovalent alcohols are advantageous over short chained and polyvalent alcohols.

To satisfy the demand for high energy content and to meet the comfort of a liquid fuel only a small range of alcohols comes into question for motor combustion. Methanol e.g. has rather low energy content as its oxygen content is 50 %, while 1-butanol shows a higher energy content as its higher proportion of C and H corresponds to an O content of 21.6 %. So far only liquid fuels are seen to have a chance on the biofuels market, because solid as well as gaseous fuels either need radical changes in motor-, storage applications and distribution infrastructure or provide a poor energy-per volume-ratio.

As the Van der Waals forces increase with the length of the alkyl group, reactivity decreases and by that, melting- and boiling points increase. 1-heptanol e.g. would provide an even higher content of energy, but merges into solid state at - 34 °C. [Kosma b; 2001]

Under severe climate conditions, however, this fuel could lead to troubles in motor- and distribution applications. 1-butanol would provide both, a liquid state of aggregation down to - 89.2 °C and high energy content, while potentially being produced biotechnologically.

The following figure points out 1-butanol meeting the mentioned requirements fairly well.

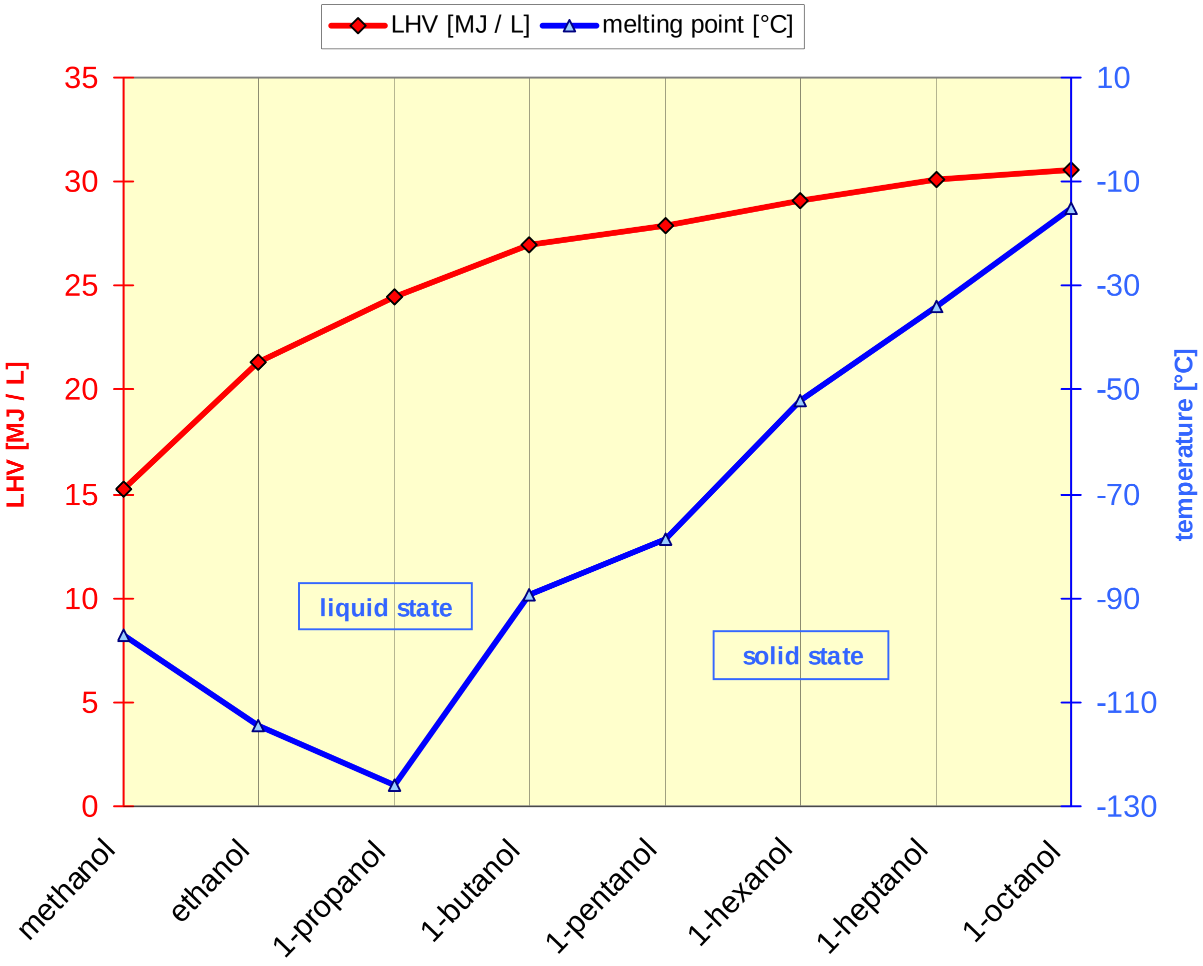


Figure 6: Lower Heating Value and melting points of monovalent alcohols;

The unexpected course of the melting points along the curve shows the influence of two chemical phenomena:

As mentioned before, the alcohols may interact via hydrogen bonds through their hydroxyl group. As the influence of the hydroxyl group decreases with the alkyl chain growing, the intermolecular power of hydrogen bonds decreases, leading to a lowering of the melting point.

In contrast to the decreasing force of hydrogen bonds, the Van der Waals-forces gain influence with growing length of the alkyl chain. This leads to an increase in the melting points after 1-propanol along the curve.

The LHV / H_i for 1-butanol amounts to 26.96 MJ / L (7.49 kWh / L).

In order to achieve the same energy output in an engine, more alcohol has to be combusted compared to petrol or Diesel, which leads to an increase in the amount of water in the of combustion.[3]

This leads to an increase in the heat capacity of the fuel gas, which manifests itself in a lower thermal load for components in the combustion chamber.

As the temperature of the fuel gas decreases, the production of thermal **NO_x** is lower, while the numbers of unburned hydrocarbons increases, compared to combustion of petrol or Diesel. [Sperling b; 1988]

Oxygen content of a fuel is another important factor for combustion and energy content. According to EN 228 fuels may not show higher oxygen content than 2.7 % (m/m). As oxygen content in Ethanol amounts to ~ 35 % (m/m) and in Butanol to 21.6 % (m/m), 1-butanol can be blended in higher rates than ethanol with gasoline within the norm EN 228.

The following table gives a comparison over 1-butanol's properties as well as chemical-physical properties of petrol and Diesel and other biofuels of interest.

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[3] compared to Diesel, 1.3 x the volume of 1-Butanol has to be combusted; compared to petrol 1.2 x the volume of 1-butanol has to be combusted;

Table 2: chemical-, physical- and safety properties of selected fuels;

properties in comparison

	unit	**1-butanol**	**ethanol**	**E85**	**petrol (DIN EN 228)**	**diesel (DIN EN 590)**
molar mass	[g/mole]	74.12	46.07	-	80-110	
density (15 °C)	kg/dm^3	0.814	0.7894	0.7845	0.720 – 0.775	0.820 – 0.845
vapour pressure (20 °C)	kPa	0.67	5.87	not determined	35 - 90	≤ 1
dynamic viscosity	mPa*s	2.95 (20 °C)	1.20 (20 °C)	not determined	5.30 (40 °C)	1.64 – 3.8 (40 °C)
boiling point / boiling range (1013 hPa)	°C	117.7	78.3	30-220	30-215	170 - 390
flash point	°C	34	12	< -21	-40	> 55
ignition temperature	°C	340	425	385	320 / 325 (winter / summer)	≥ 200
lower explosion limit (20 °C)	% (v/v)	1.4	3.1	2.2	0.8 / 0.7 (winter / summer)	0.6
upper explosion limit (100 °C)	% (v/v)	11.3	27.7	25.5	8.1 / 7.6 (winter / summer)	6.5
net calorific value per volume	MJ / l	26.96	21.34	22.1	32.2 – 32.9	35.2 – 36.3
net calorific value per volume	kWh / l	7.49	5.93	6.14	8.9 – 9.1	9.7 – 10.0
net calorific value per mass	MJ / kg	33.28	27.01	28.5	42.6 – 45.7	42.9
net calorific value per mass	kWh / kg	9.24	7.50	7.92	11.8 – 12.7	11.9
research octane number (RON)		94	129	104	95 (min)	--
motor octane number (MON)		80	103	unknown	85 (min)	--
air-to-fuel ratio		1 : 11.1	1 : 8.9	1 : 9.6	1 : 14.7	1 : 14.5
CO_2 emissions of combustion	g/l	1933	1511	1591.4	2334.8 – 2513.2	2641.6
CO_2 emissions of combustion	g/MJ	71.70	70.81	72.01	72.5 – 76.4	72.7 - 75
solubility in H_2O (20 °C)	% (w/w)	7.7	unlimited	not determined	not determined	--
solubility of H_2O (20 °C)	% (w/w)	20.1	unlimited	~ 1	0.012 – 0.02	~ 0.042
threshold limit value (TLV / MAK)	ppm (ml/m^3)	100	1000	1000	-- *	200

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* for carcinogenic substances no TLV / MAK is provided

4 Petrochemical production

Throughout the year 2007 a global consumption of 6.3 million metric tons of 1-butanol can be estimated. Since 2001, the yearly demand for 1-butanol has constantly risen approximately 3 %.

Whereas 1-butanol's use as a biofuel shall base on an environmentally sustainable way, it is important to consider current industrial production of 1-butanol for future comparison of efficiency and economic competitiveness of the biotechnological process.

Most of the 1-butanol, commonly referred to as oxo-alcohol because of mainly being produced via the 'oxo-synthesis' is widely used in the chemical industry as a base product for other chemicals, as a solvent, as plasticizer, flotation agent or other chemical and cosmetical purposes. [Dow a; 2006]

Currently almost 100 % of 1-butanol demanded by the chemical industry is produced in the field of petrochemistry (status September 2007). [Schwarz a; 2007]

1-butanol can petrochemically be produced through several methods, while only a few have present industrial importance.

- Hydroformylation (oxo-synthesis)
- Reppe process
- Hydrogenation of crotonaldehyde

Within this thesis only the ones mentioned above, which have current industrial relevance, are being introduced:

4.1 *Hydroformylation of Olefins*

The process of hydroformylation, also referred to as 'oxo-synthesis' - detected and developed in 1938 by the german chemist Otto Roelen - represents the world's oldest and with approximately 6 Mio t/a products one of the most important homogenous catalytic processes. [Münnich; 2001 S 5]

Roelen incidentally found out that alkenes react simultaneously with CO and H_2 by forming oxygenated products i.e. aldehydes. [TU Braunschweig; 2007]

The prefix 'oxo' indicates - according to IUPAC – an oxygen atom doubly bounded to carbon or another element (e.g. in aldehydes, ketones, esters). [IUPAC a; 2007]

The 'oxo-synthesis' so far is the most important production process for 1-butanol among the petrochemical production pathways mentioned above.

4.1.1 Chemical description

The process of oxo-synthesis is called homogenous catalytic as both the reactant as well as the catalyst are present in liquid phase.

Propene, usually obtained by catalytic- or steam cracking of Naphtha, is being processed into aldehydes in presence of a catalyst and syngas (synthesis gas – a gas mixture containing CO and H_2 in varying proportions).

The obtained *n*-butyraldehyde (*n*-butanal) is the most important product of hydroformylation.

Apart from the linear *n*-butyraldehyde also the branched 2-Methylpropanal (*iso*-butanal) is generated, whereas the demand for *iso*-butanal is significantly lower, so research was stressed to increase *n*-butyraldehyde yields. In the 1990's at last *n* : *iso*-ratios of 99 : 1 could be reached. [Münnich a; 2001]

Typical reactor conditions are 100 bar and 90 °C - 150 °C. [TU Braunschweig; 2007]

The resulting *n*-butyraldehyde (*n*-butanal) can immediately be hydrogenated to 1-butanol, whereas small amounts of alcohol are already generated above 140 °C. [Ullmanns a; 1974] Industrially, approximately half of the *n*-butyraldehyde is further processed to 1-butanol, the other half is being processed to 2-ethylhexanol. [Miyagawa a; 2002]

Cobalt hydro carbonyl [$Co(CO)_4H$], with the catalytic active form of Di-Cobalt carbonyl [$Co_2(CO)_8$], these catalysts are nowadays almost completely displaced by the more expensive rhodium catalysts boosting up the reaction speed by up to 10^4 times. [Ullmanns b; 1974;] [Münnich b; 2001]

Figure 7 shows the principle chemical reactions happening during Hydroformylation of propene:

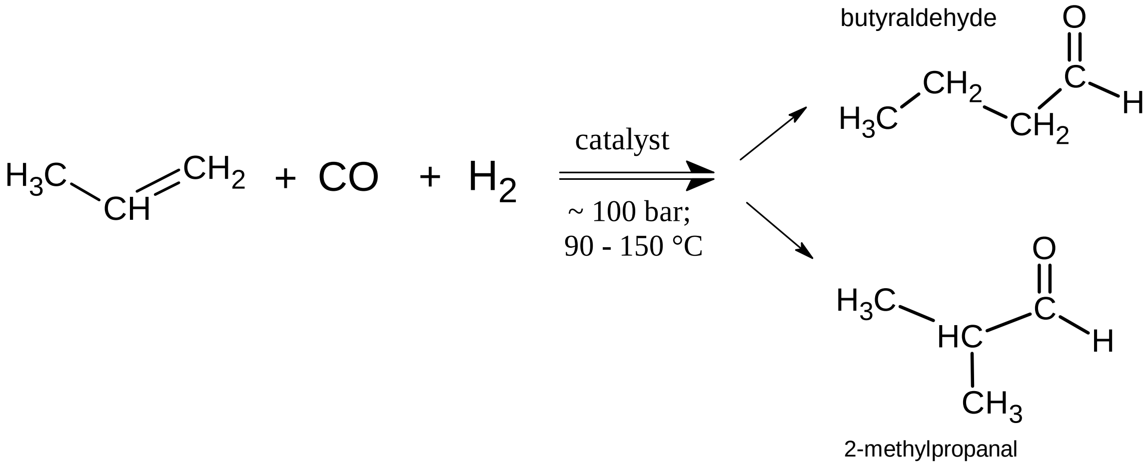

Figure 7: hydroformylation of propene;

Near the end of the 1960’s Pruett and Wilkinson introduced triphenylephosphine-rhodium-complexes. These catalysts have stabilizing properties and allowed higher yields and milder conditions of hydroformylation at approximately 90 – 110 °C and 1 – 40 bar, which lead to a decrease in expenditure for heating and compression, though rhodium catalysts require more sophisticated processes in catalyst recycling. [Kupka a; 2007]

From that the more expensive triphenylephosphine-rhodium is quickly redeemed. [Münnich b; 2001] This further developed process is described as Low-pressure-oxo-process (LPO).

To obtain 1-butanol, the butyraldehyde is hydrogenated with complex metallic hydrides, such as sodium borohydride ($NaBH_4$) and Lithium aluminium hydride ($LiAlH_4$) or by catalytic hydrogenation. [Kosma c; 2001] [Vollhardt a; 2000]

Compared to their simple hydrides NaH and LiH, $NaBH_4$ and $LiAlH_4$ show a better solubility in organic solvents, which makes them the preferred substances.

4.1.2 Technological description

The first industrial process of hydroformylation was a discontinuous process developed 1940 by ‘Oxo GmbH’, a joint venture between ‘BASF’, ‘Henkel’ and ‘Ruhrchemie’.

All of the current facilities in use are working continuously.

Table 3: properties of industrial oxo-processes; based on [Münnich c; 2001]

process	**BASF**	**Shell**	**Ruhrchemie**	**UCC (Dow)**	**Ruhrchemie-Rhône-Poulenc (OXEA)**
active complex	$Co(CO)_4H$	$CoL(CO_3)H$	$Rh(CO)_4H$	$RhL_3(CO)H$	$RhL_3(CO)H$
catalytic centre	Cobalt		Rhodium		
temperature [°C]	150 – 180	160 – 200	100 – 140	60 – 120	110 – 130
pressure [MPa]	20 – 30	5 – 15	20 – 30	1 – 5	4 – 6
products	aldehydes	alcohols	aldehydes	aldehydes	aldehydes
n / iso -ratio	80:20	88:12	50:50	92:8	95:5
by-products	medium	many	little	little	little
reconditioning of reaction mixture	different	pressure distillation	different	rectification	phase separation

Among the oxo processes the 'Shell-process', employed by the Shell Chemical Company receives a special role, as it is the only process where hydroformylation of alkenes and hydrogenation of the intermediate aldehydes take place in the same reactor simultaneously. A catalyst is used that is believed to be of cobalt type. The process is mainly established to produce C12 - C15 alcohols.

Among the conventional processes for 1-butanol production two important processes will be introduced in detail:

4.1.2.1 The UCC process

Most of the plants developed to the low-pressure-oxo-process (LPO) are working to the UCC-process – named after 'Union Carbide Corporation' where catalyst and products are separated thermally. [Münnich d, 2001]

Licensing of this process is allocated under 'Dow Chemical Company', which bought Union Carbide Corporation in 2001.

Figure 8 shows the principle scheme of the UCC process.

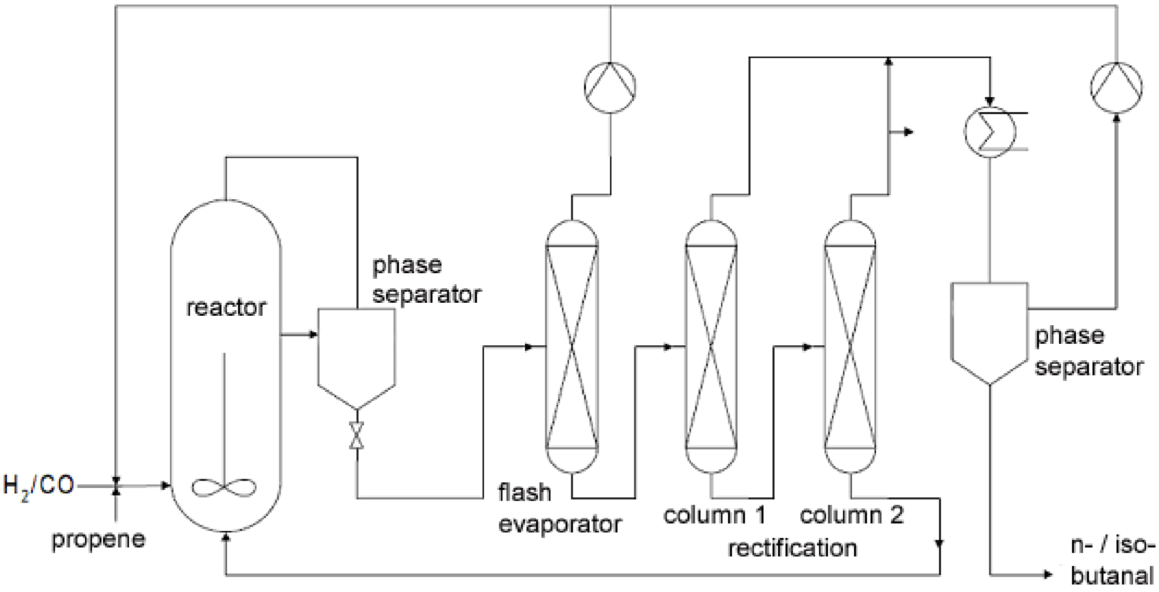

Figure 8: **scheme of the modern UCC process; own description 2007; based on [Münnich e, 2001]**

The Hydroformylation of propene takes place in liquid phase and under conditions mentioned above.

A mixture of aldehydes, the catalyst complex and highly boiling aldehyde products leaves the reactor and passes a phase separator, where gaseous products are drained back to the reactor.

The liquid phase is led into a flash evaporator, where propene, which did not undergo the reaction, is removed and led back to the reactor to undergo the hydroformylation again.

A first separation step of aldehydes and catalyst happens in the first rectification column, whereas a further separation step takes place in the second column, where the catalyst, solved in the condensate, is being led back to the reactor. The obtained product streams are recondensed, again phase-separated and leave the process as liquid products.

As rectification conditions are getting sharper with chain length of the alkene, this process can be used for olefins up to C8, because required column-conditions would otherwise seriously harm the catalyst. [Münnich e; 2001]

4.1.2.2 The Ruhrchemie-Rhône-Poulenc process

The first commercial use of water-soluble Rhodium catalysts was implemented by Ruhrchemie (RCH) and Rhône-Poulenc (RP) in 1984.

Core of this process is the liquid-liquid two phase technique where the catalyst is solved in an aquatic phase (by help of a sodium salt anchored to the ligand) and an organic phase, where *n*- and *iso*- butanal are solved. The advantage of this process is the easier separation of the catalyst by simple phase separation that lowers the energetic expenses of the process significantly as thermal and apparatus intensive methods of separation are not necessary. [Münnich f; 2001] [Kupka b; 2007]

Figure 9 shows the scheme of the RCH/RP process:

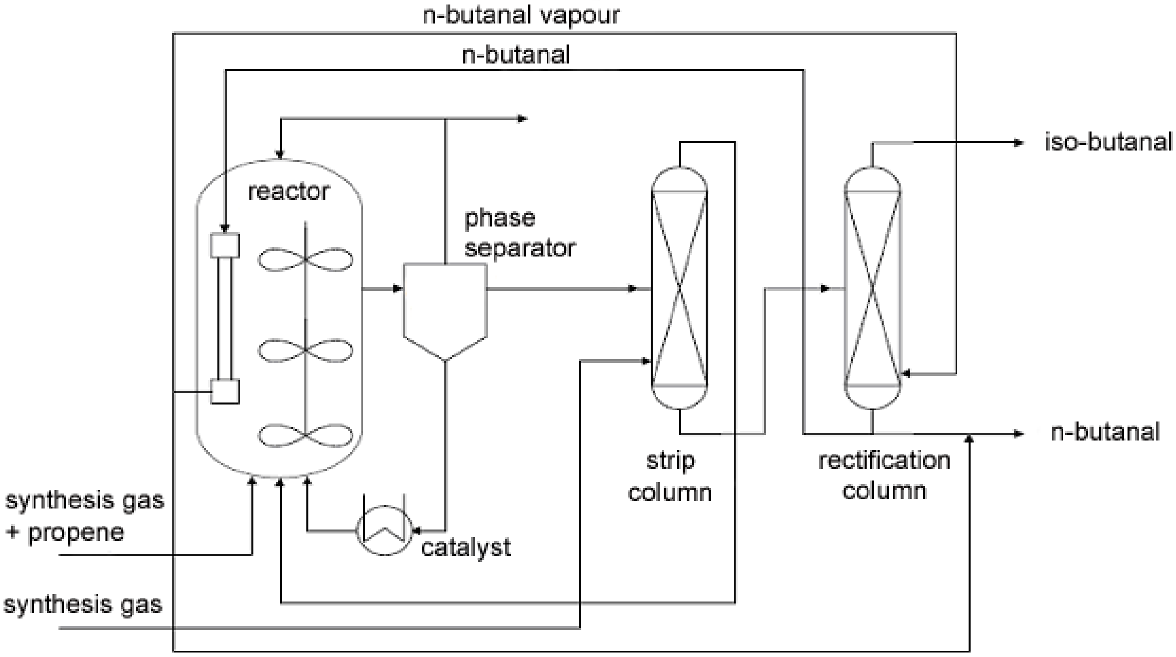

Figure 9: principle scheme of the Ruhrchemie-Rhône-Poulenc process; based on [Münnich e, 2001]

Propene and synthesis gas are continuously fed into the reactor, in which the catalyst is present in aqueous phase. The reaction happens in the barrier layer between aqueous and organic phase. After intensive stirring, the mixture is lead into the phase separator where gaseous substances that did not react as well as the catalyst are lead back into the reactor and undergo the process again.

The organic phase consisting of the aldehydes passes a strip column, where unreacted propene is separated from the aldehydes by feeding fresh synthesis gas. The following rectification step leads to a separation of *iso*- and *n*-butanal.

The required heat is provided by the enthalpy change of reaction of the hydroformylation process. [TU Braunschweig; 2007] [Münnich g; 2001] [Kupka b; 2001] Because of the decreasing solubility of higher alkenes in the aqueous barrier layer, with increasing length of the alkyl chain the process is brought down to an uneconomical level, which cannot be avoided by use of co-solvents, as losses in catalytic material would follow. As a consequence, the Ruhrchemie-Rhône-Poulenc process is not used for alkenes longer than C6. [Münnich g; 2001]

4.1.2.3 Production of aldehydes through catalytic hydrogenation

Irrespective of the processes in which the aldehydes are obtained, they have to be hydrogenated to obtain the demanded 1-butanol. This process is chemically called catalytic hydrogenation and is, in opposite to the hydroformylation, a heterogenic catalytic reaction. That implies a difference in the state of aggregation; hence the insoluble catalyst is fixed onto a carrier material with huge surface (e.g. active coal) and suspended in the reaction medium.

Palladium, nickel and platinum commonly serve as catalysts for these applications. [Universität Tübingen; 2007], [Vollhardt a; 2000]

Atomic hydrogen is bound to the catalyst and reacts with the *n*-butanal to form 1-butanol. Presence of the catalyst is necessary, as the binding energy of H_2 of 435 kJ / mole is too high, as atomic hydrogen would occur under the dominating thermal conditions. [Vollhardt b; 2000]

Figure 10 shows the chemical reaction.

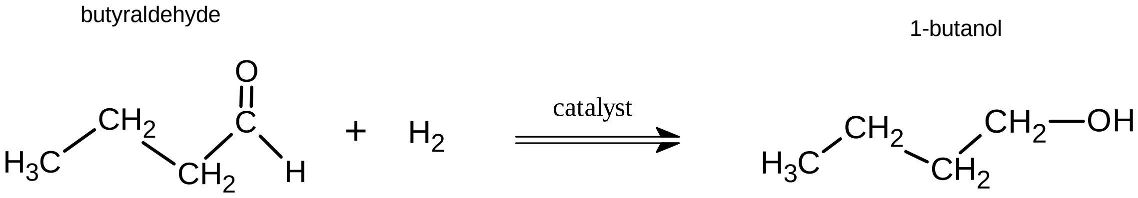

Figure 10: catalytic hydrogenation of butyraldehyde; [Vollhardt a; 2000]

4.1.2.4 Hydrogenation of aldehydes through metallic hydrides

Chemically considered, the hydrogenation process using complex metallic hydrides to obtain alcohols is a nucleophilic addition.

Hydrogen is a very weak acid, as a result the H^- -Ion (Hydride) is a very strong base, hence a good donor of electrons with a high nucleophilic power. [Sykes a; 2001]

Oxygen as a highly electronegative element leads to a polarity of the carbonyl group in the aldehyde molecule, causing a local positive partial charge at the carbon atom and resulting in an ideal target for nucleophilic species like H^-.

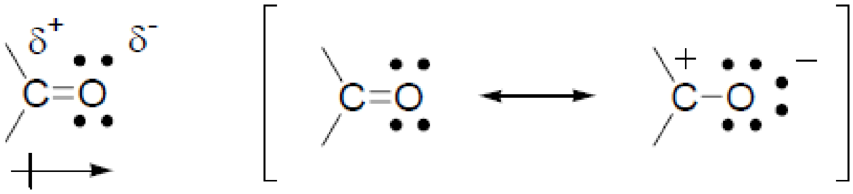

Figure 11: partial charge in the carbonyl group; [Universität Tübingen; 2007]

Depending on the chemical used as Hydride donor, different mechanisms occur:

Mechanism using $NaBH_4$:

Hydrogenation with sodium tetrahydridoborate [$NaBH_4$] is usually done in ethanol or ethanol-water-mixtures.

One H^- of the $NaBH_4$ is transferred to the electrophilic C in the carbonyl group, while the oxygen in the carbonyl group is protonated through the solvent. The chemical reaction is shown in Figure 12.

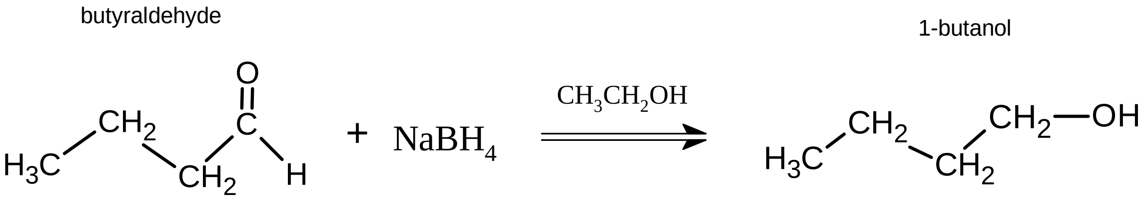

Figure 12: reduction of butyraldehyde using $NaBH_4$; product tetraethoxyborate $B(OCH_2CH_3)_4^-$ disregarded; based on [Vollhardt a; 2000]

The occurring sodium ethoxyborohydride [$NaH_3BOCH_2CH_3$] contains three further hydrides that can target three more carbonyl groups before the reaction is terminated with the presence of tetraethoxyborate [$B(OCH_2CH_3)_4^-$]. [Universität Tübingen; 2007]

Mechanism using $LiAlH_4$:

The basicity of AlH_4^- is significantly higher than of BH_4^-,as H^- is weaker bound to Aluminium which means that reduction of aldehydes cannot be done in solvents containing hydroxyl groups (-OH), as this would result in an abstraction of a proton of the hydroxyl group and lead to an intensive and vigorous production of hydrogen gas. [Sykes b; 2001]

Therefore water free ethers (e.g. diethyl ether), tetrahydrofuran or 1,4-dioxane, are in use. [Universität Tübingen; 2007]

The nucleophilic power of hydride leads to alkoxy aluminium hydride that can reduce three more carboxyl groups that are then bound to the molecule.

In a second step, aqueous solution is added, which destroys excessive reagent and hydrolysates the lithium-tetra-alkoxy-aluminium hydride and thus releases the 4 molecules of 1-butanol.

Figure 13 shows the principle of the reactions taking place.

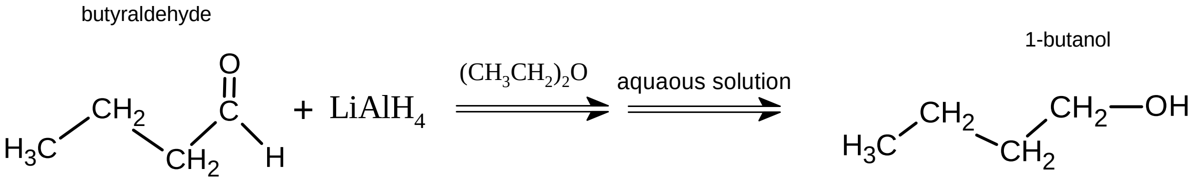

Figure 13: reaction scheme of butyraldehyde reduction using $LiAlH_4$;[4] [Vollhardt a; 2000]

4.1.3 Energy efficiency assessment for Hydroformylation processes

With exception to the “Shell-process”, all industrial oxo-processes are now working with rhodium-based catalysts.

Rhodium with a current price of 199.6 $ / g is by far more expensive than cobalt with a current price of 0.064 $ / g (state 09.2007), but less expenditure for energy, simpler and cheaper equipment, higher ratio of linear products and higher yields cleared the way for rhodium based catalysts. [Platinum Today; 2007] [BHP Billiton; 2007] [Ünveren a; 2004]

Although the RCH/RP process requires slightly higher temperatures compared to the UCC process, it is advantageous over the UCC process as no thermal recovery of the catalyst is required, catalyst leaching is negligible and overall yield is close to 99 %. [Miyagawa b; 2002] Furthermore the RCH/RP process requires about 98 % less water compared to the conventional Cobalt hydroformylation process.

The RCH/RP process can be judged as a highly developed hydroformylation process, which makes use of energy and resources in an efficient and thus economical way. [Ünveren b; 2004] [Kupka b; 2007]

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[4] Intermediate product tetra alkoxy aluminium hydride and final product LiOH are disregarded in the reaction scheme.

4.2 *The Reppe process*

Another way of producing 1-butanol from alkenes is a process named after Walter Reppe, a chemist and in the 1950s a member of the board in BASF. [BASF; 2007] Reppe developed a method of carbonylation on propene in 1942, where olefins react to the alcohol in one step directly.

4.2.1 Chemical description

Propene, carbonmonoxid and hydrogen react in presence of a tertiary ammonium salt of ferrum carbonyle hydrides to 1-butanol and 2-methylpropanole in the ratio of 86 : 14.

Figure 14 shows the reaction principle in the Reppe process:

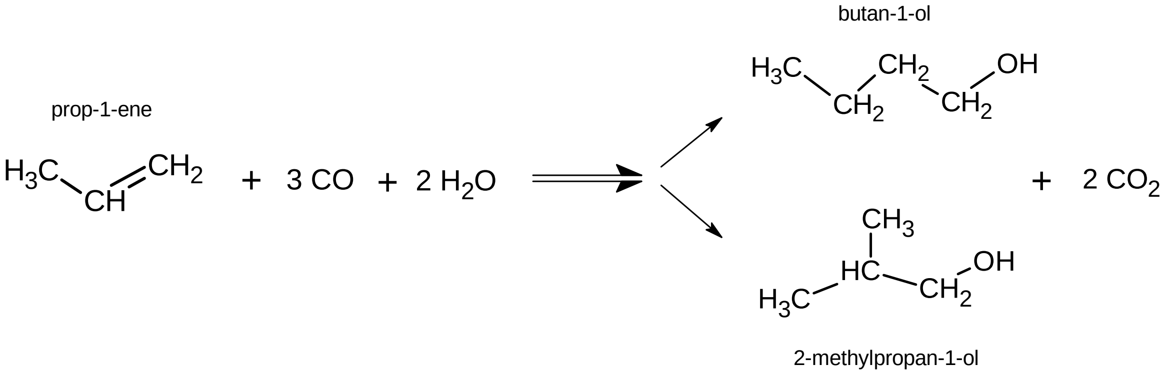


Figure 14: chemical reaction of the Reppe process

4.2.2 Technological description

The catalyst (carbonyltriferrate) concentration in the reaction solution has to be present in concentrations higher than 10 %, which is achieved by use of the dispersant agent N-alkylpyrrolidin. The process has to run under air free conditions, as the catalyst would disintegrate to iron carbonate. Conditions in the reactor are approximately 100 °C and 0.5 – 2 MPa.

4.2.3 Energy efficiency assessment of the Reppe-process

Although the milder conditions and the good *n-* : *iso-* ratio of 86**:**14 are advantageous to the conventional oxo-processes, the Reppe process did not make its way to a broad industrial implementation. The reasons are seen in the more advanced engineering necessary and the fact that by obtaining the alcohols directly, no economic synergies by selling the important C_4-aldehydes are received.

Industrial application of the Reppe process has almost completely lost importance with exception of one company in Japan (Japan Butanol Ltd.) that produced 30.000 t per year through the Reppe-process in the 1970s.

4.3 Hydrogenation of trans-2-butenal

This process – often referred to as crotonaldehyde hydrogenation – chemically considered is based on the aldol condensation of ethanal (acetaldehyde) and today has lost most of its technological importance.

4.3.1 Chemical description

The first step of the reaction is an aldol condensation of ethanal (acetaldehyde) to 3-Hydroxybutanal (acetaldol). The second step consists of acidification with acetic acid, where water is separated and the occurring crotonaldehyde is obtained by distillation.

In the last step a catalyst, commonly copper, enables the hydrogenation of the *trans*-2-butenal (crotonaldehyde) to the product 1-butanol. [Ullmanns c; 1974]

Figure 15 shows the chemical steps of 1-butanol production from acetaldehyde:

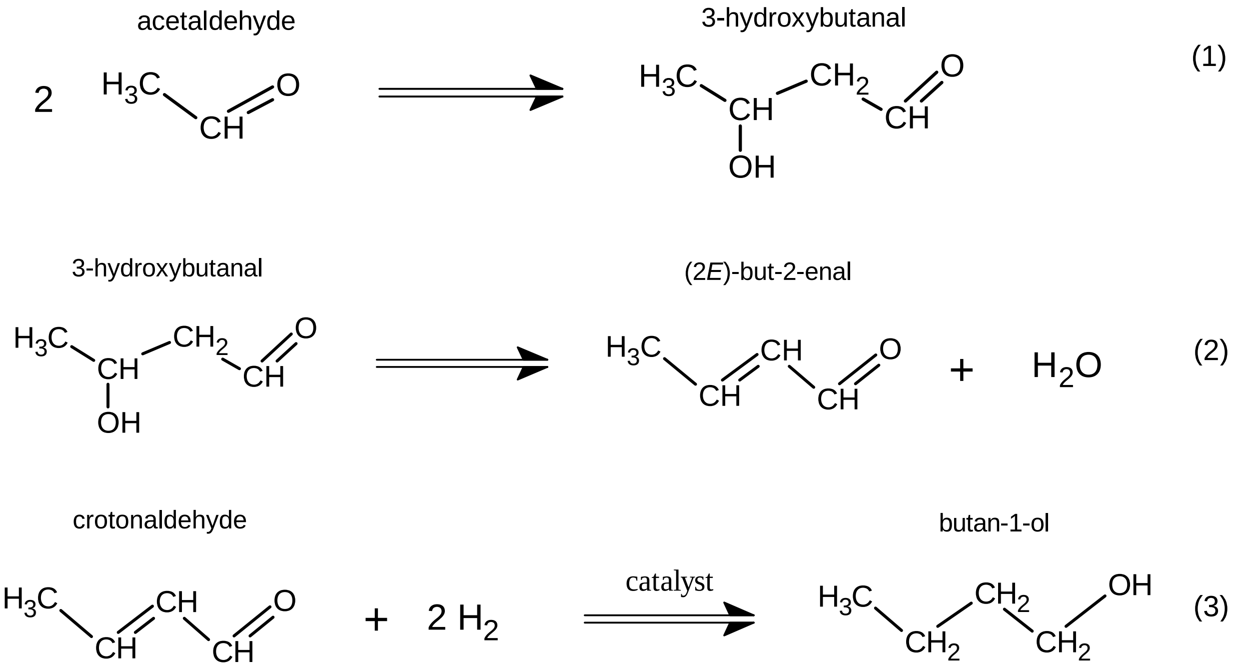


Figure 15: steps of crotonaldehyde hydrogenation: (1) aldol condensation; (2) dehydrogenation; (3) final hydrogenation;

As the crotonaldehyde process no longer is of industrial importance, no technological and energy assessment is provided.

5 Biotechnological Production of Butanol

The history of production of alcohols through micro organisms dates back more than 3000 years.

As fruits ferment naturally through micro organisms converting carbohydrates to acids or alcohols, humans dealt with the process of fermentation for thousands of years. The first chemical evidence for a fermented drink, a kind of wine, was recently found in former Shulaveri, present Georgia, dating back to approximately 5400 B.C. [University of Pennsylvania; 2007]

Fermentation then was used as a process of micro organisms preserving perishable foods. It was the French chemist Louis Pasteur who was the first to find out, that fermentation is not a process of exclusively chemical origin, but of biological entity. He noted: "*I am of the opinion that alcoholic fermentation never occurs without simultaneous organization, development and multiplication of cells…*" Anyhow, he did not know the biochemical processes behind conversion of sugars, as he further stated: "*If asked, in what consists the chemical act whereby the sugar is decomposed ... I am completely ignorant of it*." [Bionews; 2007]

Nowadays, the term **fermentation** in biotechnology includes every process which converts biological substances or materials through bacteria-, fungus- or cell culture or enzymes. Technically, fermentation processes are performed in a fermenter in liquid suspension, where the fermenting organisms are dispersed in a solution of nutrients and the products converted by the organisms are secreted into the liquid phase and can be recovered by several extraction methods (downstream-processing).

The following figure shows the typical layout of a continuous working fermenter in laboratory scale:

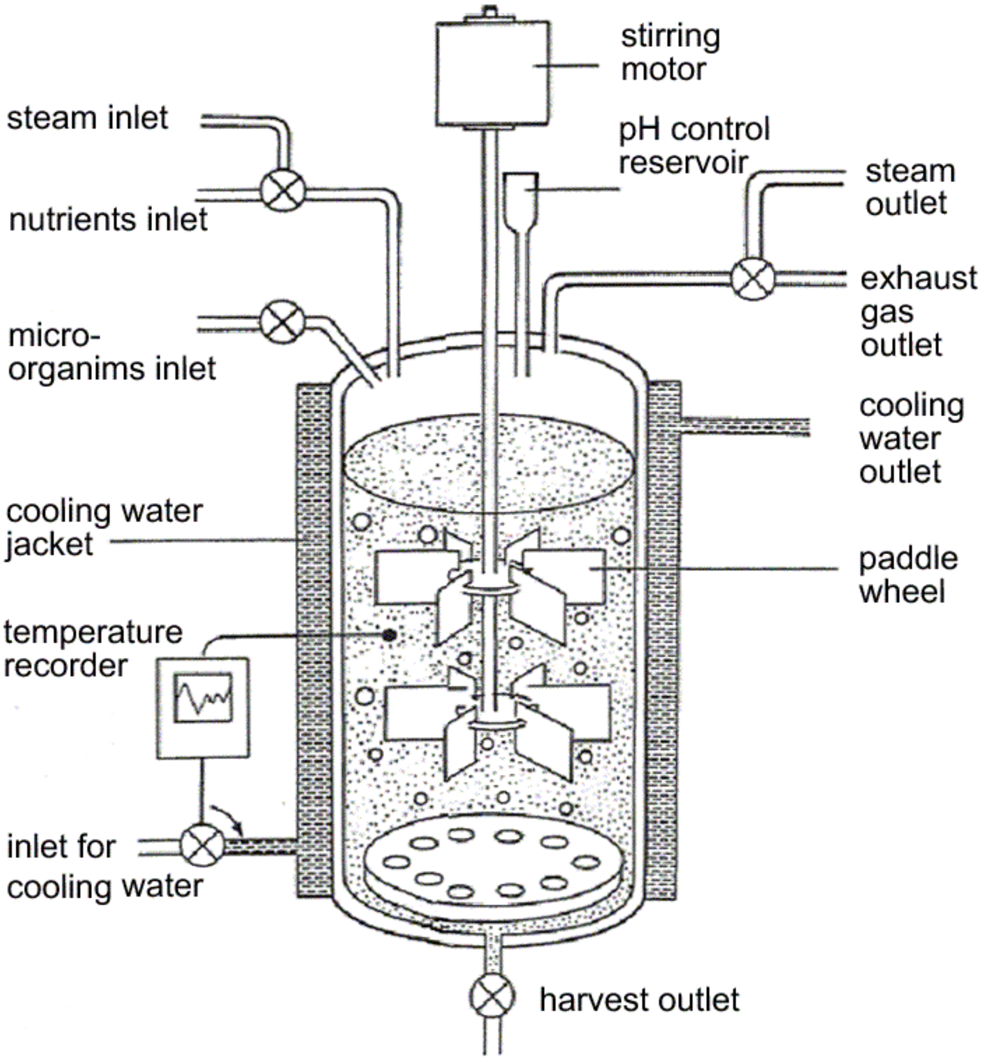


Figure 16: schematic design of a typical continuous working fermenter for anaerobe culture;

In fermentative production of 1-butanol, hexose sugars are metabolised mainly to the products **A**cetone, **B**utanol and **E**thanol through the gram-positive anaerobic genus *Clostridium*. Subsequently this kind of fermentation is called **ABE**-fermentation, whereas the type of fermentation is microbiologically referred to as ‘butyric acid fermentation’.

The genus *Clostridia* belongs to the kingdom *Bacteria*, phylum *Firmicutes*, the class *Clostridia* and to the family *Clostridiaceae* and its representatives can move autonomous by using their peritrichous arranged flagella. As a reaction on environmental stress e.g. insufficient nutrition surroundings, *Clostridia* are able to produce endospores, small, tough, non-reproductive structures that can sustain chemical and physical treatment over a long period of time (sometimes millions of years) to ensure survival of the species.

Figure 17 shows a culture of *Clostridium acetobutylicum*, one of the most important organisms for fermentative production of 1-butanol.

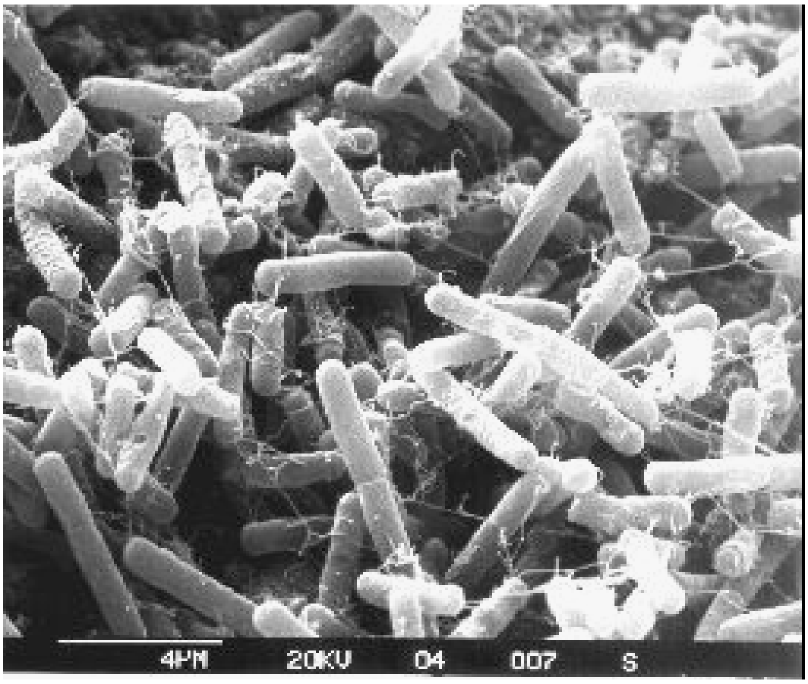


Figure 17: colonies of *Clostridium acetobutylicum* organisms under the electron microscope; [University of Princeton; 2007]

Considering the biomass that serves as feedstock for 1-butanol production, three major pathways can be differentiated shall be metabolised into 1-butanol, two fermentative processes can be divided:

- ABE-fermentation feeding starch or sugar containing biomass (1st generation technology)
- ABE-fermentation feeding biomass containing lignocelluloses (2nd generation technology)
- ABE-fermentation feeding municipal solid wastes (3rd generation technology)

Figure 18 illustrates current and future feedstock for ABE-fermentation.

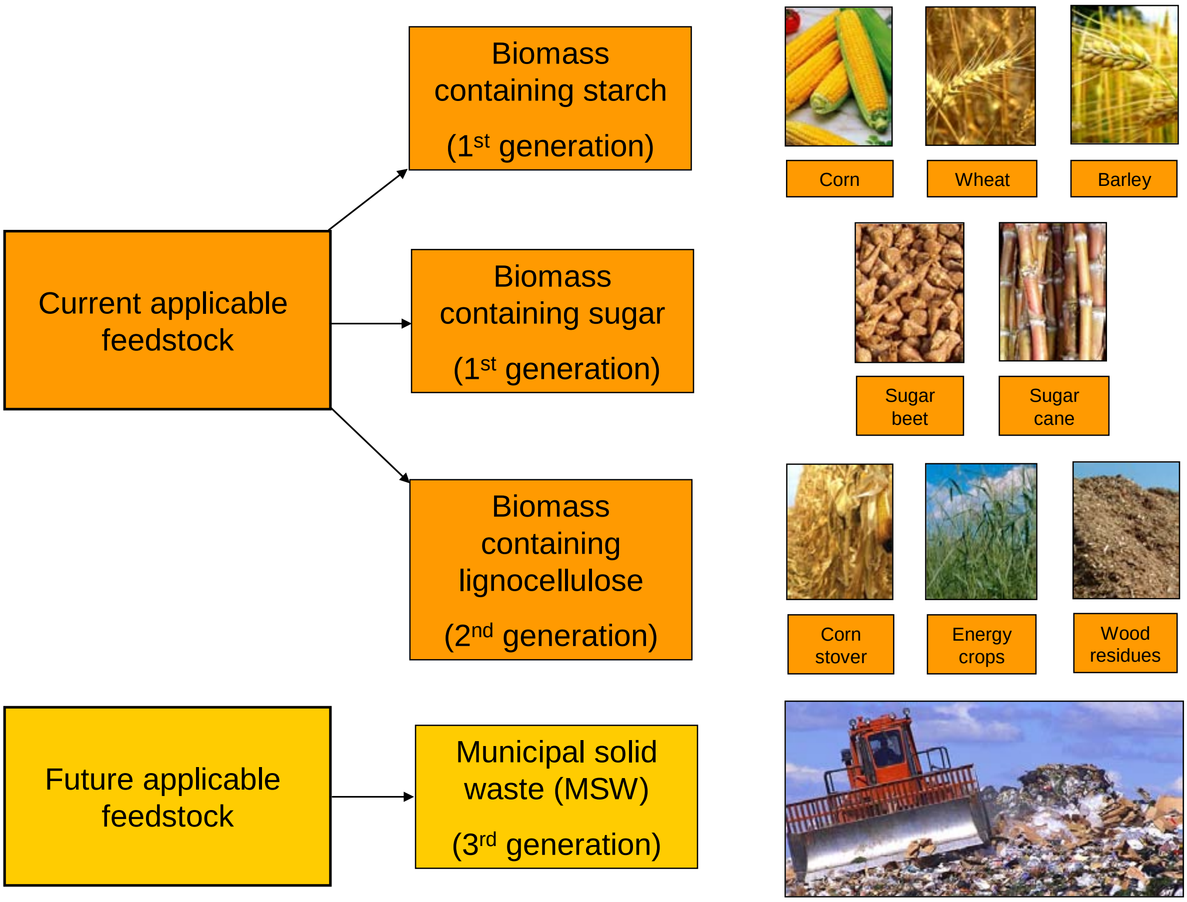


Figure 18: current and future feedstock for 1-butanol production

Not differing much on first sight, lignocellulosic feedstock poses a big challenge for research, as these materials are more resistive to biological and chemical degradation and therefore require a more severe treatment compared to fermentation of starch or sugar. Contrarily to lignocellulose-ethanol, which is still under development, lignocellulose-butanol has already been industrially established for years (see Chapter 5.3).

Decomposition and conversion to solvents 1-butanol, acetone and ethanol of municipal solid waste (MSW) or more precisely the domestic organic waste (DOW) fraction could be a potential future source for biofuels.

DOW consists of approximately 40 % of sugars, of which 25 % are glucose. Additionally, low amounts of lignocellulose biomass are present and by that DOW could be, after crushing and pre-treatment, a good feedstock for ABE-fermentation. This process is presently under academic research. [Claassen; 2000]

The layout of an industrially sized ABE-plant does not differ much from with the type of feedstock (starch, lignocellulose...) whereas pre-treatment might be required more extensively for cellulosic biomass and MSW. The design of a fermentation plant for solvent production is made up in great parts by the distillation and rectification columns for the downstream processing, where the produced solvents are separated and purified.

Figure 19 shows the scheme of an industrially sized ABE-fermentation plant:

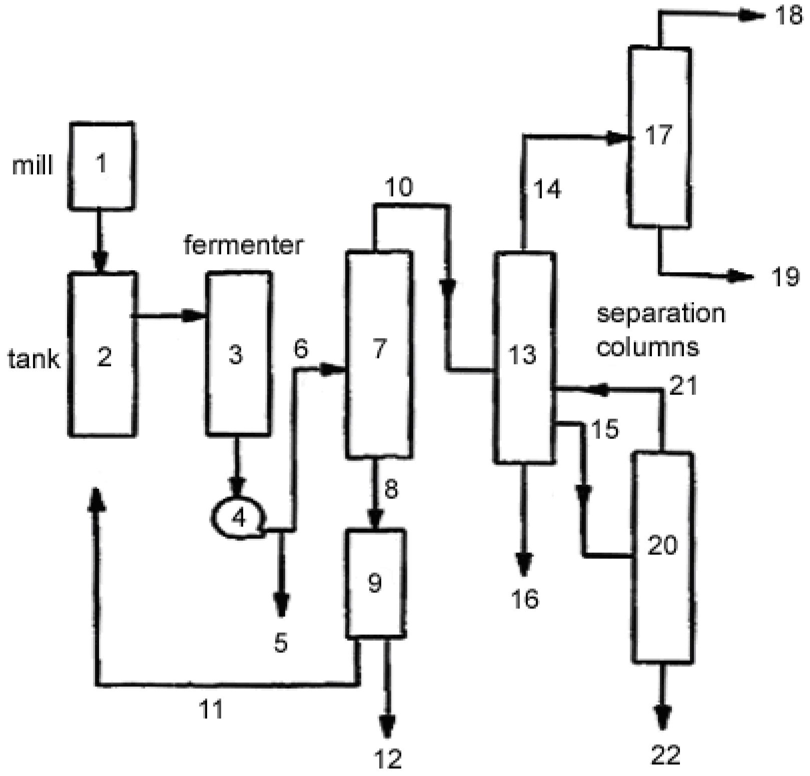


Figure 19: design of an industrial sized ABE-plant equipped with conventional downstream processing using starchy biomass (explanation in text)

In a pre-treatment step the starchy substrate (e.g. corn) is milled **(1)** and led into the medium preparation tank **(2)**, where the substrate is hydrolysed with water and sterilised to guarantee absence of any other germs that would lead to infection of the fermentation flora. The liquid medium is led into the fermenter **(3)**, in which the added *Clostridia* cultures metabolise starch to the solvent 1-butanol (and acetone, ethanol). Temperature is recorded, to ensure optimal surrounding conditions for the bacteria.

Either continuously done or at the end of the process, the fermentation broth containing cells, solvents and unmetabolised medium is led into a centrifuge **(4)**, where the cells are separated **(5)**. The supernatant containing 1-butanol, acetone and ethanol **(6)** is led into the first distillation column **(7)**, where the aqueous fermentation waste **(8)** is separated from the aqueous solvents-phase **(10)**.

Through a PTFE-membrane **(9)** water is removed from the dissolved solids and led back **(11)** to the pre-treatment. The waste stream **(12)** leaves the plant for further recycling or purification. In a splitting distillation column **(13)**, acetone and ethanol **(14)** are separated from aqueous 1-butanol **(15)**; **(16)** water; acetone **(18)** and ethanol **(19)** are separated in a third distillation column **(17)**. 1-butanol, which is forming a positive azeotrope with water (as pure water boils at 100 °C and pure 1-butanol boils at 117.7 °C), that boils at 93.0 °C is separated in an azeotropic rectification column **(20)** with help of entrainer substances (e.g. hexane). [University of Edinburgh; 2007]

While not readily purified 1-butanol **(21)** undergoes the step again, purified 1-butanol leaves the process at **(22)**.

5.1 Fermentation to 1-butanol through Clostridia feeding starch- or sugar containing biomass

Fermentation of carbohydrates to acetone, 1-butanol and ethanol is a well understood and established process that was in industrial use mainly for production of acetone. It was once the second largest biotechnological process after ethanol production through yeast. [Zverlov; 2006]

After early attempts to fermentatively produce acetone, butanol and ethanol from starch by Louis Pasteur and others tracing back to the 1860s, the ABE fermentation was developed into industrial scale in 1912 by Chaim Weizmann, chemist and later first president of Israel. Since then, the main species of choice use is *Clostridium acetobutylicum*, a saccharolytic representative of the genus *Clostridia* and sometimes referred to as the ‘Weizmann organism’.

ABE fermentation had then main importance for production of acetone that was needed in British Admiralty for production of cordite, a smokeless propellant utilised during World War I.

Butanol had no known application at that time and was either dumped or later on used for production within the lacquer industry. After the war butanol gained importance, especially because of the rising automotive industry’s demand for lacquer. The ABE-fermentation was a well established, economically competitive process in the USA.

After the Cuban revolution with the stop of exports to the USA, Acetone and Butanol production from fossil sources first became capable of competing and then outstripped the biotechnological production. However some ABE-facilities in South Africa and the USSR still existed, producing 100,000 t/a 1-butanol in the 1970s. Disintegration of the Soviet Union and the Apartheid regime in South Africa led to phase-out of commercial ABE-fermentation. Since then, biotechnological production has been refined in research within academia.

Though many laboratories pushed continuous research in the field of ABE-fermentation, commercial importance so far could not be reached again. [Schwarz b; 2007]

As 1-butanol is attracting notice for being a potential alternative to ethanol in engine application and as well can be produced via fermentation process, interest in establishing ABE-fermentation on industrial scale again is rising considerably.

Despite the number of about 40 solventogenic strains of *Clostridia*, research in butanol fermentation focuses mainly on a few species which slightly differ in their metabolic pathways, their substrates and thus in the composition of fermentation products: [Qureshi a; 2001] [Zverlov; 2006]

- Clostridium acetobutylicum
- Clostridium beijerinckii
- Clostridium butylicum
- Clostridium saccharobutylicum

As they are mesophile organisms, they grow best under moderate temperature conditions between 30 °C and 45 °C.

In a first step of the fermentation process, the starch- or sugar containing biomass is washed and foreign bodies are separated, before the biomass is milled. Depending on the size of the plant and the feedstock in use, several methods of milling are established:

The dry milling process, that is commonly used in smaller sized corn processing factories, as opposed to the wet milling process, that is implemented in larger alcohol producing factories (> 190.000 t/a). [University of Strathclyde; 2007]

The following step of autoclavation is set to produce a sterile medium and by that reducing risk of infection of the fermentation broth through other bacteria, fungi or phages. Autoclavation is a thermal process solely and done in a separate reactor, where the medium is heated under pressure in an atmosphere of saturated water vapour to 121 °C for at least 15 minutes. This is to make sure that not only living cells but also spores of thermo tolerant species are killed and the medium is free of any microbes.

In the fermenter, *Clostridia* and medium are stirred and tempered constantly while sugars are converted mainly into the products 1-butanol, acetone, and ethanol.

Three different varieties of fermentation processes are commonly differentiated [BOKU; 2007]:

- **batch culture:** no feed of nutrients after start of fermentation
- **fed batch culture:** feed of nutrients during the fermentation until reactor is completely filled up
- **continuous culture:** continuous feed of nutrients and removal of used substrate and product – a so called 'steady state'-equilibrium is engaged

With reference to an industrial application, only the process in continuous culture is seen as economically viable, as it allows producing substrate as well as downstream processing continuously and is usually more energy efficient, whereas the ABE fermentation process originally is regarded as a batch process [Zverlov; 2006]

A scheme of the ABE-fermentation process of starch- or sugar containing materials through *Clostridia* can be seen in Figure 20.

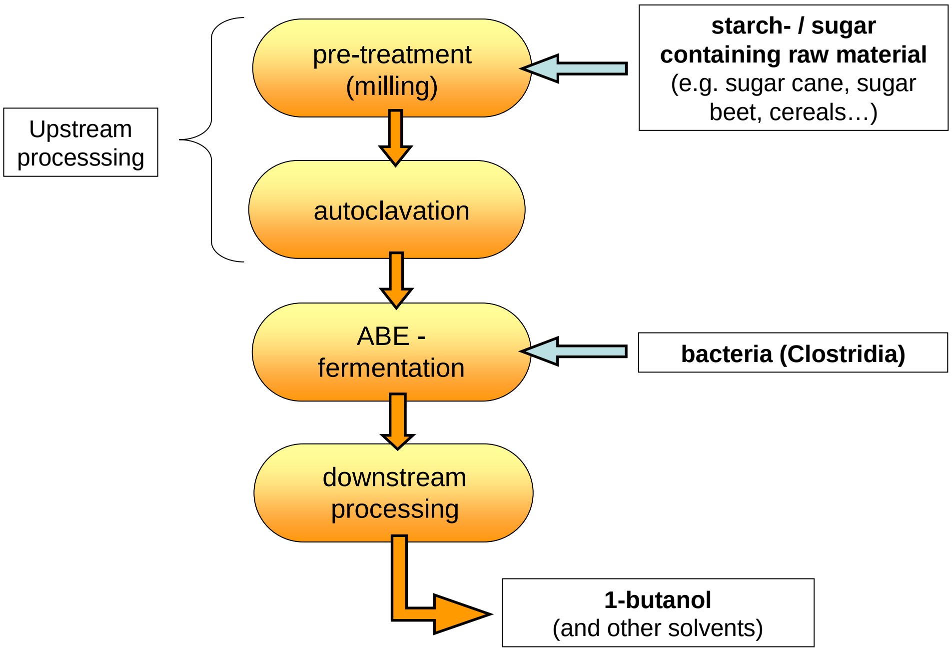


Figure 20: process scheme of current ABE-fermentation;

Starch, the main reserve substance of plants is a glucose homopolymer made of the two glucanes amylose and amylopectin.

Amylose consists of D-glucose molecules that are connected through $\alpha(1\rightarrow 4)$ bonds and represents between 15 and 27 % of the starch.

Glucose in **amylopectin** is also connected through α(1→ 4) bonds but is also α(1→ 6) linked at approximately every 25th glucose molecule and by that branched, as can be seen in Figure 21.

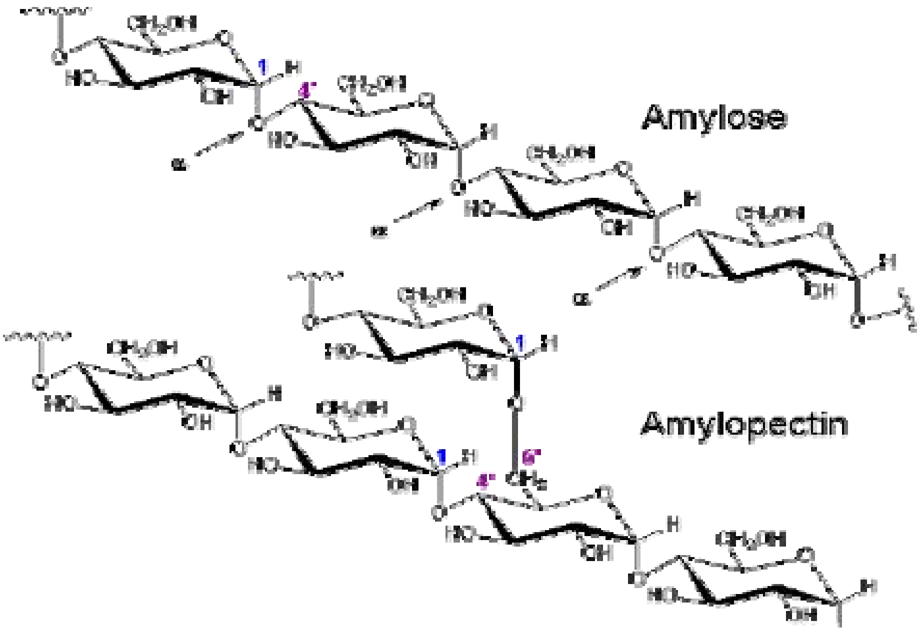


Figure 21: chemical structure of the starch's polysaccharides amylose and amylopectin

A big advantage of the 1-butanol fermentation process over ethanol fermentation, respectively of *Clostridia* over yeast (commonly *Saccharomyces cerevisiae*) is the ability of directly converting starch without need of a saccharification pre-treatment. Especially *C. acetobutylicum* and *C. beijerinckii* can decompose a variety of sugars and starch without any preliminary enzymatic hydrolysis. [Mutschlechner a; 2000]

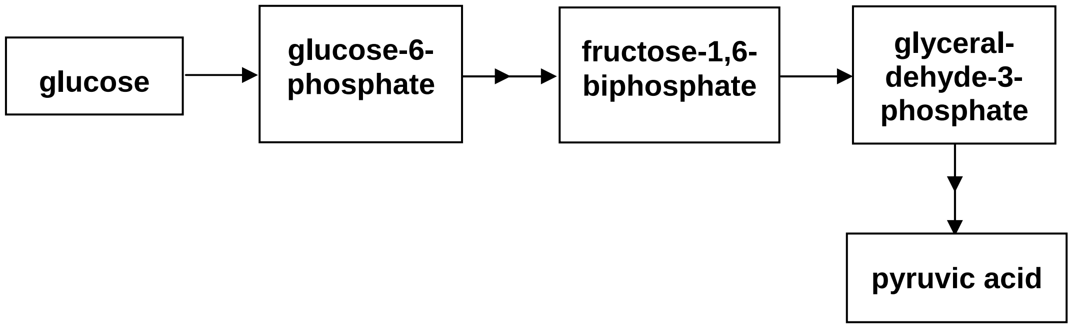
Clostridium acetobutylicum produces α-amylases and pullulanases, enzymes that hydrolyse starch to the monomer glucose and the disaccharide maltose. Maltose is further cleaved to glucose by the enzyme maltase.

In general 3 pathways are available for micro organisms to convert glucose (or generally spoken hexoses) to pyruvic acid (CH_3COCO_2H), the main intermediate compound of metabolism:

- The gylcolysis with the most common type **“Embden-Meyerhof-Parnas way”** (EM-pathway),
- The **pentose phosphate pathway** (PP-pathway)
  (also for metabolisation of pentoses) and
- The **Entner-Doudoroff pathway** (KDPG-pathway).

Clostridia use the EM-pathway for obtaining pyruvic acid, which is further metabolised to butyrate and 1-butanol.

The EM-pathway, taking place in the cytoplasm of a cell converts glucose into glucose-6-phosphate, further on into glyceraldehyde-3-phosphate and is ending up with production of pyruvic acid.



A detailed scheme of the EM-pathway showing all intermediate products with corresponding enzymes and co-factors can be seen in the Appendix section.

Pyruvic acid as a substance of central role in the metabolism is being oxidated and can be further metabolised into many products, whereas Clostridia can make use of the phosphoroclastic reaction, in which pyruvic acid is oxidated to Acetyl-Coenzyme A, commonly referred to as Acetyl-CoA, using Coenzyme A and oxidated Ferredoxine. The reaction that can be seen in the following is catalysed through the enzyme *ferredoxine oxidoreductase*. [Schlegel a; 1992]

$$\textbf{Pyruvic acid + CoA + 2 Fd (ox.)} \longrightarrow \textbf{Acetyl-CoA + 2 Fd (red.) + CO}_\mathbf{2}$$

Acetyl CoA (CH_3-CO~SCoA) is converted into Acetoacetyl-CoA through a *thiolase* enzyme *(ThlA)*. A CoA transferase also converts reinternalised butyrate and to a lesser extent actetat into Butyryl-CoA and Acetyl-CoA. This activity is dependend on the pH-value of the culture. During this *CoA-transferase* action also acetoacetat is formed, which is further metabolised into acetone and CO_2 by means of an *acetoacetate-decarboxylase*.

As excretion of butyrate and acetate lead to a drop of the surrounding pH-value, *Clostridia* undergoes a major metabolic switch at the end of the exponential growth (at approximately pH 4.5) and reduces formation of acids by uptaking excreted acetate and butyrate, forming the corresponding enzymes and converting them into the solvents acetone and 1-butanol. This switch in the metabolism avoids cell death because of toxic surrounding conditions and is often referred to as acidogenesis-solventogenesis-switch.

Formation of acetone is associated very close with production of butanol, as decarboxylation of acetoacetat leads to the loss of a potential hydrogen acceptor and subsequently other substances have to serve as hydrogen acceptors, especially already excreted butyrate, that undergoes a reduction, ending up in formation of 1-butanol.

The following scheme shows a simplified version of the metabolic pathway for production of 1-butanol and other products starting from Acetyl-CoA.

A detailed scheme showing all enzymes and intermediate products can be found in the Appendix section. [Dürre a; 2007] [Schlegel b; 1992]

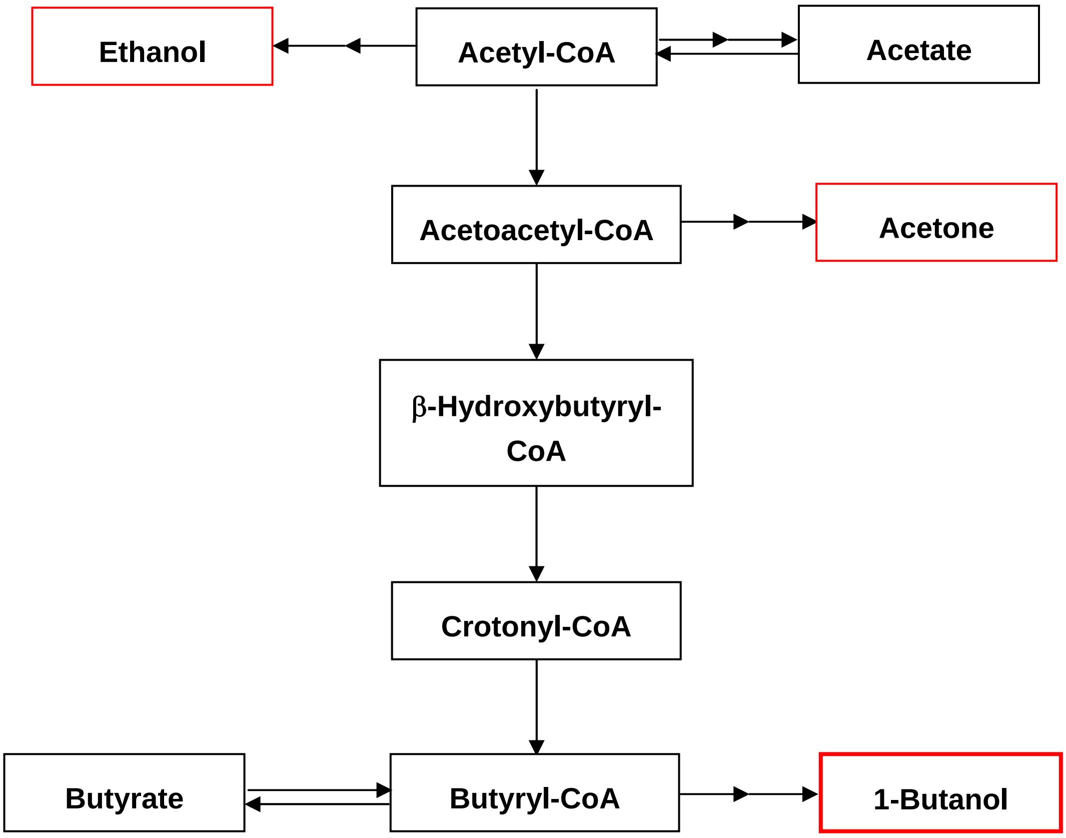


Figure 22: simplified metabolic scheme of fermentation of the genus *Clostridia*;

Clostridia obtains 4 molecules of Adenosine Triphosphate (ATP) per molecule of glucose metabolised through this process. ATP is the universal form of biochemically bound energy for the cells, which can be transported through and stored in the cells. The overall brutto reaction of butyric acid fermentation is as follows:

$$\mathbf{2}\ \text{Glucose} \longrightarrow \mathbf{1}\ \text{n-butanol} + \mathbf{1}\ \text{acetone} + \mathbf{4}\ H_2 + \mathbf{5}\ CO_2$$

The standard enthalpy change of reaction amounts to $\Delta_r H°$ = -1280 kJ / mole, which means that the reaction is exothermic, energy is released. Energy that is stored in ATP.

The composition of the solvents 1-butanol, acetone and ethanol is varying with the species, the strain, fermentation conditions and the feedstock used.

The following table is giving an overview of the product composition obtained in different laboratory experiments:

Table 4: product composition obtained from different strains of Clostridia;

		1-butanol (B)	**acetone (A)**	**ethanol (E)**
strain	source	% (v/v) of total solvents		
C. beijerinckii BA101	Qureshi, Blaschek; 2000	77.8	18.5	1.9
C. beijerinckii NCIMB 8052	Formanek, Mackie; 1997	63.4	30.3	6.2
C. beijerinckii NCIMB 8052	Formanek, Mackie; 1997	60.9	32.2	6.8
C. beijerinckii BA101	Formanek, Mackie; 1997	67.6	31.2	1.1
C. beijerinckii BA101	Formanek, Mackie; 1997	71.2	26	2.6
C. beijerinckii NRRL B592	Mutschlechner, Swoboda; 2000	60.1	32	6

As can be seen, an approximate solvent composition ratio of **butanol : acetone : ethanol = 6 : 3 : 1** is commonly obtained.

As mentioned before the formation of acetate and butyrate leads to a decrease of the pH-value in the cell broth which endangers the culture, therefore the acidogenesis-solventogenesis-switch is undertaken.

Whereas toxicity of the solvents is lower, an excess of acetone, ethanol and butanol in the cell broth leads to death of the cells as well.

The possible concentration of butanol (and the other solvents) is heavily depending on the species of bacteria used and the type of fermentation. Several laboratory experiments showed that a 1-butanol concentration of roughly 20 g per litre fermentation broth can be obtained. In continuous culture with immobilized cells the level of total solvents amounted in experiments to 15.8 g per litre and hour.

An important factor for judging efficiency of an ABE-fermentation process is the product yield that is expressed through the following equation:

$$\mathbf{Y_{P/S} = mass\ of\ products\ /\ mass\ of\ glucose}$$

In well run fermentation processes $Y_{P/S}$ of 0.48 can be obtained, while industrial fermentation processes seldomly reach higher yields than $Y_{P/S}$ = 0.37. [Formanek a; 2007] [Gapes a; 2000]

A more tangible expression commonly used to express the overall yield of a biofuel-producing process from cultivated crops is the volume of final product per hectare agricultural cultivated land. For these details see Chapter 7.3.

5.2 Fermentation to 1-butanol through Clostridia feeding lignocellulosic biomass

In addition to reserve substances like starch and saccharose, another group of carbohydrates represents the largest part of herbal material – cellulose and hemicelluloses, which give stability to cell walls and represent approximately 50 % of the overall material of a plant. Therefore, cellulose is the most abundant organic compound on earth.

Cellulose and hemicellulose are often mixed with lignin, what leads to their collecting term ‘lignocellulose’ – the heterogeneous material consisting mainly of cellulose, hemicellulose and lignin.

The following picture shows the structure of cellulose and hemicellulose in the cell wall of a plant.

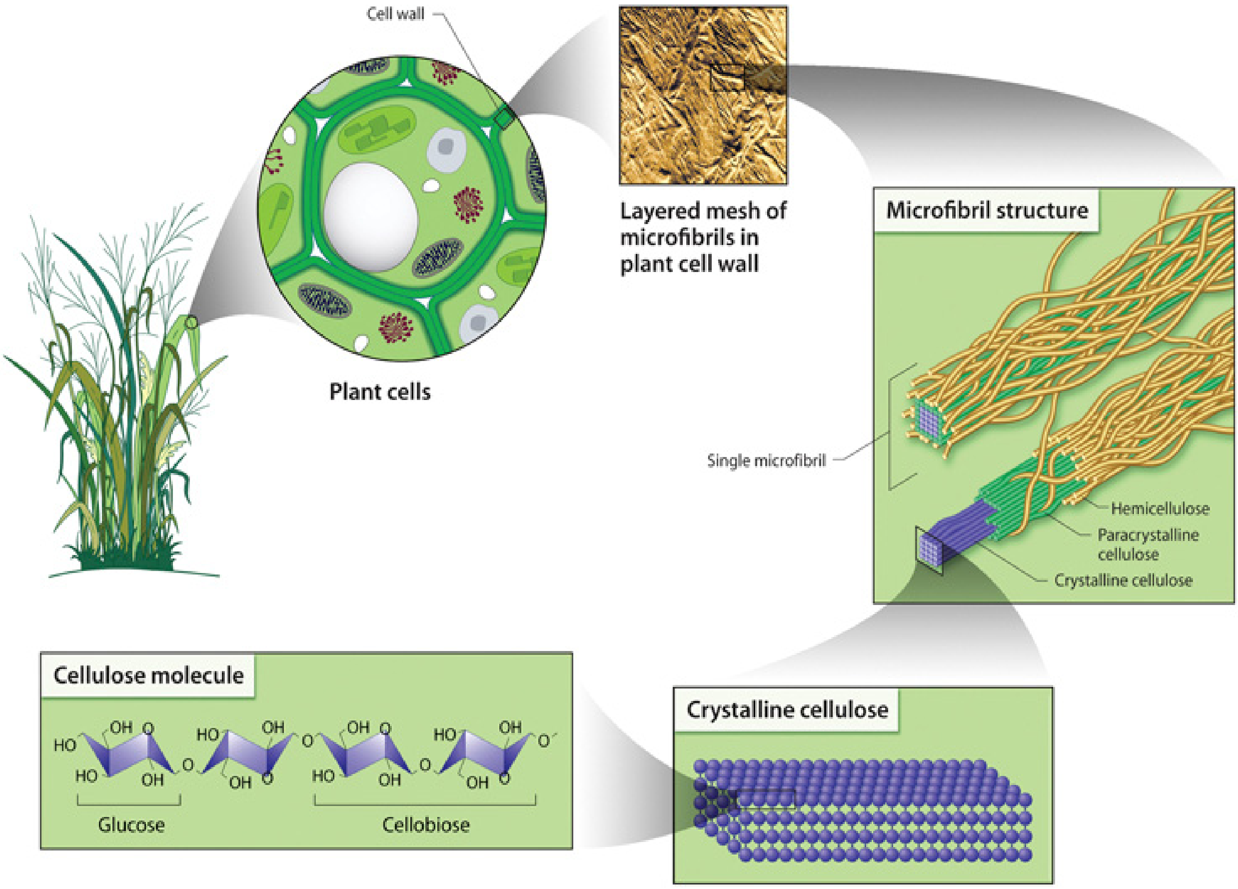


Figure 23: **cellulose and hemicellulose in the microfibrils of a plant cell wall; [Genomics; 2007]**

As can be seen in Figure 23, **cellulose** consists of unbranched glucose monomers, that are $\beta(1 \rightarrow 4)$ linked, whereas the structure-bearing elementary unit is the disaccharide cellobiose. Cellulose is partially crystalline, where amorphous (paracrystalline) cellulose covers the inner crystalline regions.

Mechanical stability of cellulose is explained by inter- and intramolecular hydrogen bonds, which associate the chains (intermolecular H-bonds) and connect the glucose molecules within the chains (two intramolecular H-bonds per molecule).

Contrarily to the homopolymer cellulose, **hemicellulose** contains miscellaneous substances and is a collecting term for carbohydrates and acids. Depending on the type of biomass, the term includes [Schlegel c; 1992]:

- **hexose sugars** - monosaccharides carrying 6 C-atoms (glucose, mannose, galactose)
- **pentose sugars** - monosaccharides carrying 5 C -atoms (xylose, arabinose)
- **hexuronic acids** - glucuronic acid, galacturonic acid, mannuronic acid

Beyond mechanical stability this leads to a strong resistance against chemical and biological treatment, which is the reason not many micro organisms are able to convert cellulose or lignocellulose material to solvents.

This is what makes industrial fermentation of lignocellulosic biomass a challenge.

Pentoses, which cannot be naturally converted from conventional ethanol producing yeast strains, however serve as a source of nutrients for *Clostridia*. Additionally to hexoses being decomposed in the EM-pathway, pentoses are metabolised through the PP-pathway, resulting in production of fructose-6-phosphate and glyceraldehyde-3-phosphate, which then enters the gylcolysis (see EM-pathway). [Dürre a; 2007] [Zverlov; 2006]

Compared to ethanol production through yeast, which cannot convert cellulosic material, a fermentation of lignocellulosic material through Clostridia could be economically more probable, as energy expenses for pre-treatment would be lower, because of the fact that *Clostridia* (e.g. *Clostridium butyricum*) show enhanced hemicellulolytic activity. [Zverlov a; 2006] Hemicellulose material, especially xylose has been shown to serve as a substrate for *C. acetobutylicum*. Recent analysis of genome sequences of *Clostridium acetobutylicum* yielded interesting findings, as genes where found that should enable *C. acetobutylicum* also to decompose cellulose material. [Dürre a; 2007]

The biochemical process of cellulose fermentation requires attack of enzymes or acids and heat, which lead to a break down of cellulose to cellobiose and further to glucose (process referred to as hydrolysis). Glucose is then led into the EM-pathway as described above and further conversion to solvents is as described in Chapter 5.1.

So far, none of the existing solvent producing strains used in fermentation (whether *Clostridia* for 1-butanol or *Saccharomyces* for ethanol) have the ability to autonomously break down and decompose cellulose. Although solventogenic *Clostridia* show *endoglucanase* activity, a complete decomposition of the complex structure of cellulose requires at least 3 enzymes, which act synergistic within the enzyme complex *cellulase* (EC 3.2.1.4):

The *endocellulase* breaks internal bonds to disrupt the crystalline structure of cellulose; the *exocellulase* cleaves units from the cellulose-ends the *endocellulase* produced, resulting in the disaccharide cellobiose which is decomposed to glucose by the 3rd enzyme complex *cellobiase* or *β-glucosidase*. [Van Kampen; 2003]

Two ways are conceivable to break down cellulose:

- **Hydrolysis through enzymes, produced by the organism itself** (intra cellular hydrolysis); organisms have to be modified molecular-biologically (e.g. through cloning mould genes coding for *cellulase*-activity from the species *Trichoderma* or *Penicillium* into *Clostridia*); these organisms are usually referred to as GMO (Genetically modified organisms)

- **Hydrolysis through enzymes and acids that are not produced by the organism** but added during pre-treatment of the feedstock (extra cellular hydrolysis); the enzymes have to be harvested from other microbes, which commonly are genetically modified as well and are ‘designed’ for the specific technical purpose.

As molecular-biological design of stems is complex, expensive and requires time of research, the near-term fermentation plants for ABE-fermentation most probable will make use of extra cellular hydrolysis.

An idealised design of an ABE plant, fermenting lignocellulosic biomass can be seen in Figure 24:

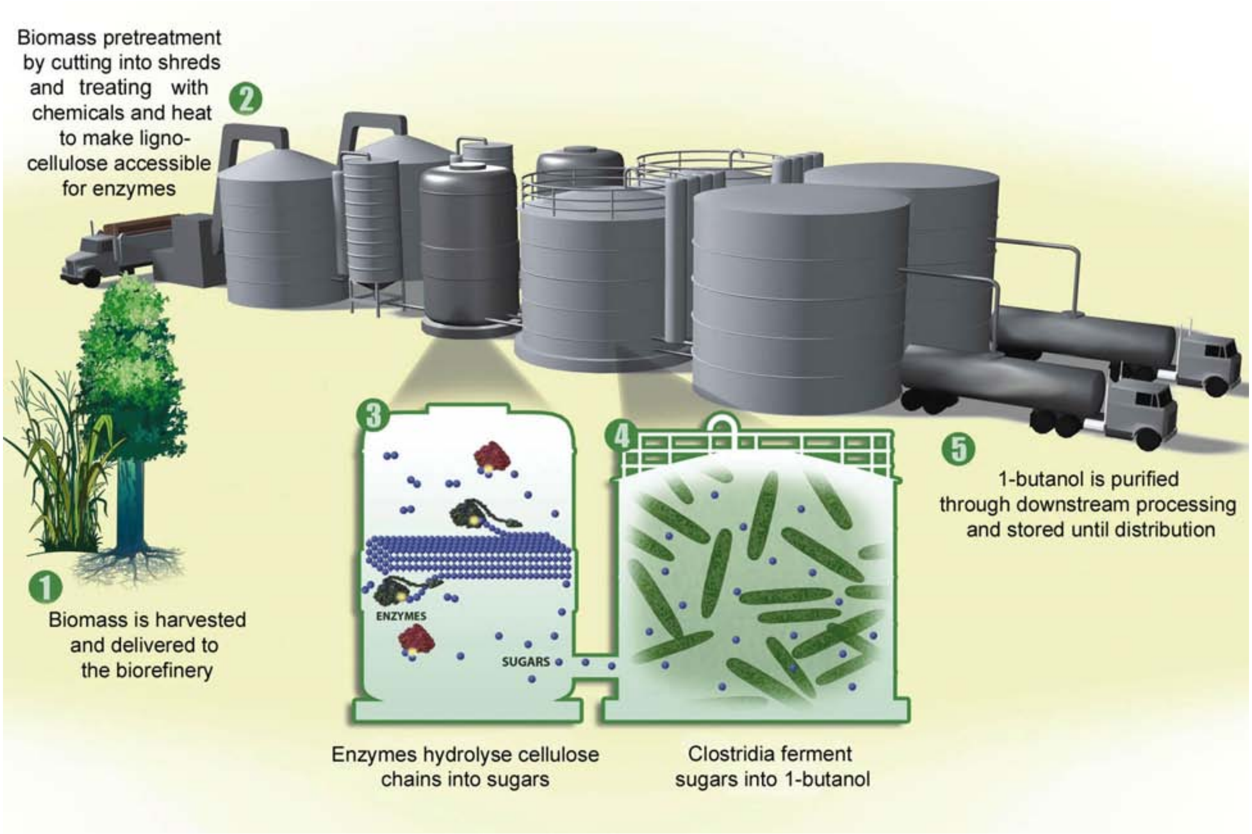


Figure 24: schematic design of an ABE-fermentation plant processing lignocellulosic biomass

Whereas no fermentation of lignocellulosic biomass is implemented in industrial scale now, extra cellular hydrolysis of lignocellulosic material and fermentation was done in large scale in Russia until end of the 1980s.

5.3 Fermentation of lignocellulosic biomass - case study of former Soviet ABE-plants

The plants, spread all over the country, with their research laboratory and head office in Nartkala (renamed in 1967; former Dokshukino), so far have been the only industrially sized plants worldwide, which used hydrolyzates of lignocellulosic wastes for fermentation of 1-butanol.

This is a major lead for production of lignocellulose-butanol over -ethanol, as lignocellulosic ethanol production so far only exists in pilot and ‘demonstration scale’ plants. [Iogen; 2007]

Little is known about the exact process of the former USSR-plants but it is noted, that the USSR-ABE-industry started industrial fermentation in 1929 using *C. acetobutylicum* strains originally in a batch process feeing starch. The process was further developed and adapted to ferment hemicellulose hydrolyzates and molasses in a so called ‘continual’ process (not a true continuous process) which was industrially used from 1961 on.

Hydrolysis was performed with 1% (v/v) sulphuric acid and temperatures between 115 – 25 °C to avoid complete degradation of pentoses (xylose, arabinose), where higher fermentation yields could be obtained compared to a complete hydrolysis under harsher conditions (this was due to lower toxic by-products in the hydrolyzate).

The plants where designed for extensive use and production of by-products, a biorefinery concept where hydrogen, vitamin B12, biogas and animal feed where produced, which can be seen in Figure 25. It might be interesting to note, that CO_2 occurring during the fermentation process was processed to dry-ice and sold, too.

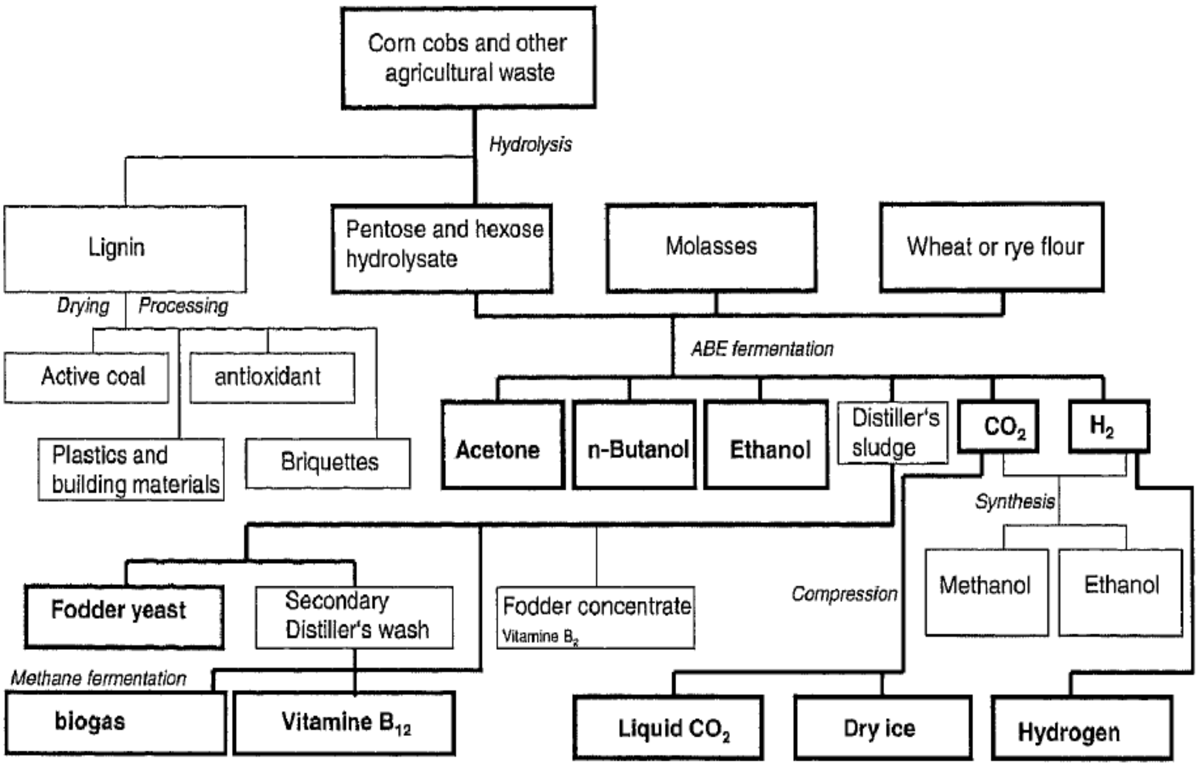


Figure 25: concept of the ABE-fermentation plants in Russia; only products and by-products in bold boxes where realised; [Zverlov; 2006]

The scale of production (per year) can be cited exemplary on the ‘Evremovo’-plant:

Table 5: ***mass of feedstock and products achieved in the ‘Evremovo’-plant; according to [Zverlov; 2006]***

input	**amount**
molasses and lignocellulose hydrolyzate	40.500 to (starch equivalent)
output / products	
1-butanol	8.550 to
acetone	4.140 to
ethanol	2.310 to
CO_2	13.1 million m^3
biogas (mainly CH_4)	11.0 million m^3
H_2	8.7 million m^3

Although the process of converting lignocellulosic waste material was used in industrial scale and its products had broad clientele, all plants where shut down and the fermentation facilities dismantled with dissolution of the USSR.

Subsequently the majority of the know-how of the ABE-process with lignocellulosic biomass was lost.

Researchers within academia and as well as industry try to again establish and improve the process of ABE-fermentation in industrial scale.

5.4 Challenges in ABE-fermentation

A common problem in establishing industrial processes is the up-scale from a pilot plant on laboratory to industrial sized measure. Fermentative processes require accurate attention and wide experience as fermentation means to deal with bio-organisms that quickly can adapt to changing surrounding conditions, which implicates a certain variation in the function of fermentative processes.

Some of the most challenging aspects in ABE-fermentation from lignocellulosic biomaterial as well as starch or sugar containing biomass in industrial scale are:

- **Reducing the costs for downstream processing** through new methods of concentrating and separating the products; it should be noted that the energy required for purification of the products from ABE-fermentation through distillation is higher than for ethanol fermentation by yeast, as the heterogeneous products in ABE-fermentation require multi-level distillation and azeotropic rectification. Azeotropic rectification is needed as well in ethanol purification, but the boiling point of the azeotrope 1-butanol / water amounts to 93.0 °C compared to 78.17 °C of the ethanol / water azeotrope. A potential arrangement of the distillation arrangement of an ABE-plant can be seen in Chapter 5, Figure 19.
- **Establishing a stabile, efficient fermentative process**; Problems often reported in western ABE-fermentation plants were infections through bacteriophages, which can be avoided or significantly reduced by keeping strict sterilisation conditions and using robust strains of bacteria. An average duration of 4 weeks for a continuous process is seen as a sufficiently long to show economical advantages.
[Gapes a; 2000] [New a; 2007] [Zverlov; 2006]
- **Increasing the quantity of products** in the fermentation broth; depending on the strain and the type of fermentation 1-butanol yields between 10 and 23 g L^{-1} could be obtained in laboratory and industrial plants. In continuous culture solvent yields between 0.58 g $L^{-1}h^{-1}$ and 15.8 g L^{-1} h^{-1} (with immobilized cells) could be obtained.
[Qureshi a; 2001] [Qureshi b; 2000] [Zverlov; 2006]

As a result of the challenges mentioned above, lots of effort is put into implementing new technologies of downstream processing like pervaporation, liquid-liquid extraction and other separation and purification technologies. Pervaporation indeed looks promising as it separates ABE selectively from the broth and is not harming the bacterial culture. [Qureshi c; 2001]

Pervaporation means a membrane separation process, where the solution is led through a membrane and by that separated. The characteristic property of pervaporation is a phase change at the membrane, in that way that the retentate remains liquid while the permeate is led away in gaseous state.

Molecular- and plant biotechnology is trying to adapt *Clostridia* genetically as well as physiologically towards hyper-butanol production and more robust strains. [Blaschek a; 2007]

Although the process of ABE-fermentation looks promising, some problems might arise when scaled up on industrial level, especially regarding the changes in the process when bacteria switch their metabolism from production of acids (butyric acid) towards production of solvents (1-butanol). This switch is followed by a rising pH-value and should go along with reducing the temperature in the bio-reactor. It takes a lot of experience to detect the switch in large sized reactors and is usually observed through changes in the translucence of the fermentation broth. See also chapter 6.2 for details.

6 Fuel production prospects – 1-butanol in comparison with ethanol and petrol

The shift towards bio derived fuels is motivated not only by the threat of short-running oil reserves, but outcome of a multiplicity of aspects, as discussed in chapter 2.1.

Precisely stated, reserves of fossils for production of fuels will last longer than commonly expected, as ongoing findings and technological progress make exploitation of unconventional fossil findings like oil tars or oil sands economically feasible.

Rising of proved reserves can be seen in the following figure, whereas it has to be noted that the data should be seen against the background of current economical limitations, which are not considered in any form.

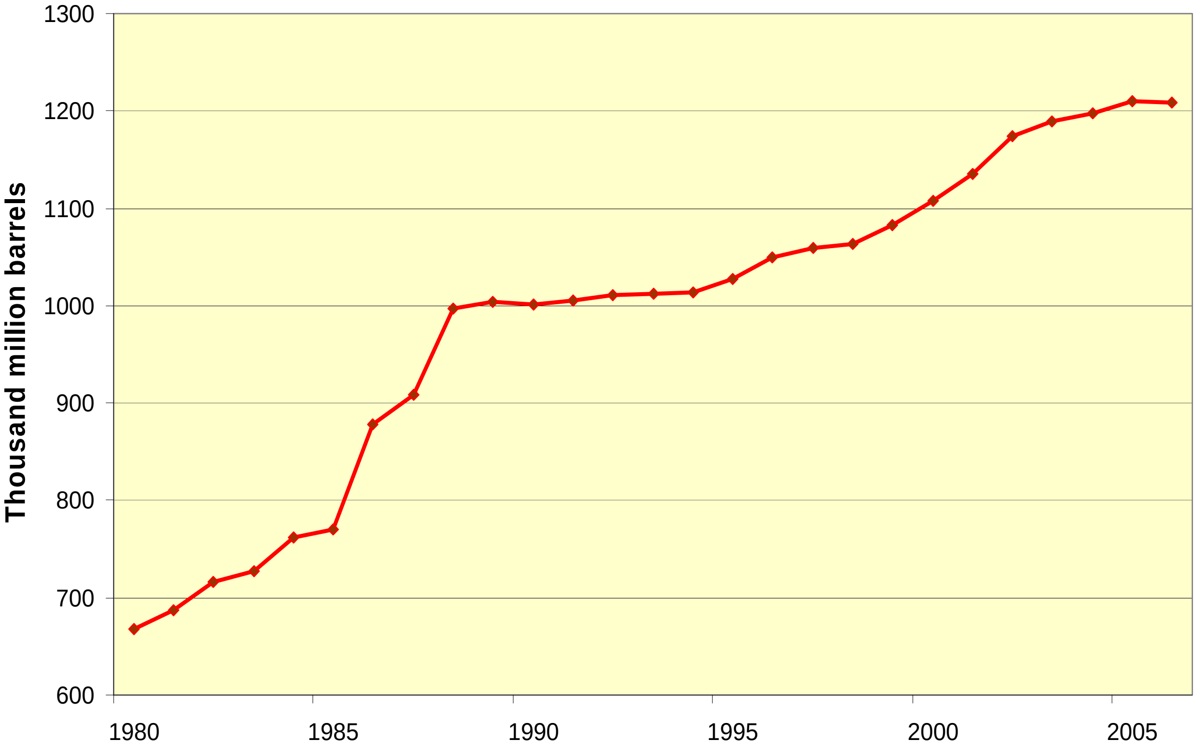


Figure 26: proved reserves of oil in thousand million barrels; [BP c; 2007]

Geologists assume the peak of oil production (often referred to as ‘oil peak’ or ‘peak oil’) in between 2000 and 2020, whereas the Association for the Study of Peak Oil and Gas (ASPO) states it to be very likely that the peak happens presently. [ASPO; 2007]

Implementing a ‘new’ fuel demands enormous endeavour along the whole process chain, starting from an economical production and refining, logistics that can handle the fuel safely without lowering the quality, ending up in an engine, which burns the fuel efficiently without any major drawbacks compared to today’s fuels.

This is the main reason why the plenty of biofuels which could be produced is shrinking to a manageable number of fuels which are being considered as potential petrol replacement. The dominating biofuels are biodiesel and ethanol, where ethanol counts for 86 % of the total biofuel production.

World liquid fuel production in 2006 was contributed by biofuels in the range of 1 % (v/v). When considering the increase in liquid fuels from 2005 to 2006, a surge in biofuel production of 17 % (v/v) can be observed. [Worldwatch a; 2007]

In 2003 the European Union adopted a directive, which means a binding law for member states, in which the implementation of biofuels or other renewable fuels within the transportation sector shall be promoted. The targets where given on a time-dependent basis, and a proportion of 2 % (energy content) should have been placed on the markets by end of 2005.

For 2010 a target of 5.75 % market share in the transportation sector was adopted. National targets are partially more ambitious as Germany for example tries to achieve a national share of biofuels of 6.75 % in 2010.

It might be interesting to note that the European-2%-target for 2005 could only be achieved by Sweden and Germany.

In January 2007 the European Commission announced plans to adopt a 10 % binding target for biofuels in 2020. [VDA; 2007] [Lahl; 2007]

6.1 Petrol production prospects

The current rise in fossil fuel prices mainly is not by virtue of rising production costs but because of speculations at the stock markets and a great demand for oil in the USA and China. [Aral a; 2007]

In 2004 the costs for production of 1 litre of petrol amounted to 0.32 € in the USA and to 0.34 € in the EU in 2004. Subsequently the main share of the final price to pay by the customer is from stock market speculation and government taxes.

Figure **27** shows the development of fuel prices before taxes in Germany (not inflation-adjusted):

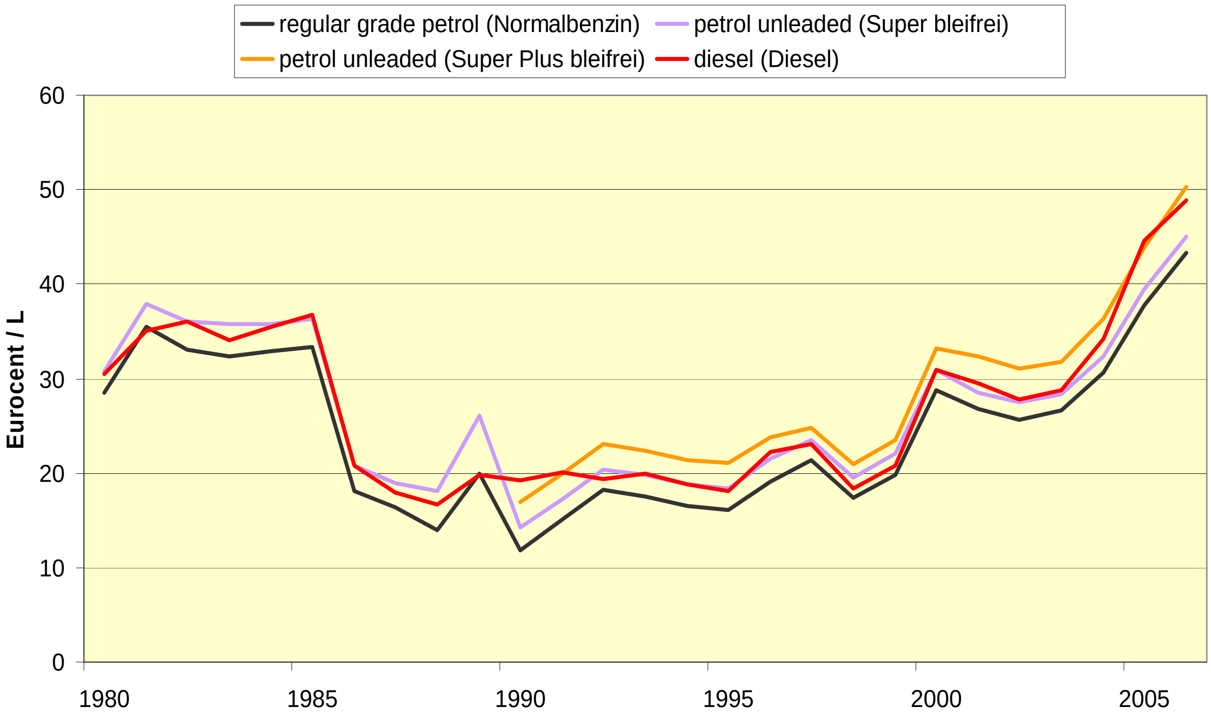


Figure 27: fuel prices before taxes in Germany since 1980; [Aral b; 2007]

Nevertheless petrol will play a major role as a fuel in motor application at least on a mid-term range, whereas there is requirement to drastically reduce its relevance against the background of several negative aspects discussed in the Introduction section.

The International Energy Agency (EIA) is projecting an annual growth in the global primary energy demand between 1.3 % and 1.8 % in the period 2005 – 2030.

Requirements will be covered in large parts by fossil oil, whereas the rate slightly differs depending on the scenario observed. The IEA modelled a '**reference scenario**' where they assume that there are no new energy-policy interventions by governments (referred to as a 'business as usual scenario'). This scenario is intended to provide a baseline vision of how global energy markets are likely to evolve if governments do nothing more to affect underlying trends in energy demand and supply.

Moreover they had presumed an '**alternative policy scenario**', where The Alternative Policy Scenario takes into account those policies and measures that countries are currently considering and are assumed to being adopted and implemented, taking account of technological and cost factors, the political context and market barriers.

This would reduce primary energy demand in 2030 to 16,000 megatons oil equivalent. [IEA a; 2007] Figure 28 shows the shares for the most important sources of energy projected to 2030 according to the IEA reference scenario, the ‘business as usual scenario’ respectively.

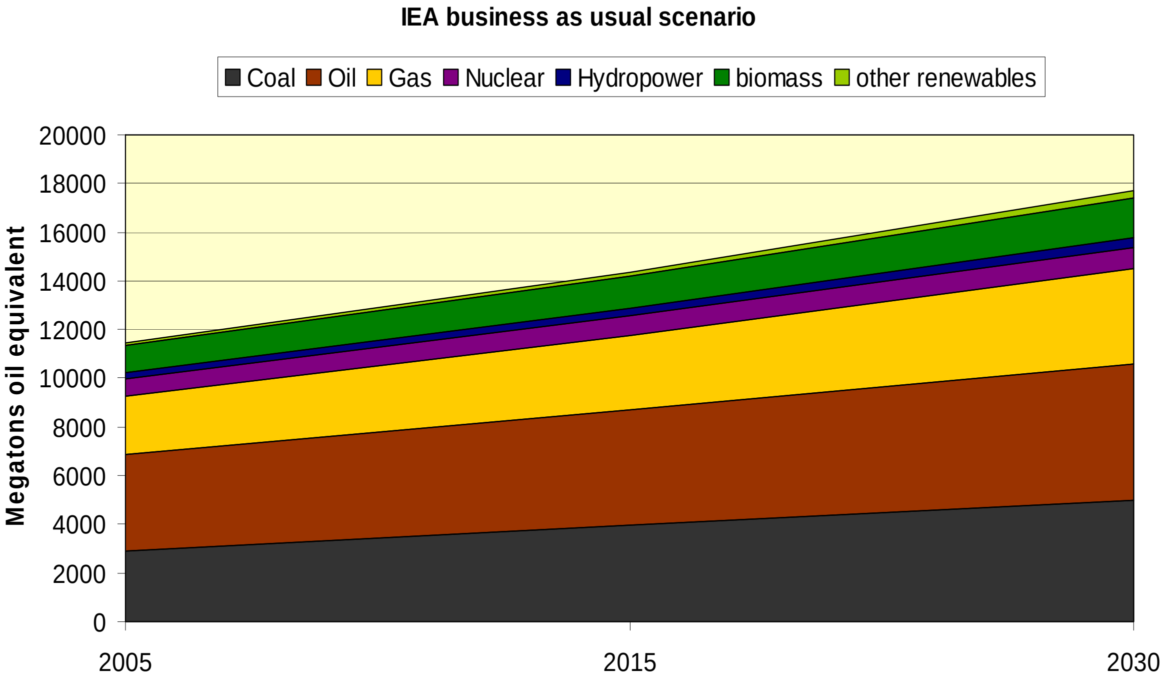


Figure 28: world’s primary energy demands between 2005 and 2030; [IEA b; 2007]

Transportation will stay the main driver of oil demand in most regions. Globally, transport’s share of the total primary oil use will rise from 47 % in 2005 to 52 % in 2030.

This scenario makes clear that although biofuels take an increasing share of the market for road-transport fuels, oil-based fuels continue to hold capital importance, as their share will fall from 94 % in 2006 to 92 % in 2030. Worldwide, consumption of oil for transportation is projected to grow by 1.7% per year over the projected period 2005 - 2030. [IEA c; 2007]

A rising energy demand in the transportation sector of about 0.7 % annually between 2010 - 2020 and an almost constant level between 2020 - 2030 is also expected in the European Union (EU 27), and will amount to roughly 422 megatons oil equivalent (17.66 EJ) in 2030.

6.2 Ethanol production prospects

Ethanol is currently produced from starch or sugar containing crops and counts for 86 % of the worldwide total biofuel production.

Production capacities of ethanol more than doubled between 2001 and 2006, when they amounted to 38,200 million litres. The main producers of ethanol are the USA (18,300 million litres), Brazil (15,700 million litres), the EU (1,550 million litres) and China (1,300 million litres). [Worldwatch a; 2007]

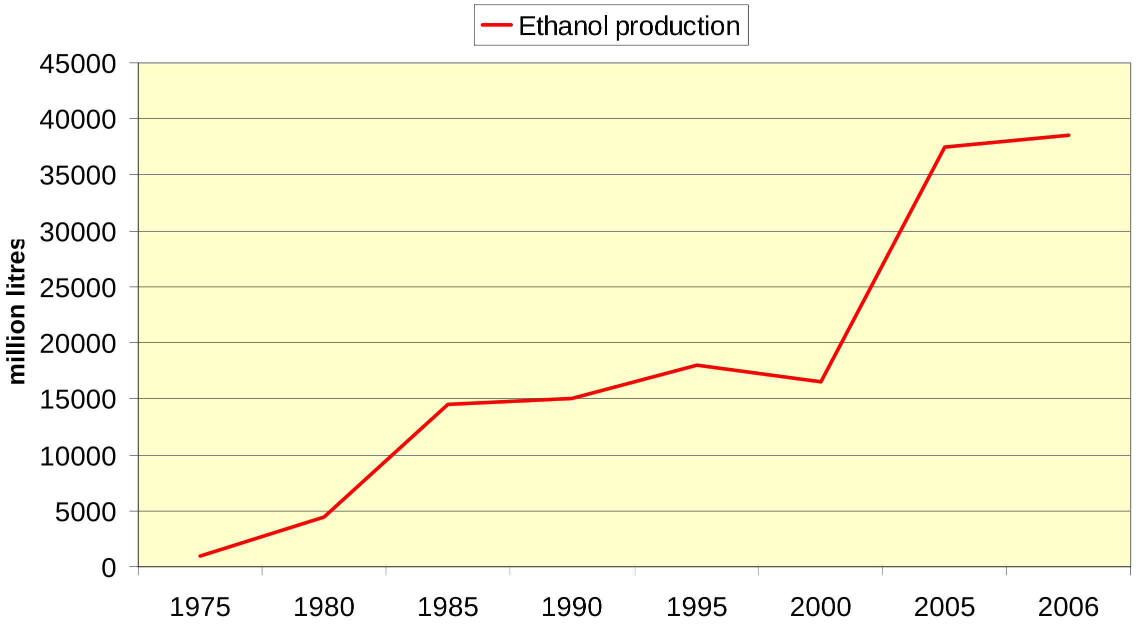


Figure 29: global production of ethanol 1975 - 2006; [Worldwatch a; 2007]

Depending on the type and price of biomass, the quantities and grade of implementation of the process, production costs can widely vary. Subsequently ethanol production costs vary geographically, as ethanol from sugar cane is being produced for 0.18 €/L, while ethanol production from wheat in the European Union costs approximately 0.47 €/L. In the USA, where ethanol is mainly being produced from corn, production costs amount to 0.24 €/L. [Worldwatch b; 2007]

For proper comparability of production costs of petrol and their bio-derived substitutes, it is important to consider energy equivalence, as a consumer’s overall fuel costs (mileage) and engine performance is dependent on the energy content of the fuel. Considering energy equivalence of petrol, production costs of ethanol - with exception of the Brazilian market - are higher than the ones of petrol. This leads to a necessity of governmental subsidies to promote implementation and use of ethanol in the market.

A joint evaluation of the Well-to-Wheels energy use and greenhouse gas emissions for a wide range of potential future fuels and powertrains options was performed in 2003 (and updated in 2006) by EUCAR, the 'European Council for Automotive Research and Development', CONCAWE, 'The oil companies' European association for environment, health and safety in refining and distribution' and JRC, the European Commission's Joint Research Centre. In the following, the study will be referred to as 'CONCAWE WTW-study'. Within this study cost calculations for production of several biofuels in a Well-to-Tank approach were also made.

The following table shows the production costs of ethanol per petrol energy equivalent according to different sources.

Table 6: ***cost scenarios for ethanol production; prices for fuel from 2nd generation feedstock are shaded;***

Ethanol production costs		**details**	**source**
per litre	**per energy equivalent of petrol** [5]		
0.18 €	0.27 €	**current production costs**; **Brazil**; ethanol form sugar cane	Worldwatch b
0.22 €	0.33 €	estimated costs ethanol from wheat straw; oil at 50 €/bbl; wheat straw at 37 €/t	CONCAWE a
0.24 €	0.36 €	**current production costs**; **USA**; ethanol form corn	Worldwatch b
0.36 €	0.55 €	estimated costs ethanol from sugar beet; oil at 50 €/bbl; sugar beet at 26 €/t	CONCAWE a
0.37 €	0.56 €	estimated costs ethanol from wheat; oil at 50 €/bbl; wheat at 100 €/t	CONCAWE a
0.38 €	0.57 €	estimated costs ethanol from wood waste; oil at 50 €/bbl; wood waste at 53 €/t	CONCAWE a
0.47 €	0.70 €	**current production costs**; **EU**; ethanol form wheat	Worldwatch a
0.48 €	0.72 €	estimated costs ethanol from farmed wood; oil at 50 €/bbl; farmed wood at 81 €/t	CONCAWE a
0.51 €	0.76 €	estimated costs ethanol from wheat; oil at 50 €/bbl; wheat at 150 €/t	CONCAWE a
0.64 €	0.95 €	estimated costs for ethanol from lignocellulose; oil at 50 €/bbl	FNR a

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[5] 1 litre of ethanol is assumed to contain 0.67 the energy of 1 litre of petrol

Detailed assumptions for the WTW-study can be seen in the appendix of this thesis.

It can be seen that production of ethanol broadly varies between 0.27 € and 0.95 € (per energy equivalent of petrol).

An increase in the prices for fossil fuels clearly has a positive impact on the direct competitiveness of biofuels, but it must be considered that rising prices of conventional fuels commonly means an increase of expenditure costs in the process chain of biofuels as well (cultivation, transportation).

Although relatively low production costs for ethanol from wheat straw are assumed in the WTW-study, it should be noted that the production of ethanol from lignocellulosic biomass is not established yet on industrial scale, and by requiring higher expenditure for pre-treatment (to make cellulose accessible for yeast) will lead to higher prices when compared to conventional production (at least shortly after implementation). The german agency '*Fachagentur für Nachwachsende Rohstoffe e.V.*' is assuming a price of production for ethanol from lignocellulose in Europe of about 0.64 €/L. [FNR a; 2006]

6.3 1-butanol production prospects

1-butanol production from renewable biomass so far is not established on industrial scale, as politics, investors as well as industry until recently focused more on ethanol as a renewable substitute for petrol.

Butanol production via fermentative processes was heavily used between 1912 and the 1950s in the USA, Canada, Japan and South Africa. Only in Russia were production vessels in operation until the 1980s, producing approximately 100,000 t 1-butanol per year. Extrapolating the available data of demand back to the 1980s, the Russian production would have amounted to approximately one eighth of the worldwide demand.

Cheap oil prices and changing political surrounding conditions in Russia and South Africa then ceased renewable butanol production and so the current industry's global demand for 1-butanol (~ 6.3 million metric tons) is mainly provided by petrochemical production.

Currently butanol from renewable sources, the so called 'bio-butanol', is produced in pilot plants within academia and demonstration plants originally serving as ethanol plants. Generally speaking, it is possible to reconstruct ethanol producing facilities to butanol producing facilities, as the fermentation processes of the organisms (*Clostridia* strains for 1-butanol production and *Saccharomyces* strains for ethanol production and) are in a way similar.

BP and DuPont announced in a press release on the June 20th, 2006 to bring 'bio-butanol' on the UK-market in 2007. Therefore an ethanol fermentation plant in Wissington should have been reconstructed to produce 1-butanol.

However, those plans were dropped and a planned ethanol site in Kingston upon Hull shall now serve as demonstration facility for butanol fermentation. The start-up is now scheduled for early 2009. [Daily; 2007] [BP b; 2006] [New a; 2007]

As the above mentioned WTW-study did not reckon production of 1-butanol, this was done within this thesis, where scientific data obtained from literature was processed in a spreadsheet program according to the calculations made in the WTW-study.

The results obtained from the calculation as well as prices estimated in scientific literature are shown in Table 7:

Table 7: cost scenarios for butanol production; prices for fuel from 2nd generation feedstock are shaded; ("ABE-yield" equates to $Y_{P/S}$)

1-butanol production costs		**details**	**source**
per litre	**per energy equivalent of petrol** [6]		
0.20 €	0.24 €	estimated costs butanol from corn; corn at 56 €; gases are sold; 7.1x10^5 € for waste water treatment	Qureshi d
0.21 €	0.25 €	estimated costs butanol from corn; corn at 56 €/t, gases are sold; 2.1x10^6 € for waste water treatment	Qureshi d
0.27 €	0.32 €	estimated costs butanol from corn; corn at 140 €/t, gases are sold; 7.1x10^5 € for waste water treatment	Qureshi d
0.31 €	0.37 €	estimated costs butanol from corn; corn at 56 €/t, gases are not sold; 2.1x10^6 € for waste water treatment	Qureshi d
0.32 €	0.38 €	estimated costs butanol from corn; corn at 50 €/t, batch fermentation; ABE-yield: 0.42	Qureshi e
0.38 €	0.45 €	estimated costs butanol from corn; corn at 84 €/t, batch fermentation; ABE-yield: 0.42	Qureshi e
0.42 €	0.50 €	estimated costs butanol from a grass rooted plant; corn at 56 €/t, gases are sold; 7.1x10^5 € for waste water treatment	Qureshi d
0.51 €	0.60 €	calculated costs according to WTW-study butanol from corn; oil at 50 €/bbl, corn at 173 €/t, batch fermentation; ABE-yield 0.42	CONCAWE / Qureshi e

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[6] 1 litre of 1-butanol is assumed to contain 0.84 the energy of 1 litre of petrol

0.54 €	0.64 €	calculated costs according to WTW-study butanol from corn; oil at 50 €/bbl, corn at 150 €/t, batch fermentation; ABE-yield 0.42, less credits	CONCAWE / Qureshi e
0.60 €	0.72 €	calculated costs according to WTW-study butanol from corn; oil at 50 €/bbl, corn at 150 €/t, batch fermentation, ABE-yield 0.42; no credits	CONCAWE / Qureshi e
0.62 €	0.74 €	estimated costs butanol from a grass rooted plant; corn at 140 €/t, gases are not sold; 2.1x10^{6} € for waste water treatment	Qureshi d
0.67 €	0.8 €	estimated costs butanol from corn; corn at 168 €/t, batch fermentation; ABE-yield 0.42	Qureshi e
0.68 €	0.81 €	calculated costs according to WTW-study butanol form corn; oil at 50 €/bbl, corn at 173 €/t, batch fermentation; ABE-yield 0.42; no credits	CONCAWE / Qureshi e

It can be seen that production of 1-butanol might vary between 0.24 € and 0.81 € (per energy equivalent of petrol).

Comparing with the current and estimated prices of ethanol (see Table 6) and allowing some variation in the calculations, the **production prospects** on a petrol-equivalent-basis **of ethanol and 1-butanol are of equal magnitude**.

It might be interesting to note that the average price of corn in the current year amounts to roughly 155 $ per tonne, but is not directly correlated with prices of crude oil.

For details of the calculations, see the Appendix section.

The costs of fermentative production of butanol (as well as of other fermentative obtained fuels) depend on several factors. Those are:

- **Substrate costs:** The expenses for feedstock contribute the major factor to the costs of butanol or any other fermentative produced fuel. More than 60 % of the total production costs are being chipped in by the substrate in fermentation processes using 1st generation feedstock. [Gapes b; 2000] Feedstock costs for 2nd generation biofuels using lignocellulosic biomass are projected to bring down the overall process costs significantly, as low value agricultural biomass, wood residues and MSW are available at little or no costs. [Worldwatch c; 2007]
- **Oil price:** It sets the prices for conventional fuels which might be used within the process chain (e.g. in crop cultivation, transportation) and influences the costs of virtually all other products or services.

- **Downstream processing:** As the products of ABE fermentation are obtained in aqueous solution, a lot of energy goes into the purification and separation of the products. It should be noted that the separation of the mixture of water, 1-butanol, acetone, ethanol and solids requires complex multi-level distillation processes, as well as azeotropic rectification. For details of the downstream processing see Chapter 5.3.
- **Sale of by-products:** Besides the product 1-butanol, a lot of by-products are obtained from the fermentation process, as has been shown in Chapter 5.2. These by-products (mainly acetone, ethanol, hydrogen, cell cake and CO_2) can be recovered and sold without extraordinary expenditure. CO_2 can be sold or captured in CCS (Carbon Capture Sequestration) -equipped plants. Depending on the selling of these credits, the overall production costs can be reduced.

As mentioned in Chapter 5.1 the Yield $Y_{P/S}$ is an important factor to judge efficient fermentation processes. Yields over $Y_{P/S} = 0.4$ are quite common in fermentation processes on laboratory scale, while many industrial process yields amount to approximately $Y_{P/S} = 0.37$.

If yields in fermentation fell to $Y_{P/S} = 0.25$ or lower, the process would is no longer be economically feasible. [Gapes a; 2007]

Continuous fermentation processes are broadly established for industrial processes and are seen to require an approximate duration period in ABE-fermentation of four weeks to be economically advantageous.

An economical production of lignocellulosic 1-butanol (2nd generation 1-butanol) is potentially closer than economical production of 2nd generation ethanol, as 1-butanol production from lignocellulosic waste material was already established in industrial scale (see Chapter 5.3 for details).

6.4 Near term prospects for 2nd generation biofuels

Whereas several companies are promising to establish cellulose derived fuels within the next few years or had planned to launch industrial production of these fuels in the past, cellulosic conversion technologies are seen to be approximately 8 – 15 years away from supplying a significant share to the world's liquid fuel demand.

There is indication that biofuels processed through **biochemical pathways** such as fermentation are likely to begin commercial expansion within the next **8 – 10 years**, while the **thermo-chemical conversion methods**, such as Fischer-Tropsch pathways seem to operate commercially slightly later, in approximately **10 – 15 years**.

Though the technologies for converting lignocellulosic biomass into fuels are becoming increasingly cost competitive, the establishment of 2nd generation biofuels on the market will hinge greatly on how much and in what way governments support the technologies and help risk-averse investors to place their money in building a significant number of cellulosic conversion plants.

Production of biofuels is seen as being economically competitive to conventional petrol, when oil prices are resting higher than 50 – 70 $ / bbl. As the current oil price of approximately 90 $ / bbl (December 2007) is largely caused by stock market speculations, investors are not sure that the prices for fossil fuels will on the short term remain high enough for cellulosic conversion technologies to operate competitive. [Worldwatch d; 2007] [IIASA; 2007]

It might be interesting to note that the average oil price (sort ‘Brent’) for the current year 2007 amounts to 71.50 $ and for the first time crossed the 100 $-barrier in early 2008.

Especially the future of 1-butanol as a biofuel is heavily depending on the will of the ethanol industry and involved stakeholders to adapt existing ethanol plants for ABE-fermentation and to construct new butanol plants.

Therefore it can be foreseen, that a potential shift from ethanol production to 1-butanol would probably rather happen as an evolution rather than a revolution.

6.5 Long term potential for 2nd generation biofuels

Diversity of calculation results regarding long term biofuel potential is relatively high, due to different calculation methods, underlying basic data and conversion factors[7]. Depending on the feedstock and the technology of how the biomass is converted into biofuel, conversion factors between 0.34 (current factor ethanol from wood) and 0.6 (hydrogenation from vegetable oil) are estimated. [VES a; 2007]

For calculation of the biofuel potential after conversion (see Table 8) a potential average conversion factor of 0.45 was assumed. This stands in contrary to the calculations through the OECD which assumed a rather conservative average conversion factor of 0.35, which seems too low against the background of the present conversion rate data of the VES.

Conversion factors especially for ABE-fermentation (utilising glucose) are calculated to amount to 0.40, while Formanek, Mackie and Blaschek have shown that *C. beijerinckii* BA 101 can achieve 1-butanol conversion rates of 0.75. [Formanek b; 2007]

Estimations for the technical potential of biomass for energy production vary greatly. The ‘German Agency of Renewable Resources’ (FNR) and ‘Worldwatch’ estimate the worldwide potential of bio-based energy to amount to 40 EJ (roughly 9 % of the world’s

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[7] The conversion factor is the energy content of a fuel obtained from an energy content biomass. This can be described through the equation $Y = MJ_{LHV\ fuel} / MJ_{LHV\ biomass}$

total energy), while the OECD “Round Table on Sustainable Development” assumes a potential of biofuels only to account for roughly 43 EJ in 2050.

OECD as a result assumes biofuels to achieve a market share of almost a quarter of the total liquid fuels market in 2050, where 11 % would come from 1st generation biofuels and 12 % would be provided through the more advanced 2nd generation biofuels. [OECD a; 2007]

It has to be questioned, however, whether this potential can be realised, as concerns regarding a potential ‘fuel versus food’ crisis might limit the potential of conventional 1st generation biofuels (For details regarding food-versus-fuel see Chapter 7.1)

Table 8 shows the detailed assumptions for the worldwide biofuel potential in 2050 (OECD-data adjusted; values in EJ):

Table 8: ***total (oven dry) biomass and biofuel potential for the year 2050 (values in EJ); [OECD b; 2007]***

	Potential from additional land	**Crop residues potential**	**Forest residues potential**	**Organic wastes**	**Total biomass potential**	**Total biofuel potential after conversion [8]**
USA	0.7	5.0	14.3	0.5	20.5	4.6
South & Central America	62.0	4.3	16.8	0.9	84.0	18.9
Europe & Russia	10.1	5.8	16.9	1.1	33.9	7.6
Africa	43.8	6.3	18.2	1.4	69.7	15.7
Asia	- 18.6[9]	12.8	20.6	6.0	20.8	4.7
Oceania	11.2	0.6	3.8	0.1	15.7	3.5
World total	**109.2**	**34.8**	**90.6**	**10**	**244.6**	**55.0**

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[8] It is assumed that half of the biomass is used for biofuels production at an average conversion efficiency of 45 %

[9] negative number because more land is cultivated than potentially available for rain-fed cultivation because of irrigation; not rounded to zero as food imports are likely to be needed from other regions with affections on their land use

It can be seen from the table, that 2nd generation biofuels more than double the world's biomass potential, as crop residues, forest residues and organic wastes are not suitable for biofuels of the 1st generation. According to this calculation approximately 29 % of the world's total transport fuel demand of approximately 187 EJ could be provided through biofuels.

However the 'World Business Council for Sustainable Development' assumes that biofuels could worldwide contribute after conversion approximately 100 EJ of energy. [WBCSD; b 2004]

It becomes clear that the varieties calculated in several scenarios sometimes differ more than 100 %, which shows the uncertainty and variety of these long term assumptions.

It should be noted that the potentials mentioned in the table are technical potentials and would be partially scaled down because of economical restrictions (e.g. economic transportation distance of biomass).

7 Well-to-tank Integration for 1-butanol from biomass

A ‘Well-to-tank’ integration is an analysis, where energy consumption, GHG-emissions as well as emissions of harmful substances are observed from the beginning of the fuel production (‘Well’ stands synonymously for oil well and marks the start of production) to filling the tank of a customer’s car in the context of the fuel’s own energy density.

The ‘Well-to-tank’ (WTT) analysis implies observation of the process chain along the production, refinery and distribution, as Figure 30 illustrates for biomass derived fuels.

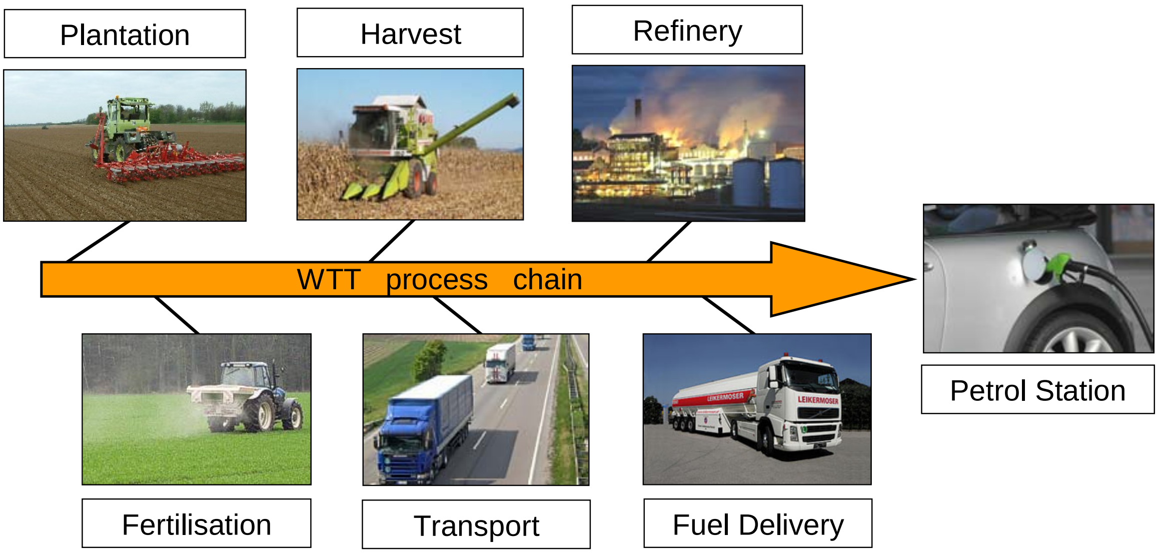

Figure 30: Illustration of the Well-to-Tank process chain

In the following, the several ecological and economical aspects that play a role in the Well-to-tank process chain are being elaborated.

7.1 Food-versus-fuel aspects of biofuel crop cultivation

The biomass that delivers the carbohydrates which are converted into the solvent 1-butanol can either be cultivated on purpose or be collected from agricultural (e.g. corn stover) or wood residues.

Cultivation of crops on agricultural land for biofuel production is necessary for processes in which only the starchy or sugar containing fraction of the plant can be used. These processes are referred to as 1st generation biofuels (see Chapter 2.2 for details).

Expansion of biofuel programmes will globally increase the demand for agricultural products. As currently no processes making use of 2nd generation feedstock are established, a rising demand in biofuels means an increase of arable land serving for biofuel crop cultivation.

Currently, virtually the earth's entire arable surface is already in use. The global surface amounts to 13.4 Gha, of which 3.9 Gha is captured by forests, 3.5 Gha is used as grass land, 0.2 Gha are urban settlements, 1.5 Gha is used as arable land and large parts of the remaining 4.2 Gha are consisting of deserts, mountains and other land that is unsuitable for productive use. The OECD estimates 0.44 Gha as an upper limit that could be made available for dedicated bio-energy crop cultivation in 2050. The FAO (Food and Agriculture Organization of the United Nations) warned in the year 2000, that models used to calculate land availability tend to overestimate the amount of land which could be used for agriculture by 10 – 20 %. [OECD c; 2007]

In this regard, 1st generation biofuels will especially have a significant future impact on the agricultural economy.

Within this context a 'food versus fuel' dilemma is discussed frequently. The concern is that land that would otherwise serve for food production might become fuel production land and leave the world's poorest people hungry.

This concern has to be taken serious, whereas it might be too simplistic: As a result of governmental subsidies and policies in industrialised countries, market prices for many agricultural goods like sugar beet, corn and wheat often fall under their costs of production and by that prevent a liberal trade (in response to agreements under the WTO).

These low prices of agricultural goods have a great impact on small-scale producers in developing countries and lead to excess production of agricultural goods in industrialised countries.

The move to biofuel programs can help to absorb excess supply, and through higher commodity prices, bring profit to rural areas worldwide, (due to most of the suitable land being located in Africa and South & Central America) particularly to developing countries. Many of the world's 800 million undernourished people are farmers or farm labourers, who could benefit from an end to 'commodity dumping'.

It should be noted, that profit of farmers by biofuel-programmes depends on the embodiment of biofuel crop cultivation. It is more likely that farmers will more benefit, if production of biofuel is designed on a small-scale, labour intensive manner, than in large plantations of monocultures controlled by big companies.

The 'food-versus-fuel' debate will be significantly diminished, when biofuels can be produced from lignocellulosic biomass (2nd generation biofuels).

With 1-butanol, 2nd generation biofuels could be quicker implemented in the market than ethanol from lignocellulose, as 1-butanol from lignocellulosic biomass was already established in industrial scale (see Chapter 5.3 for details).

Though 2nd generation feedstock would diminish a fuel vs. food competition, cellulosic feedstock could also put pressure on food supplies, particularly if enormous demand for biofuels strains the limits of agricultural potential and productive land. [Worldwatch e; 2007]

Consequently specific standards for cultivation of biofuel-dedicated biomass are essential to avoid negative impact on the food- and agricultural sector.

7.2 Environmental impacts of biofuel-plant cultivation, transportation and refinery

Regardless of the intended application, agricultural cultivation has significant impact on the environment, mostly on water, air-quality/climate and biodiversity.

Impacts on water:

While crop cultivation of corn, wheat, sugar beet and sugar cane requires no additional water besides rainwater in the central parts of Europe, the middle west of the USA and the centre-south of Brazil, agricultural cultivation in many countries is heavily dependent on irrigation. In Europe especially Spain, Portugal, France, Belgium and Greece have to irrigate their agricultural areas, which leads to a partial drawdown of groundwater, dry up of wetlands or oxygen deficiency in rivers.

Different kinds of plants require specific amounts of water for growth: [Karl; 2003]

- Corn takes up approximately 300 L of water per kg dry matter
- Wheat takes up 300 – 400 L of water per kg dry matter
- Sugar beet takes up 350 – 500 L of water per kg dry matter
- Miscanthus takes up approximately 300 L of water per kg dry matter
- Poplar and willow take up approximately 800 L of water per kg dry matter

It can be seen that not only the more discussed plantation of crops, but also cultivation from short rotation forestry (poplar and willow), partially require huge amounts of water, which could run short if cultivated in improper areas.

When judging the impact of a specific crop on the aqueous environment, the plant's demand for fertilizing agents has to be considered, especially nitrogen fertilizers (commonly made from natural gas), which can cause, if used excessively, eutrophication (overload with chemical nutrients) of surface waters due to the increased load of nutrients.

Projects in Brazil have shown that the filter cake obtained after fermentation serves as a good substitute for fertilizers and helps creating value from waste streams.

Generally spoken grasses (e.g. switchgrass) and lignocellulose coppice have a less demand in nitrogen and by that would be favourable not only for water but also for the climate (see 'Impacts in air quality / climate' in this Chapter).

But not only water uptake and use of fertilizers during plantation has to be considered. The biotechnological refinery process and pre-treatment require huge amounts of water and results in large volumes of nutrient-rich waste water. To keep fermentation temperatures under moderate levels (30 – 40 °C) high amounts of water are required for cooling, which means that high amounts of warm water which can, if released into local streams, alter ecosystems and even lead to fish mortality. In Brazil or example, 3,900 litres of process-water are required per tonne of sugar cane utilised.

As fermentation processes happen in liquid state, water has to be added in the medium preparation step, which ends up as nutrient-rich wastewater that has to be cleaned and recycled as would otherwise lead to eutrophication of rivers and local streams by affecting the water's dissolved oxygen content. [Worldwatch f; 2007]

Impacts on air quality / climate:

The air quality is affected through biofuel processing along the whole Well-to-tank chain, as cultivation of crops emits greenhouse-relevant substances, transportation through trucks emits GHGs and fermentation produces CO_2, NO_x, SO_x, VOCs (Volatile Organic Compounds) and particulate matter.

A recently published study examined the N_2O-release from nitrogen fertilizer use in biofuel crop cultivation. It was found out that when taking into account the GWP of N_2O (see Chapter 2.1 for details) and the positive effect of saving fossil fuels, the current established biofuels such as biodiesel from rapeseed and ethanol from corn can contribute as much or even more to global warming by N_2O emissions than burning of fossil fuels (biodiesel's global warming effect is approximately 1.0 – 1.7 times larger than the positive effect from saving fossil fuel; ethanol's global warming effect is slightly lower amounting to 0.9 – 1.5 times the global warming effect of fossil petrol). Approximately 1 % of the fixed nitrogen input from the fertilizer is released in the form of N_2O.

This contribution to global warming by biofuels can only be reduced by making use of plants that have much lower demand for N, as perennial grasses, like switch grass and miscanthus, but especially lignocellulosic plants would be favourable.

For biodiesel, production from oil palm might have a moderate positive effect for the climate, when rainforests do not have to be cleared for cultivation. [Crutzen; 2007]

It was proven, that corn-ethanol plants in Iowa (USA) have emitted probable cancer-causing chemicals such as formaldehyde and toluene.

VOCs mainly occur during the process of blending 1-butanol or ethanol with petrol, whereas they nowadays can be efficiently collected in newly erected plants. Occurrence of VOCs is more of interest in low blending rates of ethanol with petrol, as the rise of vapour pressure of the blend between 1 % and 5 % implicates a higher volatility of components, resulting in evaporative emissions. 1-butanol shows significantly lower tendency forming VOCs, as it has a lower vapour pressure and does not show any significant vapour pressure anomaly when blended with petrol.

It should be noted that much of the air pollution that is associated with biofuels comes from burning fossil fuels (in USA, Germany, China and others mainly coal) for process heat and power of the bio-refineries (see Chapter 9 for details). Subsequently, well designed bio-refinery concepts in which waste streams (like distiller’s sludge) are used for process heat and power would significantly lower the costs of the biofuel production process, while decreasing environmental impact.

However fermentative processes from an air-quality point of view can be justified advantageous over biodiesel production processes, which require hexane for oil-extraction from plants and seed. Although the air pollutant hexane is recycled as much as possible, it is assumed that approximately 10 kg of hexane are emitted into the air per tonne of oil obtained from soybean (besides other pollutants).

Transportation of biomass is usually done by trucks and biofuel delivery as well is commonly done by trucks. An exception is Brazil, where biofuels are mainly delivered via pipeline.

As demand for bio-derived fuels increases and consumption of biofuels exceeds the own production in some countries, a rising amount of feedstock and biofuels will be transported over longer distances, especially by ships. Shipping on the one hand is a relatively energy efficient way of transporting goods, but also means a major source of pollution, due to a lack of regulations governing emissions from maritime transport.

Impact on biodiversity:

As mentioned before, land availability for biofuel dedicated crops tends to be overestimated. As a consequence, land that was untapped nature more and more is being converted to agricultural land.

The biggest threat of expanding land for cultivation of biofuel crops or any other use is the irreversible conversion of virgin ecosystems.

Consequences are rarely known but studies suggest that deforestation causes the annihilation of many species and their habitats, affects the hydrological cycle on regional scale (reduction of precipitation) and the climate on global scale.

Currently, especially the rainforests of Malaysia, Indonesia and Brazil are at great risk to lose significant parts of their unique flora and fauna.

Drivers of rainforest-clearing in Malaysia and Indonesia are mainly plantation of soybeans (which still are more used for food rather than fuel) and oil palm. Soybean production is inducing an expansion of pasture land for cattle into new forest areas, while plantation of oil palm directly into former rainforest areas is one of the leading causes of rainforest destruction in Southeast Asia.

It is calculated that approximately 32,000 ha of forest in the Malaysian region *Sabah* are cleared every year for plantation of oil palm. [WWF; 2007]

It should be noted that soybean or oil palm are not cultivated for 1-butanol production, but biodiesel products. However, it shall be observed in terms of an integrated observation of a environmental effects of biofuels on the whole.

Besides biodiesel, production of ethanol from 1st generation feedstock can also have a significant impact on a countries' ecology.

Brazil, as one of the worlds dominating ethanol producers (secondary to the USA) is heavily expanding land for sugar cane production and by that replacing pasture land and small farms planting varied crops for large monocultures. The *Cerrado*, Brazil's wild savannah that covers more than one quarter of the land area and is home to half of the countries endemic species that cannot be found anywhere else, is supposed to be the future expansion area for sugar cane production. Concerns are rising that an expansion of agricultural production into this complex ecosystem could result in irreversible ecological damage (also because vast stretches of the *Cerrado* as well as rainforest are replaced by soybean cultivation). [Worldwatch g; 2007]

Broadly spoken the same statements as noted for ethanol would apply for 1-butanol production, as 1-butanol can be produced from the same feedstock as ethanol. However, as mentioned in Chapter 5.3, it seems 1-butanol is closer to become a 2nd generation biofuel than ethanol making use of lignocellulosic biomass as lignocellulosic 1-butanol had already been established, and by that, future negative impact on biodiversity, water and climate from cultivating feedstock can be assumed to be significantly lower.

Relative to fossil fuels, the impacts of biofuels resulting from cultivation, transportation and refinery are generally significantly smaller. Anyhow, as cultivation of biomass dedicated for biofuel production is rapidly boosting, while little is known about the overall environmental impacts of biofuel-crop plantation, future research has to be done in this field, while some institutions already demand a deceleration of biofuel programmes (e.g. the ‘Umweltrat’ of the German Federal Government).

A potential future positive contribution to the world’s climate without major negative impacts on environment and biodiversity is heavily dependant on an elaboration of binding standards and certification schemes for agriculture and cultivation of biofuel dedicated plants and (as biofuel trade will massively increase within the next years) trade of biofuels to assure a better overall sustainability of the Well-to-tank value chain.

To increase crop yields per hectare and the need for water and pesticides, cultivation of genetically modified (GM) crops is one promising measure. GM crops are plants which have their genetic make-up altered by means of molecular-biological engineering that does not involve conventional, natural methods of breeding.

As of 2003, approximately 80 % of the US soybean crop and roughly 40 % of its corn crop where genetically modified. While a positive effect in reduction of pesticides and especially herbicides is controversial and some studies cite that chemical treatment has increased with GM crops, cultivation of GM crops is increasing worldwide.

A coexistence of conventional plants and GM plants is seen as implausible, as bees and wind can carry GM pollen over long distances, ‘contaminating’ conventional as well as ‘organic farmed’ plants.

Subsequently any benefits of GM crops must be weighed carefully against the risks they pose to wild-life, biodiversity and human health.

Additionally in much of Asia and several European countries, there is considerable opposition against the cultivation and processing of genetically modified plants. This could also pose a potential future threat for promoting 1st generation biofuels with respect of their social acceptance.

2nd generation biofuels would significantly diminish the issues addressed above, as these biofuels make use of residues and wastes and would not cover much of the land for production of feedstock.

7.3 Economical aspects of biofuel-plant cultivation, biomass transportation and 1-butanol delivery

Biomass that serves as 1st generation feedstock is cultivated on purpose and thus is accumulated relatively evenly. Biofuel refineries are commonly located nearby areas of agricultural cultivation and crops are partially processed automatically (cleaning, threshing etc.) directly on site to keep transportation costs and overall energy input low. Issues regarding an energy efficient transportation of the feedstock are therefore of secondary importance.

As feedstock of the 2nd generation, especially wood residue, is accumulated irregularly, consideration of an energy efficient transport is of great importance not only when deriving the economical potential from a technical potential but also when it comes to judging the overall efficiency of an energy conversion act, commonly expressed through the EROEI-factor (Energy Returned On Energy Invested). EROEI is the ratio of amount of usable energy obtained from an energy resource to the energy to be expended for acquiring the energy resource.

From that point of view, transportation of 2nd generation biomass is very important to consider, as a process could end up requiring more energy solely for transportation of biomass, as can be obtained from the biofuel after conversion.

If chopped wood is not being pre-processed on site, the economic transportation distance is limited to 200 km. When wood residues are processed and transported as wood chips, the maximal economic transportation distance rises, whereas the most efficient way and thus the greatest economical transportation distance can be achieved, when woody biomass is transported in form of pellets. The lower the transportation distance, the lower the GHG-emissions and subsequently the better the overall well-to-wheel efficiency [OECD c; 2007] [Verenum; 2007]

Among the factor $Y_{P/S}$ for judging efficiency of a fermentative process (see Chapter 5.1) and the EROEI, a more practical factor often used to judge the overall efficiency of converting biomass to biofuel is the **volume of biofuel** that is **obtained from a mass of biomaterial**.

As corn is mostly used in the USA for producing ethanol, it became common practice to quote the overall yield of ethanol in US Gallons[10] per bushel of corn[11].

To evaluate 1-butanols' competitiveness over its closest "competitor" ethanol, the calculations were derived from "gallons per bushel of corn" and converted into litres per hectare.

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[10] 1 US Gallon corresponds to 3.79 L

[11] 1 bushel of corn corresponds to 25.40 kg

The following table shows the yields of ethanol and / or 1-butanol (shaded) per energy equivalent of petrol currently obtained.

***Table 9:* 1-butanol yields (shaded) per area compared to ethanol yields per area;**

Feedstock / Product	Crop yield (per acre)	Yield of product per hectare	**Yield per hectare (in energy equivalent of petrol)**	source
corn / ABE	~ 150 bushel (USA)	1,594 L BuOH 808 L Acetone 423 L EtOH /ha	~ 1,622 L (excluding acetone)	adapted from [Formaenk c; 1997]
wheat / ethanol	---	2,560 L EtOH / ha	~ 1,715 L	[FNR b; 2006]
corn / ethanol	~ 131 bushel (EU)	3,063 L EtOH / ha	~ 2,052 L	adapted from [Ethanolproducer; 2007]
corn / ABE	~ 150 bushel (USA)	1,824 L BuOH	~ 2,171 L *	adapted from [Ramey; 2004]
corn / ethanol	~150 bushel (USA)	3,506 L EtOH / ha	~ 2,350 L	adapted from [Ethanolproducer; 2007]
corn / ABE in fibrous bed reactor	~ 131 bushel (EU)	3,063 L BuOH	~ 2,573 L *	adapted from [Ramey; 2004]
corn / ABE in fibrous bed reactor	~150 bushel (USA)	3,507 L BuOH	~ 2,946 L *	adapted from [Ramey; 2004]

It can be seen that the output of 1-butanol from conventional ABE-fermentation is clearly lower than for ethanol fermentation, as the additional products acetone and ethanol are obtained as well. Acetone is excluded from calculation of the “energy equivalent of petrol”, as it is not regarded as a potential fuel blending component in significant amount. Thus yields of 1-butanol and ethanol from ABE fermentation are roughly 20 % lower compared to conventional ethanol fermentation (on a petrol-equivalent basis).

If taking production of acetone into account (which can be sold to the chemical industry), the productivity of ABE-fermentation amounts to ~ 2,825 L and by that shows a higher overall conversion efficiency than ethanol fermentation from corn.

Ethanol production from sugar beet and sugar cane gives higher yields, as yields from sugar beet roughly amount to 5,000 L EtOH / ha and yields from sugar cane amount to roughly 6,000 L EtOH / ha. [Worldwatch h; 2007] These observations could not be compared to 1-butanol yields due to lack of data.

Data marked with (*) should be accepted under reserve, due to the fact that these yields were obtained in a demonstration plant using non-established fermentation technology (Immobilized cells in a fibrous bed reactor) feeding additional substrate (butyrate) besides corn.

There is no reliable data regarding yields from 2nd generation feedstock only, thus it is not being considered in this calculation.

8 Tank-to-wheel integration for 1-butanol

A ‘Tank-to-Wheel’ (TTW) integration observes the aspects of storing and combusting a fuel, most commonly dealing with several aspects of combustion in an ICE (internal combustion engine). The main aspect of a Tank-to-wheel analysis is of technical nature, but economical and environmental aspects like mileage and emissions have to be considered in a comprehensive TTW-integration as well.

The main technical parts that are affected by a TTW-integration can be seen in Figure 31.

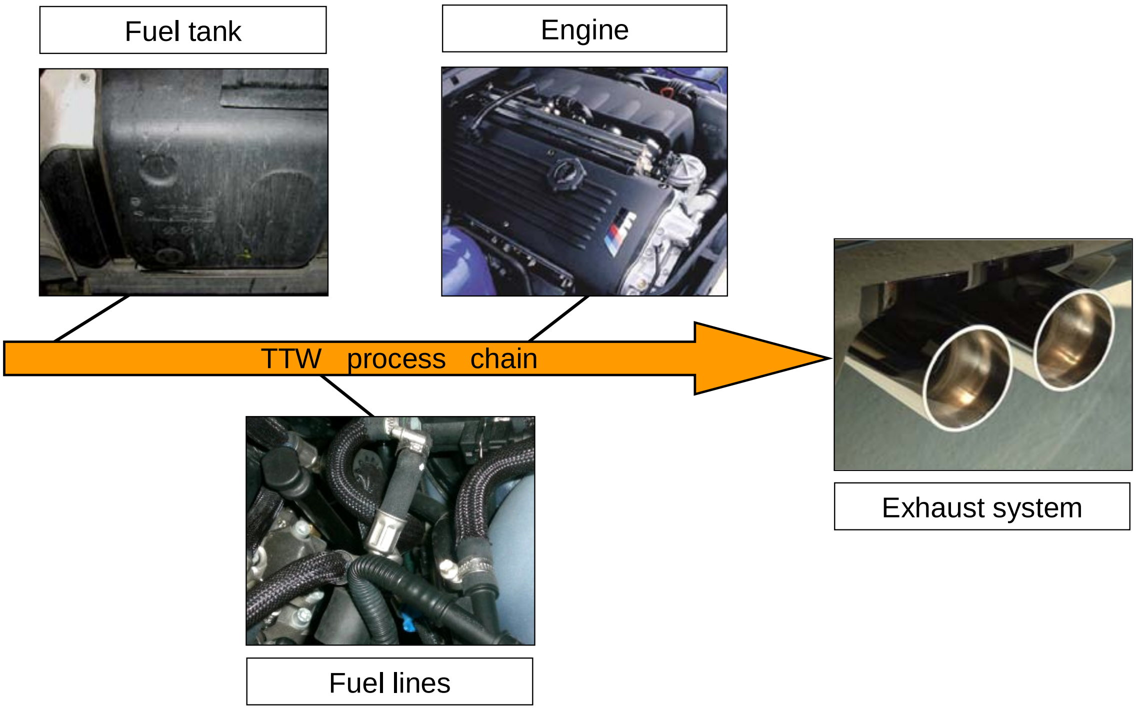

Figure 31: main technical parts along the TTW process chain

With help of a TTW-integration it becomes clear whether the proposed fuel can be used pure or blended, with or without need of additives, in conventional or modified diesel or petrol engines. The following chapters will give an insight into the TTW-balance of 1-butanol and compare observed data with other biofuels of interest (especially ethanol blends).

8.1 Technical aspects of combusting 1-butanol in internal combustion engines

1-butanol as a liquid hydrocarbon is seen as a potential biofuel candidate on a mid-term range, as it does not require any major changes in on-board storage and engine periphery, in contrary to potential long-term biofuels like liquid hydrogen (LH_2).

A higher volumetric power density of roughly 27 MJ / L compared to ethanol (21 MJ / L) or other alternative fuels like CNG, allows a more efficient on-board storage and reasonable travelling distances between refuelling stops.

Similarity with the conventional fuels petrol and diesel determines whether a potential biofuel can be used either in pure form or has to be blended with conventional fossil fuel to satisfy the European fuel standards for petrol (EN 228) and for diesel (EN 590).

8.1.1 Combustion of pure 1-butanol

Similar to the use of other alcohols like ethanol, combustion of pure 1-butanol requires changes in the layout of the powertrain. Pure alcohols show significantly lower vapour pressures than petrol and thus ignition improvers have to be added to the alcohol or cylinder block heating systems have to be implemented to ensure cold-start ability.

Not only vapour pressure but also enthalpy change of vaporisation (heat of vaporisation) is of importance for engine-start under cold conditions. Heat of vaporisation is the energy that is necessary to transfer a substance into gaseous state. From that point of view 1-butanol is superior to ethanol, as 1-butanol’s heat of vaporisation amounts to 584 kJ / mole and is significant lower than ethanol’s heat of vaporisation amounting to 837 kJ / mole. The intersection of these two factors should be observed in future studies to note the thermal conditions in the combustion chamber and to evaluate 1-butanol’s advantage over other alcohols concerning this issue.

Moreover, corrosion and elastomer compatibility is an important issue in combusting alcohols in automotive engines. Especially storage and combustion of pure alcohols requires special materials of fittings, gaskets and filters, as alcohols tend to associate with the synthetic material and increase weight and volume and properties.

Alcohols as solvents have a significant ‘cleaning’ effect on all parts of the tank, fuel line and the engine. This has to be considered especially with ICEs, which so far have been running on conventional petrol or diesel and shall then be adapted for (pure) 1-butanol (or other alcohols). Firmly bonded deposits can be solved through alcohols and lead to a quicker clogging of filter pores. This could lead to shorter car-service intervals.

While little is known about the combustion behaviour of pure 1-butanol in spark ignition engines, higher viscosity and higher heat of vaporisation potentially would demand adaptation of the fuel injection nozzles and would lead to a slower rate of fuel vaporisation.

Combustion of pure 1-butanol would have one significant disadvantage over ethanol, which is due to the higher boiling point of 1-butanol, which amounts to 117.7 °C. Internal combustion engines allow marginal amounts of unburned fuel to leave the combustion chamber around the piston rings (‘blow-by’) into the bottom of the crankcase and because of dilution reduce the oil’s ability for lubrication.

However, combustion of pure 1-butanol as well as other alcohols doesn’t seem to be under consideration in the automotive sector at least on the mid-term.

8.1.2 1-butanol as a blending component in compression ignition engines

Some studies (e.g. Sperling Ernst; ‘*Die Verbrennung von n-Butanol-Dieselkraftstoff-Gemischen im Vorkammer-Dieselmoto”*’) claim 1-butanol is a potential blending component for compression ignition (CI or diesel) engine application, as evaluation of butanol-diesel blends in practical testing did not show any major problems on the short-term.

Nevertheless 1-butanol will not serve as an alternative fuel for conventional diesel in Europe under current conditions, as the flash point of pure 1-butanol (34 °C) is significantly lower than the one of diesel and by that is bringing down the flash point of a 1-butanol-diesel blend under the minimal value that is demanded by EN 590 already in ‘weak’ blends, which could be shown within this thesis (see the Appendix section ‘Results from laboratory testing’, available only in BMW-internal version).

An adaptation of the EN 590 is seen as improbable, as a flash point lower than 55 °C for diesel fuels would result in classification into another storage-safety class, which would mean major changes in refineries as well as storage tanks and petrol stations.

The low flash point moreover is a main technical problem of alcohol-diesel blends. However 1-butanol is more capable of meeting the demand after an ignitable diesel-blend and several testing showed no ignition-misses during combustion in slightly adapted engines running on 1-butanol-diesel blends up to 70 % (v/v).

Anyhow, taking a closer look at the combustion process reveals the occurrence of ignition delay, which leads to a thermodynamic disadvantageous combustion in the chamber, which means a lower efficiency for the engine. To compensate for the low flammability of alcohols, engine adaptation in respect of achieving a temperature increase of the combustion chamber wall would be necessary.

Emissions of nitrogen oxides could be reduced in the order of 3 - 4 % per 10 % (v/v) of 1-butanol, while a reduction in particulate matter (PM) of about 6 - 7 % per 10 % (v/v) and a reduced tendency for coking could be achieved in experiments. [Sperling c; 1988]

It should be noted that whereas alcohol-diesel blends might not have a bright future in the individual traffic in the near term, modified diesel engines running on almost pure alcohol are already locally established in public transport.

Stockholm’s public transport company ‘SL’ (*Storstockholms Lokaltrafik AB*) is currently operating approximately 500 busses, which are running on 95 % hydrous ethanol (*‘Etamax D’*) and 5 % of an ignition improver (*‘Beraid’*) to initiate combustion. While a drop in fuel economy of about 40 % (v/v) (approximately 26 % energetic) has been reported by the manufacturer ‘Scania AB’, SL reports higher maintenance costs as well. [Akzo Nobel; 2007]

8.1.3 1-butanol as a blending component in spark-ignition direct injection engines

Both, alternative fuels and spark-ignition direct injection (SIDI, also referred to as DISI) engines completed a lot of research during the last years, but few studies have addressed the intersection between alcohol based fuels and modern SIDI engines.

SIDI engines have been developed to optimize fuel consumption and power output with simultaneous reduction of emission, in other words to increase efficiency of the combustion process.

Current modern and future engine concepts are likely to run on blended alcohols like 1-butanol blends and ethanol blends.

3 main types of SIDI engines have been developed over the last years, the

- **air guided SIDI engines**, where the fuel is transported to the spark plug through a generated charge flow
- **wall guided SIDI engines**, where the fuel is fed to the spark plug through a suitable shaped combustion chamber wall or piston
- **spray guided SIDI engines**, where fuel is injected into the combustion chamber directly to the spark plug by means of a piezo-injector. This system is given the highest prospects of reducing emissions and increasing thermal efficiency as moistening of the combustion chamber wall can be significantly reduced and it allows an optimal fuel-mixture generation through multiplex injection.

Figure 32 shows the arrangement of the piezo-injector and placing of the fuel in a spray guided SIDI engine.

Figure 32: arrangement of injector and spark plug in a BMW SIDI engine

1-butanol is commonly given the best prospects as a blending agent for petrol in unmodified conventional spark ignition engines and modern SIDI engines, despite that alcohols generally offer several properties differing from petrol, which can be seen in Chapter 3.1. These differences have to be considered in any technical tank-to-wheel analysis, as fuel lines, gaskets, combustion characteristics, and emissions are affected. To reduce effects of the differing properties in unmodified petrol engines and anyhow benefit from the positive effects of renewable fuels, blending is one path to meet these targets.

Storage of 1-butanol or 1-butanol-petrol blends is not differing significantly from in car-storage of conventional petrol as 1-butanol shows low water hygroskopy and by that does not lead to corrosion. This contrasts with ethanol, which shows significant water affinity and thus a higher tendency for corrosion.

It should be noted that even though plastic tanks are established within the automotive industry since the 1980s, steel tanks might again gain in importance as migration of fuels through plastic tanks is becoming more and more an issue, especially for SULEVs (Super Ultra Low Emission Vehicle).

A potential evaporation of fuel out of the tank especially occurs in ‘weak’ ethanol-petrol blends between 0.5 % and 5 %, as vapour pressure increases because of the lower number of hydrogen bonds between ethanol molecules. This sometimes is referred to as ethanol's 'vapour pressure anomaly'.

1-butanol with its longer alkyl chain shows lower influence of the hydroxyl chain and because of a higher number of Van-der-Waals forces offers a significantly lower vapour pressure without any significant vapour pressure anomaly in any blending ratio with petrol.

During transportation of the liquid fuel along the fuel lines, there is frequent contact between alcohol components and plastic components, thus interaction with elastomers is important to being considered in TTW-integrations.

1-butanol with its lower LHV than petrol has a higher viscosity of 2.95 mPa*s compared to petrol (around 0.44 mPa*s), which would result in a slightly longer injection time. This certainly would not be of major importance in 'weaker' blends; however it should be considered that especially spray-guided SIDI engines (e.g. BMW engines with 'High Precision Injection') are very sensitive to the time between end of fuel injection and spark initiation. [Smith a; 2007]

What has been stated in Chapter 8.1.1 might as well become of importance for 1-butanol-petrol blends, depending on the 'strength' of the blend: Pure 1-butanol, with a boiling point of 117.7 °C could lead to dilution of the motor oil on the long term, because ICEs allow marginal amounts of the fuel and gas to leave the combustion chamber into the crankcase. The higher boiling point of 1-butanol would avoid boil-off during daily driving and might reduce the oil's lubrication ability.

The most significant difference between petrol and alcohols recognised by the driver is a lower cruising range. The differences in the range certainly correlate with the ratio of the blend.

Ethanol with a LHV of about 5.9 kWh per litre offers roughly 1/3 less energy per litre than pure petrol (~ 9 kWh / L).

1-butanol with a LHV of about 7.5 kWh per litre can offer higher a higher cruising range in any blending ratio in comparison to ethanol. The higher energy content of 1-butanol is mainly due to a lower mass content of oxygen (1-butanol: 21.6 %; ethanol: 34.7 %).

The RON (Research Octane number; 'ROZ' in german convention) is a measure for the autoignition resistance of a petrol fuel. A higher octane number implicates higher activation energy to start combustion and subsequently it is less likely that a given pressure in the combustion chamber leads to irregular combustion or self-ignition. 1-butanol has an octane rating of 94 and would practically not change the octane rating if blended with petrol rated RON 95 (EN 228 'Ottokraftstoff Super'), but reduce octane rating of petrols with higher octane rating like EN 228 'Ottokraftstoff Super Plus'.

Ethanol has an octane rating of 104 and thus introduces the possibility of higher compression ratios and thus could offer higher thermal efficiency.

8.2 Environmental aspects of combusting 1-butanol in internal combustion engines

The level of emissions from burning alcohols in ICEs depends on the technology of the engine, the driving cycle, the exhaust system and on the ratio of blend.

Various studies agree on the statement that biofuel use significantly reduces emissions of controlled pollutants and toxic emissions on a tank-to-wheel basis.

Nevertheless future research has to be done to evaluate the specific influence of the factors mentioned above as the level of emissions differs from study to study.

Significant reduction of **CO_2-emissions** from the combustion process cannot be obtained through blending petrol with alcohols. Combustion of pure 1-butanol leads to formation of roughly 1930 g CO_2 per litre, which equates to 71.70 g CO_2 per MJ. Combustion of petrol leads to formation of 2318 g CO_2 per litre which equates to 73.8 g CO_2 per MJ. The same applies for ethanol, which combusts to ~ 70.80 g CO_2 per MJ (1510 g CO2 per litre).

However it should be noted that CO_2-emissions from renewable sources like biotechnologically produced 1-butanol are commonly being considered as environmentally neutral as their carbon stems from biomass (for details see Chapter 9). CO_2-emissions are currently not affected by any emissions standard, but plans in the EU as well in some states in the USA are announced to include CO_2 in future emission standards.

Emissions of sulphur oxides (SO_x) have been reduced significantly over the last decade through catalytic hydrodesulphurisation and no longer display a major issue in vehicle emissions. SO_x implicates the oxides of sulphur, whereas SO_2 is of primary importance in vehicle emissions. A definite reduction in sulphur content was important because of air-quality matters, as toxic SO_2 would otherwise occur during combustion, and as sulphur would favour corrosion and lead to inefficiency of the catalytic converter.

As a result the European Union since January 1st, 2005 no longer allows sale of petrol and diesel with sulphur content higher than 50 ppm (50 mg/kg) and furthermore fuels with maximum 10 ppm have to be offered. From the beginning of 2009, the maximum content of sulphur in any petrol and diesel sold for car use may not exceed 10 ppm. [EU a; 2008]

Blending of petrol through alcohols, independent of the type, would reduce the content (and emissions) of sulphur, as alcohols do not contain any sulphur. The reduction of sulphur oxides would correspond proportional to the content of alcohol in the blend. SO_x-emissions are not affected by emission standards.

Emissions of nitrogen oxides (NO_x) are commonly affected by emission standards and their emission from road transportation is going to be further reduced. Current values allowed by emission standard ‘Euro 4’ amount to 80 mg/km for petrol powered cars and 250 mg/km for diesel powered cars. ‘Euro 5’, which will come into force on September 1st, 2009 demands a maximum value of NO_x-emissions of 60 mg/km for petrol vehicles and 180 mg/km for diesel vehicles. NO_x are precursor substances to ground level ozone, particulate matter (PM) and ‘acid rain’, therefore their treatment is of particular importance. Immissions from NO_2 and NO mainly stem from diesel vehicles.

It should be noticed, that while in chemical terms NO_x includes all binary oxygen-compounds of nitrogen (NO, NO_2, N_2O, and the instable N_2O_3, N_2O_4, N_2O_5), emissions regulations specify NO_x as the sum of NO_2 and NO and is calculated as NO_2-equivalent.

Formation of NO_x is divided into three sources, ‘thermal NO_x’, ‘fuel NO_x’ and ‘prompt NO_x’. NO_x from combustion of petrol or petrol blends mainly derive from thermal NO_x (90 - 95 %) and prompt NO_x (5 - 10 %).

Although 1-butanol, like all alcohols, does not contain any N and by that reduces emissions of fuel NO_x in petrol as well as diesel blends, several studies come to different conclusions. Most of them state that at least ethanol-blends emit slightly higher amounts of nitrogen oxides; however there are exceptions and evidence that NOx-emissions from 10 % ethanol-blends range from a decrease in the range of 10 % to an increase of about 5 % relative to pure petrol. [Worldwatch i; 2007]

Hydrocarbons (HC) can be observed in the exhaust gas from engines that are suffering from incomplete combustion processes.

Not much is known about emissions of hydrocarbons from 1-butanol combustion, therefore evaluation through practical testing is suggested.

Moreover, it appears to be very important to further evaluate the potential of 1-butanol-petrol blends especially in spark ignition engines.

9 Well-to-Wheel integration for 1-butanol

The previous chapters have given insight in specific expenditures of 1-butanol production and the impacts of biofuel-crop plantation on the environment as well as the technical and environmental issues regarding combustion of 1-butanol either neat or blended. Observed data for 1-butanol has been compared with other biofuels of interest.

The following Well-to-Wheel (WTW) analysis covers the impact and outcome of 1-butanol and competing biofuels of interest in a more general context over the whole process chain of production and consumption.

The potential of reducing GHG-emissions, while offering reasonable energy density, is one of the key drivers for biofuels and a WTW-analysis is the basis for assessing the impact of a fuel and to judge its environmental performance.

By means of a WTW-integration, it becomes more evident, whether a potential biofuel adds more greenhouse gases to the environment than use of neat fossil fuel or can account to a significant reduction of anthropogenic GHG-emissions.

Moreover, the costs of a given reduction in greenhouse gases are commonly evaluated by Well-to-Wheel integrations, which are somewhat similar to lifecycle analyses.

The following figure shows the GHG-emissions of 1-butanol and other biofuels of interest compared to the GHG-emissions of petrol and diesel on a well-to-wheel basis (production, distribution and consumption). For clarity reasons, the figure has been put on the following page.

The CO_2-emissions from combustion of biomass derived fuels are disregarded, as they are being considered as CO_2-neutral.

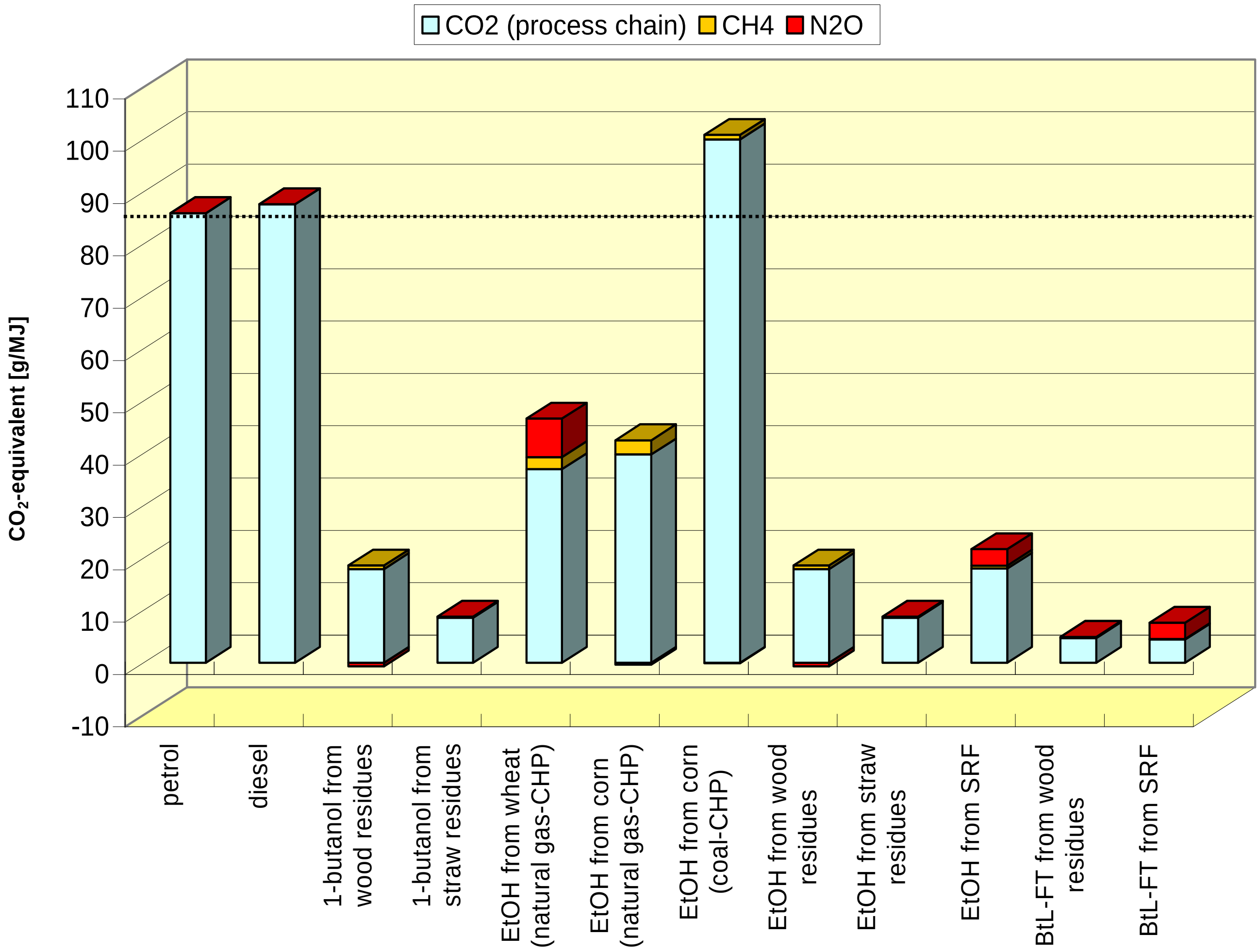

Figure 33: GHG-emissions of 1-butanol and other biofuels over the process chain [12] in CO_2-equivalents [VES b; 2007]

It can be seen from the diagram that production of ethanol from corn (supply of energy and heat through coal) ends up having a higher impact on the atmosphere than the combustion of pure petrol (the dotted line indicates the borderline, when petrol-similar biofuels start emitting more GHG than production and combustion of neat fossil petrol).

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[12] Abbreviations in Figure: CHP – combined heat and power; SRF – short rotation forestry; BtL – biomass to liquid; FT – Fischer-Tropsch process

This especially applies for ethanol production in the USA, as most of the ethanol there is produced from corn and energy from coal holds the highest share in the U.S. heat and power generation sector. [DoE; 2006]

It can be seen that 1-butanol production from 2nd generation sources like wood residues or agricultural wastes (like straw or corn stover) significantly can contribute to a reduction of GHG-emissions on a well-to-wheel basis. 2nd generation ethanol lies within the range of 1-butanol in terms of the environmental impact in contrary to 1st generation ethanol.

Still, there could appear significant difference in GHG-emissions between 1-butanol and ethanol, as 1-butanol requires less effort within the WTT-process chain. This is because 1-butanol requires significantly less expenditure in refineries, as pipe systems do not have to be prepared rigorously for continuous absence of water.

As has been noticed in Chapter 5.3 and Chapter 6.3, 2nd generation 1-butanol is potentially closer to economical production than 2nd generation ethanol. While so far no fermentation plant is commercially producing 1-butanol, the following assessment shall provide insight into the role 1-butanol could play in the European biofuels market.

The ‘European Commission - Directorate General for Energy and Transport’ assumes a final energy demand in the European transport sector of 16.38 EJ in 2010, which will rise to roughly 17.66 EJ in 2030. This corresponds to an assumed increase in passenger transport activity of 1.4 % annually until 2030.

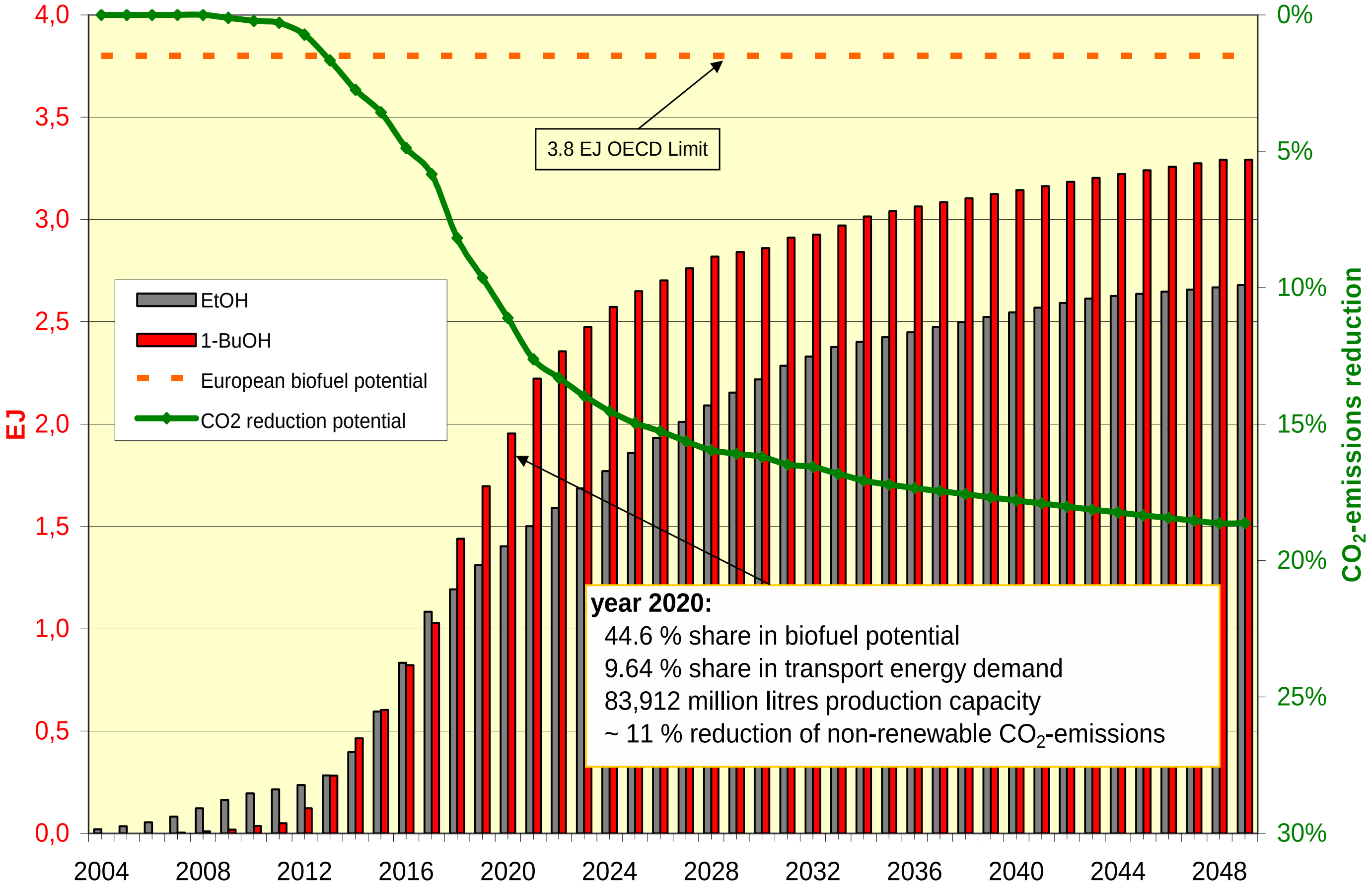
To evaluate the potential of 1-butanol it is important to note that the facilities for production of ethanol can be reconstructed to ABE-fermentation facilities. However, it should be also noted that the production of 1-butanol in adapted facilities would be approximately 40 % lower, compared to former ethanol production, because of produced ‘by-products’ acetone and ethanol (which of course would be sold as well, but are disregarded within this assumption). The yield for 1-butanol is expected to increase due to molecular biotechnological forthcomings within the next decade

Figure 34 shows the potential of 1-butanol in the European transportation sector until 2030 under the following assumptions:

Ethanol production in the European Union increased by roughly 60 % annually since 2004; Ethanol facilities, which are currently under construction show capacities of about 4000 million litres, which are being considered as well. Growth rate however, will decrease due to economic limitations but is seen to rise again when processing of 2nd generation feedstock reaches economical viability. This is assumed for the year 2014, which is seen realistic in several studies (for details see Chapter 6.4). A conservative growth rate between 20 % and 50 %, which is below actual growth, has been taken into account.

The OECD assumes a maximum biofuel potential of 3.8 EJ in 2050 and as ethanol currently accounts for roughly 86 % of the biofuels market, a conservative market share of 70 % is assumed for the year 2050, which leads to a maximum potential of 2.66 EJ in 2050.

For 1-butanol production a start up-phase between 2008 and 2010 is assumed, where ethanol facilities are adapted and processes established. Production of 1-butanol with a realistic 1-butanol-yield of 0.6 and a fraction of 5 % for ethanol production which is used for ABE fermentation between is presumed. Start of processing of 2nd generation feedstock however is seen to start in 2012, two years earlier than for ethanol. This is considered as possible, as 2nd generation 1-butanol already has been established before. Annual augmentation then is assumed to lie in the range of ethanol production. Simultaneously an increase in 1-butanol-yield to 0.8 is presumed, which will rise to 1.0 in 2013. A continuous increase in the fraction of ethanol facilities, which are used for 1-butanol is assumed, which will reach 50 % in 2014 and amount to 97 % in 2050.



3.8 EJ OECD Limit

year 2020:
44.6 % share in biofuel potential
9.64 % share in transport energy demand
83,912 million litres production capacity
~ 11 % reduction of non-renewable CO$_2$-emissions

Figure 34: scenario of 1-butanol production compared to ethanol production

It can be seen that the potential of an earlier introduction of 2nd generation technology, combined with the higher energy content and increasing use of ethanol capacities for 1-butanol production could lead to production numbers in the order of ethanol at around 2014 and would significantly outstrip ethanol production from 2020 on.

If these values are scaled to the EU's assumptions for the total energy demand in transport, 1-butanol compared to ethanol could cover the energy demand in transport as follows. [EU b; 2005]

Table 10: potential of 1-butanol or ethanol meeting the future energy demand in European transport

	2010	**2015**	**2020**	**2025**	**2030**
1-butanol	0,11 %	2.75 %	9.64 %	14.52 %	16.09 %
ethanol	~ 1 %	2.35 %	7.45 %	10 %	12.19 %
final energy demand in European transport [EJ]	16.38	16.86	17.60	17.71	17.66

It should be noted, that these calculations only take domestic production into account, imports are not being considered. Certainly 1-butanol and ethanol values cannot be added, as 1-butanol is regarded being an ethanol substitute.

It becomes clear that the higher energy density of 1-butanol combined with earlier implementation of 2nd generation technology could significantly facilitate the EU target for a 10 % biofuel proportion (based on LHV) in 2020. A consequent development and usage of production facilities as well as focus in research for achieving higher 1-butanol-yields in fermentation is just as important as a decision to concentrate future endeavour on 1-butanol in collaboration with politics and industry.

Several analyses in different countries showed, that biofuels are currently a relatively expensive measure of reducing emission of climate relevant gases. A positive exception is ethanol produced from sugar cane in Brazil, which currently amounts to less than 50 € per tonne of GHG-emissions reduction.

The estimations for the emissions reduction costs in € per metric tonne of CO_2-equivalent can be seen in Figure 35.

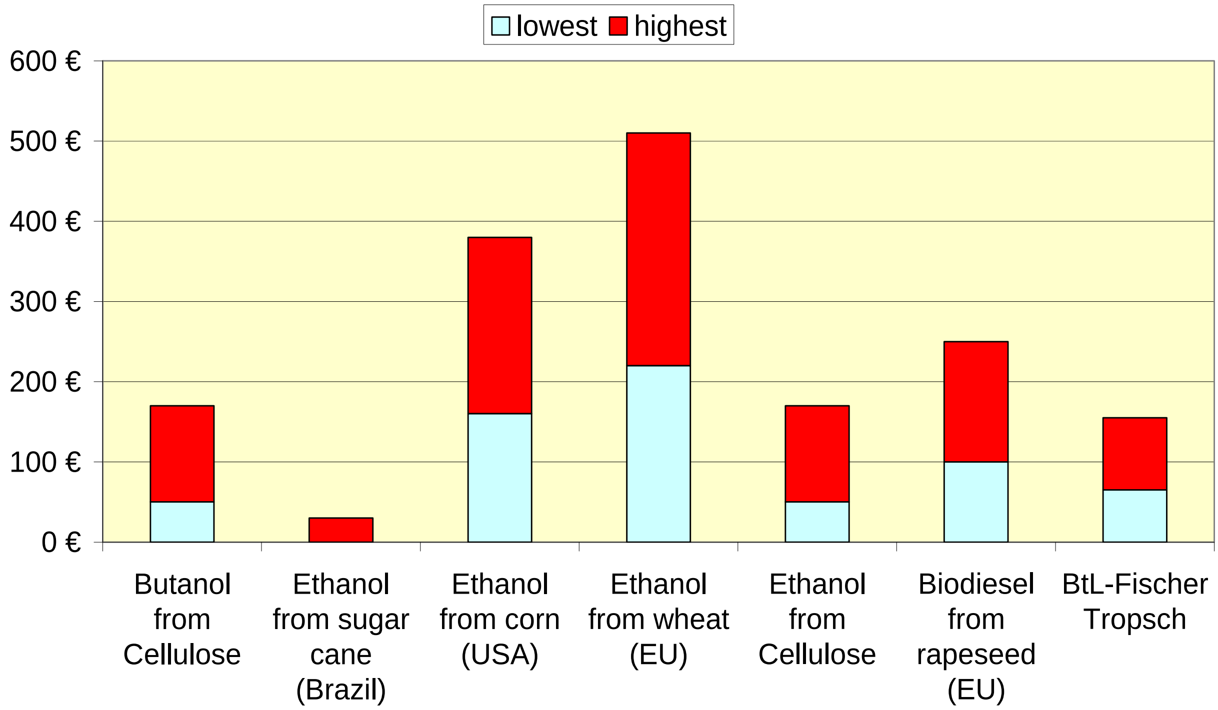


Figure 35: GHG-emissions reduction costs in € per tonne CO_2-equivalent

Especially current production methods for ethanol from corn or wheat feature costs, which assumingly lie in between 200 € and 510 € per tonne of reduced GHG-emissions, depending on higher or lower GHG-emissions reduction estimates. [Worldwatch j; 2006] Greenhouse gas emission reduction costs of 2nd generation 1-butanol are assumed to lie within the range of cellulosic ethanol, as the production processes are quite similar. Depending on the type of process chosen for downstream processing, reduction costs might be subject to variations.

The Well-to-Wheel analysis for 2nd generation 1-butanol showed that a significant reduction of GHG-emissions compared to other biofuel production pathways can be achieved, while combining the potential to significantly attribute to the EU-biofuels targets with comparable low emission reduction costs, which lie in the range of other 2nd generation methods.

10 Conclusion and discussion

A rising awareness against negative impacts on the environment from burning fossil derived fuels and limited oil deposits in combination with a growing instability of oil supply leads to an increasing interest and research of biofuels. Liquid biofuels are seen as one promising path for assuring tomorrow's mobility while having little or no negative impact on the environment.

Ethanol currently is the leading biofuel on the globe, but shows properties, e.g. hygroskopy and comparatively low energy content, which are disadvantageous for fuel substitution and throughout the distribution process.

As a consequence, research is stressed on developing fuels, which can be blended with petrol and feature the advantages of ethanol (production from renewable biomaterials), without the drawbacks noted above.

Butanol, specifically 1-butanol therefore has gained in attraction the last years and is now seen as one potential substitute for ethanol.

1-butanol is a monovalent alcohol just like ethanol, but contains a butyl group instead of the ethyl group. This slight difference on molecular basis, leads to significant differences in chemical and physical properties and by that diverse behaviour in engine application.

The major advances of 1-butanol over 1-ethanol from a chemical and technical point of view **are a significant higher energy content** (LHV) of approximately 30 % (1-BuOH ~27 MJ/L EtOH: 21.3 MJ/L) **and a lower hygroskopy**, which allows delivery of 1-butanol in established logistic systems.

Although neat 1-butanol offers quite a low vapour pressure of 0.67 kPa, blends with petrol show a significantly higher vapour pressure, because of reduced intermolecular forces between 1-butanol molecules. However, there is no vapour pressure anomaly as known from ethanol blends.

One other physical factor might especially gain in importance for combusting 1-butanol. 1-butanol offers a boiling point of 117.7 °C, which might lead to problems when unburned 1-butanol accumulates in the motor oil as a consequence of 'blow-by'. Oil temperatures of more than 115 °C are hardly achieved in daily driving; therefore dilution of the oil might become an issue, depending on the blend's 'strength'.

As 1-butanol should serve as a renewable substitute for petrol it is important to consider a sustainable pathway of production. Practically all of the world's 1-butanol currently is being produced petrochemically, meaning syntheses for production start from fossil material. The most important production method nowadays is the so called hydroformylation of olefins or 'oxo-synthesis'.

Crude oil derived propene therefore reacts with synthesis gas (a gas mixture of H_2 and CO) and forms butyraldehyde, which is further hydrogenated to 1-butanol. The ‘oxo-synthesis’, as well as other petrochemical production pathways are energy intensive and produce considerable amounts of by-products.

In the beginning of the 20th century, when oil was known as a rather expensive product, 1-butanol production was established on a biotechnological pathway – the fermentation from starch to the products acetone, 1-butanol and ethanol through the bacterial organism ‘*Clostridium acetobutylicum*’.

Although having been outstripped by petrochemical production in the second half of the century in almost every part of the globe, huge effort is set into re-establishing the biotechnological production methods of the so called ABE-fermentation from sugar- or starch containing biomaterial.

During **ABE**-fermentation *Clostridia* strains convert glucose and even pentoses under absence of oxygen into the products **A**cetone, 1-**B**utanol and **E**thanol. The common ratio in the fermentation broth is B:A:E = 6:3:1

Commonly the substrate sugars come from starch- or sugar containing plants like corn, wheat, sugar cane or sugar beet, they can be easily ‘accessed’ by the microbes. By using only the sugar- or starch containing parts of the plant (1st generation feedstock), the biggest fraction of the whole plant is lost. However these parts like stems, leaves and roots contain glucose as well, but in a hardly accessible form for the micro organisms. Currently, heavy effort is done in research to develop technologies for making this lignocellulose-fraction accessible for the organisms. Lignocellulosic material used for conversion to biofuels commonly is nominated as 2nd generation feedstock.

1-butanol could be years ahead in respect of serving as a 2nd generation biofuel, as fermentation from lignocellulosic material, which so far is not available for ethanol production, has already been established in the former Soviet Union until the 1980s.

Research within academia and industry is trying to adapt and improve the known process to satisfy today’s demands. This especially applies for reduction of energy usage, establishment of a stable fermentation process and improvements in product yield and purification (downstream processing). Price of feedstock, type of downstream processing and sale of by-products are the main factors that affect the fermentation costs.

The global demand in primary energy will annually grow between 1.3 % and 1.8 % until 2030, while crude oil exploration is estimated to currently reach ‘oil peak’ and significantly will decline, leading to further price increase.

Therefore it is important to estimate the production capacity and costs for 1-butanol in comparison to ethanol or other biofuels. Implying that production of 1-butanol will have the same limitations like ethanol, but 2nd generation feedstock being already established in 2012 (for ethanol: 2014), then 1-butanol could outrun ethanol production at around 2019 and contribute approximately 9% to the European transport energy demand in 2020, which will amount to 17.60 EJ. The calculations are based on the OECD’s estimations of a biofuel potential in Europe (and Russia) of about 7.6 EJ.

Production costs of 1-butanol are estimated to **vary between 0.24 € and 0.81 €**, while ethanol broadly varies between 0.27 € and 0.95 € (each per energy equivalent of petrol). So to say, the costs lie in the same magnitude.

The **Well-to-Tank** integration, which was also done within this thesis, addresses the impacts of biofuel production (especially 1st generation biofuels) from plantation, via refinery and delivery to the car’s tank. The food-versus-fuel debate, impacts on environment and the influence of genetically modified organisms on biodiversity are discussed and economical aspects like yields per hectare and profitable biomass transportation distances figured out as well.

The **Tank-to-Wheel** integration observes aspects of storing and combusting neat or blended 1-butanol. While 1-butanol is potentially serving as a petrol blending agent in modern SIDI-engines, combustion of pure 1-butanol and 1-butanol’s usage in compression ignition engines (diesel engine) is covered as well, but doesn’t seem to be very promisingly. In a technical comparison of ethanol and 1-butanol it becomes clear, that 1-butanol shows better material compatibility and offers a higher cruising range. Vehicle emissions are observed as well and while CO_2-emissions (which are considered as renewable, as the carbon only is derived from biomass) are of equal range, SO_x-emissions decline and HC-emissions seem to rise in comparison to fossil fuel. Emissions of NO_x are clearly dropping for 1-butanol blends, while the situation seems unclear for ethanol blends to rise or fall.

The overall **Well-to-Wheel** analysis in the thesis points out, that the GHG-emissions over the whole process chain for 2nd generation 1-butanol might amount to 10 - 20 g CO_2eq per MJ, which is roughly 80 % less than conventional petrol and more than 50 % less than current 1st generation ethanol production methods.

From a cost perspective, one tonne of saved GHG-emissions through production and combustion of ethanol from wheat costs maximum 500 € in the EU. GHG-emissions reduction costs for 2nd generation 1-butanol would amount to maximum 170 € per tonne and would lie in the range of 2nd generation ethanol or BtL-fuels.

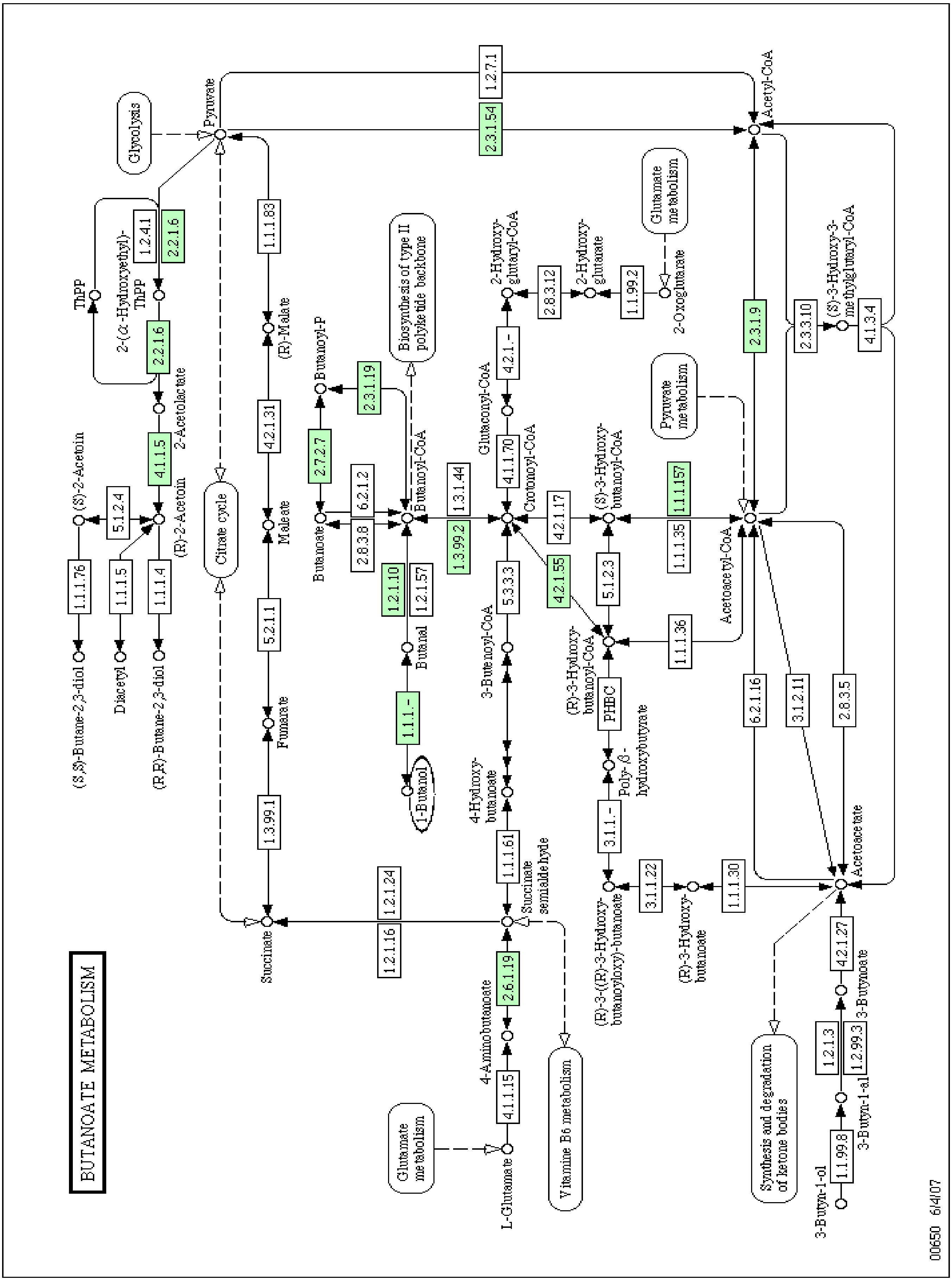
The outcome of this thesis is that 2nd generation 1-butanol is a promising candidate for substituting not only petrol but also 1st generation ethanol and that 1-butanol can significantly contribute to a cost-effective and sustainable reduction of greenhouse gases in the automobile transport sector.

Appendix

Selected calculation assumptions for production cost scenarios (Chapter 6)

	Ethanol from wood waste	**Butanol from corn**	**Butanol from corn**	**Ethanol from farmed wood**	**Butanol from corn**	**Ethanol from wheat grain**	**Butanol from corn**
	Concawe WTW 2006	Qureshi and Blaschek (paper 3)	Qureshi and Blaschek (paper 3)	Concawe WTW 2006	Qureshi and Blaschek (paper 3)	Concawe WTW 2006	Qureshi and Blaschek (paper 3)
	oil @ 50 € / barrel, wood waste @ 53 € / t	oil @ 50 € / barrel, corn @ 173 € / t, batch, C. beijerinckii, ABE yield 0,42	oil @ 50 € / barrel, corn @ 150 € / t, batch, C.beijerinckii, ABE yield 0,42; 0 credits	oil @ 50 € / barrel, farmed wood @ 81 € / t	oil @ 50 € / barrel, corn @ 173 € / t, batch, C. beijerinckii, ABE yield 0,42	oil @ 50 € / barrel, wheat @ 150 € /ton	oil @ 50 € / barrel, corn @ 173 € / t, batch, C.beijerinckii, ABE yield 0,42
years	15	15	15	15	15	15	15
t product/a	156000	121596	121596	156000	121596	100000	121596
PJ/a	4,2	4,05	4,05	4,2	4,05	2,7	4,05
h/a	8000	8400	8400	8000	8400	8000	8400
MW	145	133,82	133,82	145	133,82	93	133,82
MWh/a	1160000	1124087	1124087	1160000	1124087	744000	1124087
	wood waste (0 % moisture)	*Corn (14 % moisture)*	*Corn (14 % moisture)*	*farmed wood (0 % moisture)*	*Corn (14 % moisture)*	*Wheat grain (13 % moisture)*	*Corn (14 % moisture)*
€ / ton	53	173	150	81	173	150	173
t/a	677000	514000	514000	677000	514000	338000	514000
M€/a	35,881	88,922	77,1	54,837	88,922	50,7	88,922
M€/a							
M€	227	80,27	80,27	227	80,27	66	80,27
M€/a	27,24	9,63	9,63	27,24	9,63	7,92	9,63
M€/a	12,1	3,61215	3,61215	12,1	3,61215	14,8	3,61215
kt/a						114	
€/t						82	
M€/a		24,98	0		10	9,35	
M€/a	75,221	77,18655	90,34455	94,177	92,16655	64,072	102,16655
€/GJ	17,91	19,07	22,33	22,42	22,78	23,73	25,25
€/kWh	4974,93	5298,30	6201,50	6228,64	6326,57	6591,77	7013,00
€ / L	0,382	0,514	0,602	0,479	0,614	0,506	0,681

Metabolism pathways of Clostridium acetobutylicum (Chapter 5.1)



Results from laboratory testing (BMW internal)

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