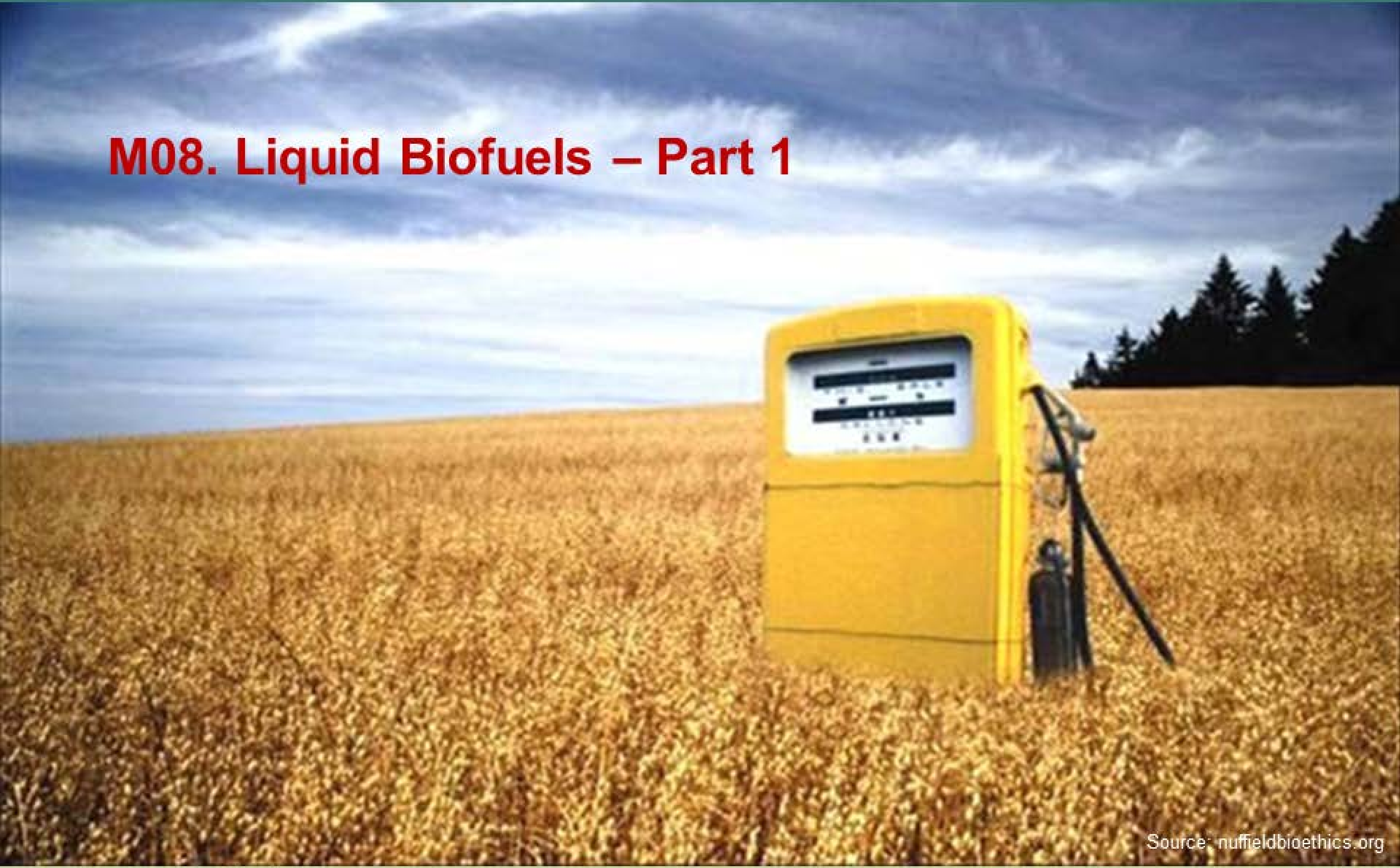
M08. Liquid Biofuels – Part 1



Source: nuffieldbioethics.org

Liquid Biofuels

- Introduction
- Vegetable oils
- Biodiesel
- Bioethanol
- Thermochemical produced biofuels
- Biofuels Policy
- Economy and ecology

Introduction

- Definition and history
- Classification
- Development

Definition and history
of liquid biofuels

... are **recent** fuels (not fossilized) of organic origin that are **liquid** at a processing and /or during energetic use.

They are made of several energy **plants** and/or their parts, of wood and other **products, by-products and residues** of organic origin.

In 1860, the German engineer **N. A. Otto** used **bioethanol** for the first time in an engine (**Otto engine**).
In 1912, Rudolf Diesel developed the **Diesel engine**. His first attempts were with gasoline, but later he used petroleum and also **vegetable oil**.

Source: http://de.wikipedia.org/wiki

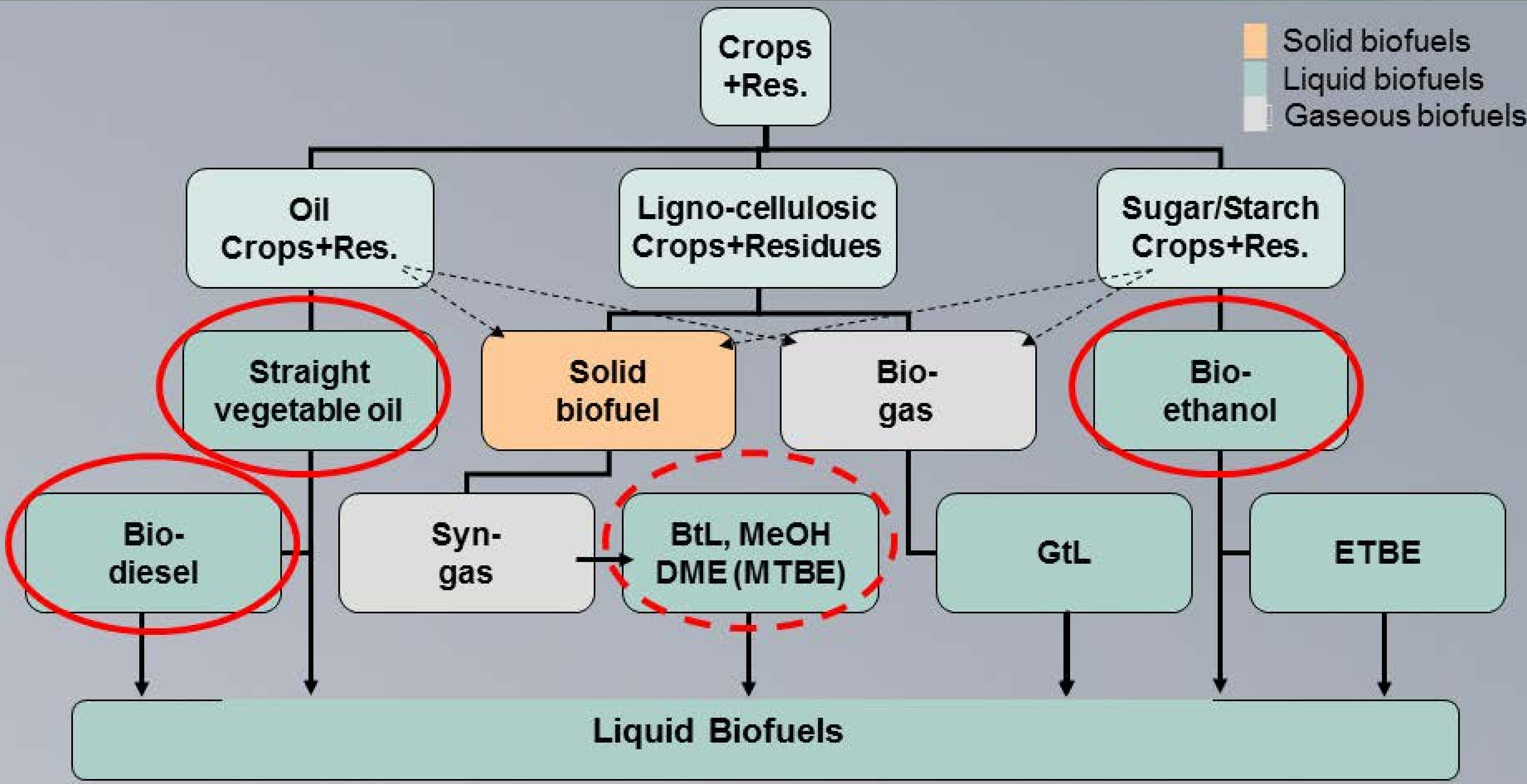
Technical terms:

SVO	Straight Vegetable Oil
PPO	Pure Plant Oil
FAME	Fatty Acid Methyl Ester = Biodiesel
FAMAE	Fatty Acid Mono Alkyl Ester = Biodiesel
FAEE	Fatty Acid Ethyl Ester = Biodiesel
VOME	Vegetable Oil Methyl Ester = Biodiesel
RME	Rape (Seed) Methyl Ester = **Biodiesel**
PME	Pflanzenölmethylester = Biodiesel
AME	Altfettmethylester = Biodiesel

Technical terms:

EtOH	**Ethanol**
MeOH	Methanol
ETBE	Ethyl Tertiary Butyl Ether
MTBE	Methyl Tertiary Butyl Ether
DME	Dimethyl Ether
BTL = BtL	**Biomass-to-Liquid**
FT-Diesel	Fischer-Tropsch Diesel
HTU-Dies.	Hydro-Thermal-Upgrading Diesel
GTL = GtL	**Gas-to-Liquid**

Classification of liquid biofuels
by feedstock and final product



BtL…Biomass-to-Liquid, GtL…Gas-to-Liquid, ETBE… Ethyl tert-butyl ether, MTBE…Methyl tert-butyl ether, MeOH…Methanol, DME…Dimethyl ether. Pyrolysis oil, HTU-Diesel (Hydro Thermal Upgrading), ethanol and hydrogen from ligno-cellulosic species are not considered here because of their minor practical relevance in the near future.

Source: renac

Classification of liquid biofuels
by technology

go green ltd.

1st Generation	2nd Generation	3rd Generation

1st Generation

- **Vegetable oil**
- **Biodiesel**
- **Bioethanol**
- Green diesel*
- Bioethers**
- etc.

* Similar to biodiesel, but produced by fractional distillation.

** MTBE (methyl-tertiary-butyl-ether) or ETBE (ethyl-tertiary-butyl-ether) made from bioethanol

2nd Generation

- FT fuels (Fischer-Tropsch)
- BioDME (Dimethyl ether)
- Biomethanol
- Butanol, Isobutanol
- DMF (Dimethylformamide)
- HTU diesel
- Mixed alcohols
- Wood diesel
- Pyrolysis oil (Bio-oil)
- etc.

3rd Generation

- Ethanol from living algae
- etc.

2nd Generation:
Thermochemically produced liquid biofuels (bio-synthetic liquid fuels) are made not only from solid but also from gaseous biofuels (e.g. syngas, biogas), called **Gas-to-Liquid (GtL).** When solid biomass is the source of the gas production the process **is also** referred to as **Biomass-to-Liquids (BtL)**.

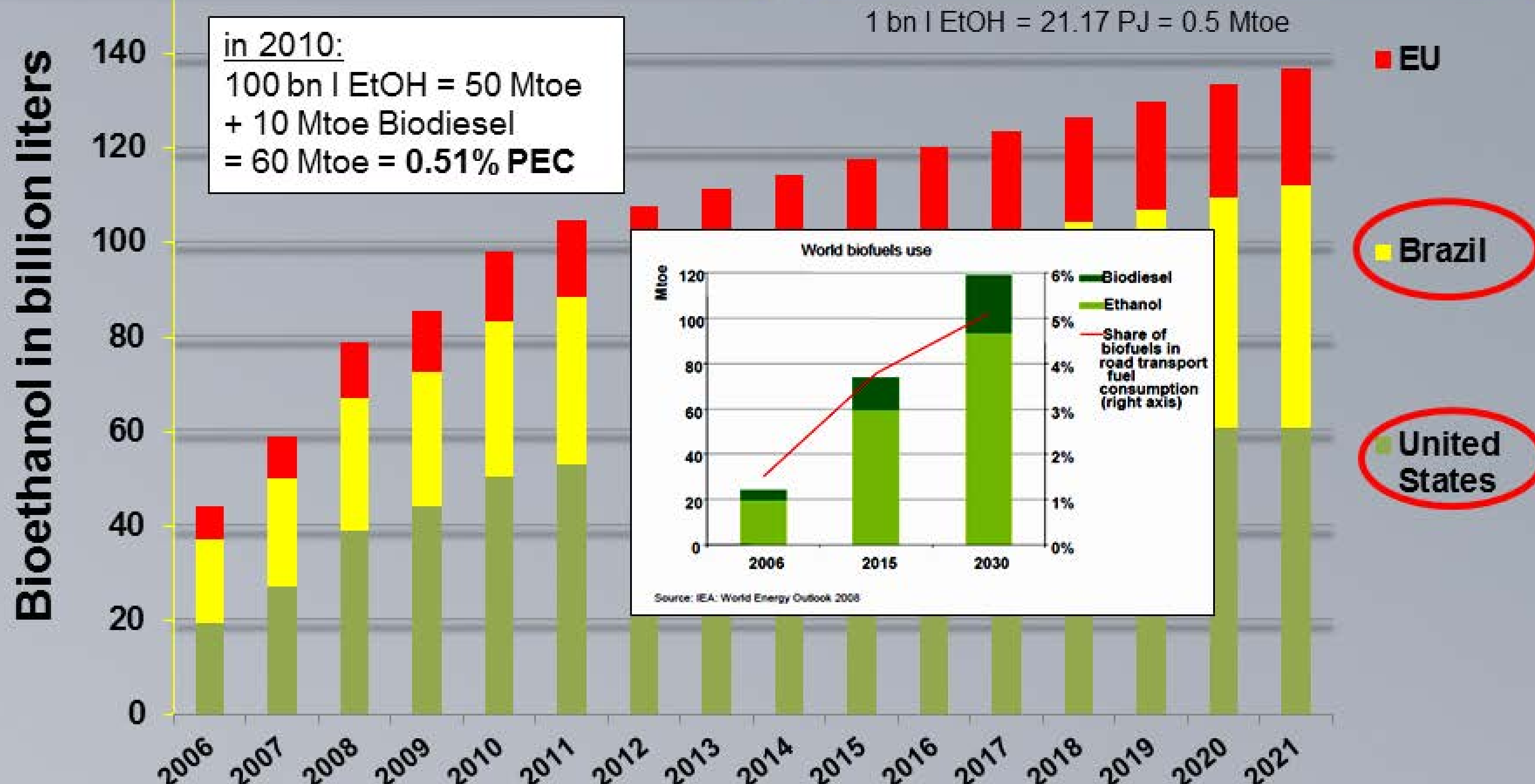
The second generation biofuels are under **development**, although it must be noted that most or all of these biofuels are **synthesized** from intermediary products such as syngas using methods that are identical in processes involving conventional feedstocks, first generation and second generation biofuels. The distinguishing feature is the technology involved in producing the intermediary product, rather than the ultimate off-take.

Source: http://en.wikipedia.org/wiki/Second_generation_biofuels

Development of global production
of liquid biofuels

Share of biofuels on road transport fuels
in 2010: **3.0%** (≈0.5% PEC)
in 2020/30: 4 - 6% incl. 2nd generation biofuels
in 2050: ≤ 27% according to IEA (2011)

Objective of biofuels share in <u>Germany</u>
in 2020: **10...12%** (**7%** GHG reduction)
accord. to EU Strategy of Decarbonisation
and German Biokraftstoffquotengesetz



Source: renac

Vegetable oils

- Productivity of oil crops
- Production technologies
- Fuel characteristics
- Energetic utilisation
- Experiences and examples

Feedstock
of vegetable oils and biodiesel

Coconut oil

Sunflower oil

Palm oil

Jatropha

Used fats & oils

Soy

See also lesson „Bioenergy Feedstock“.

Productivity of oil crops

A rough survey

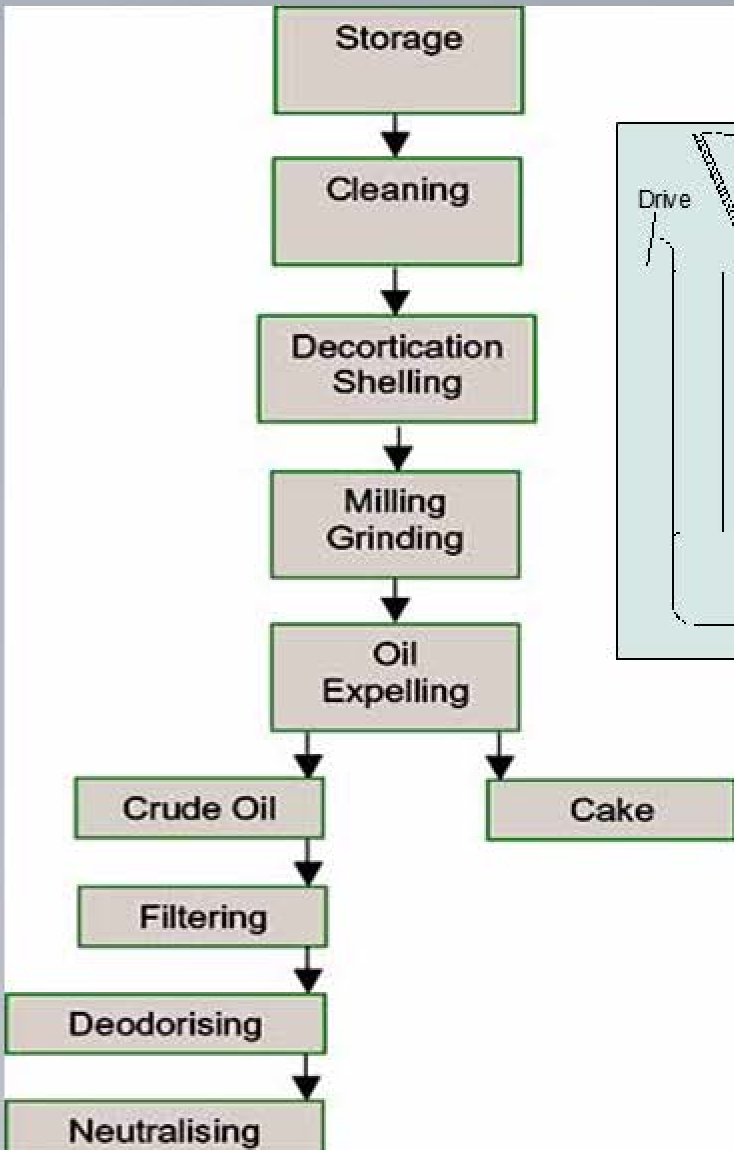
Crop	kg oil/ha/yr	litres oil/ha
algae (open pond) [3]	80000	95000
avocado	2217	2638
brazil nuts	2010	2392
cacao (cocoa)	863	1026
calendula	256	305
camelina	490	583
cashew nut	148	176
castor beans	1188	1413
chinese tallow	3950	4700
coconut	2260	2689
coffee	386	459
Copaifera langsdorffii [1]		12000
coriander	450	536
cotton	273	325
euphorbia	440	524
flax (linseed)	402	478
hazelnuts	405	482
hemp	305	363
jatropha	1590	1892
jojoba	1528	1818

Crop	kg oil/ha/yr	litres oil/ha
kenaf	230	273
lupin (lupine)	195	232
macadamia nuts	1887	2246
maize (corn)	145	172
Millettia pinnata[2]	9000	
mustard seed	481	572
oats	183	217
oil palm	5000	5950
olives	1019	1212
opium poppy	978	1163
peanut	890	1059
pecan nuts	1505	1791
pumpkin seed	449	534
rapeseed	1000	1190
rice	696	828
safflower	655	779
sesame	585	696
soybean	375	446
sunflowers	800	952
tung tree	790	940

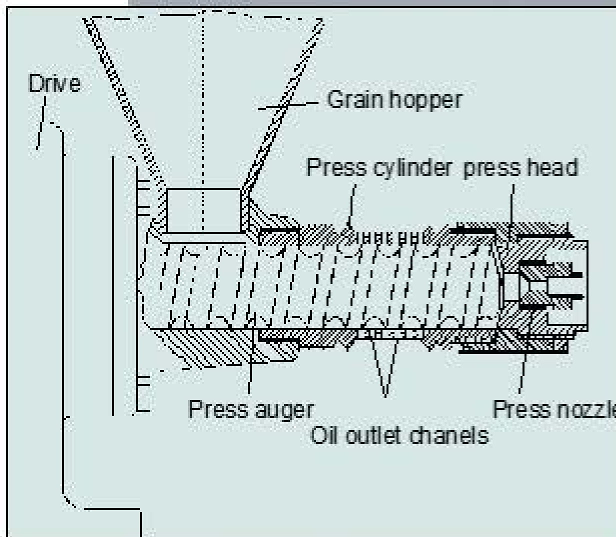
Source: http://en.wikipedia.org/wiki/Table_of_biofuel_crop_yields

See also "Bioenergy Feedstock"!

Technology of oil production
including extraction process



Oil press = Expeller = Screw-type press



The relevant part of the seed may be placed **under pressure** to "extract" the oil, giving an **expressed oil**. → The **most used method** worldwide, for **decentralized (small) production**.

$80^{\pm 10}$% of oil content

Oils may also be extracted from seeds **by dissolving** parts of seeds in water or another solvent. The solution may be separated from the plant material and concentrated, giving an **extracted or leached oil**. → **The highest oil output.** (modern technology, for **centralized production**)

≤ 99% of oil content

Source: renac

Extraction efficiency
of the lab Piteba oil expeller

Crop	Sunflower (black oil seed)	Rapeseed / Canola	Cocoa beans (undecortitated)	Walnut (kernel)	Oil palm kernel
Extraction efficiency	76...84 %	75 %	65 %	89 %	68 %
Crop	Shelled groundnut	Niger seed / noog	Jatropha	Linseed / flaxseed	Babassu
Extraction efficiency	70 %	84 %	77 %	85 %	85 %
Crop	Hemp seed	Safflower	Hazelnut		
Extraction efficiency	68 %	78 %	81 %		
Crop	Almond	Beechnuts	Coprah (oil)		
Extraction efficiency	89 %	77 %	87 %		

Source: http://www.piteba.com

Big expellers in industry achieve higher values!

Fuel parameters of vegetable oils
used in in engines (1)

- ✓ **Density** determines the volumetric **calorific value** among with the calorific value (the mass) and therefore fuel consumption.
- ✓ **Heating/Calorific value (LHV)** determines the content of energy, which can be transformed into the engine and consequently the **power and consumption.**
- ✓ **Kinematic viscosity** characterizes the power to run, and dose the fuel flow and thus the **course of combustion**, **power and consumption**. Too high Viscosity cause ignition of the injection nozzles. **Depends on temperature!**
- ✓ **Cetane number** determines the **course of combustion** (tendency to beat) and therefore the **power, consumption and engine wear.**
- ✓ **Pour point = Solidification point** of determining the **temperature** at which the oil starts to become **solid** and cause problems in flow and dose. A mixture with additives can prevent the solidification of the fuel.

Fuel parameters of vegetable oils
used in in engines (2)

- ✓ **Flash point** is the **minimum temperature** to which the pure liquid fuel must be heated so that the vapour pressure is sufficiently high **for an explosive mixture** to be formed with air when then the liquid is allowed to evaporate and is brought into **contact with a flame, spark or hot filament**. Vegetable oils have an ignition point higher than the diesel. So they need good materials and good radiators.

- ✓ **Another point: (Auto-)Ignition Temperature** is the minimum temperature to which the fuel-oxidiser mixture (or a portion of it) must be heated in order for the combustion reaction to occur **without an external flame**. Flashpoints are lower than ignition temperatures.

- ✓ **Iodine number** determines the **unsaturated fatty acids** (number of double bonds). Oils with high iodine numbers harden **(form resins)** with high temperatures and/or with influence of **oxygen and ultraviolet radiation**. They cause resins in the tank **(storage problem)**, in tubes and in the injection system.

- ✓ **Index of acidity = Number of neutralization** (total acid number TAN) indicates the value of oil acidity and the corrosion potential. Mixed with diesel oil (primary) **cause soap** and reduce the durability of **fuel filters** and **motor oil.**

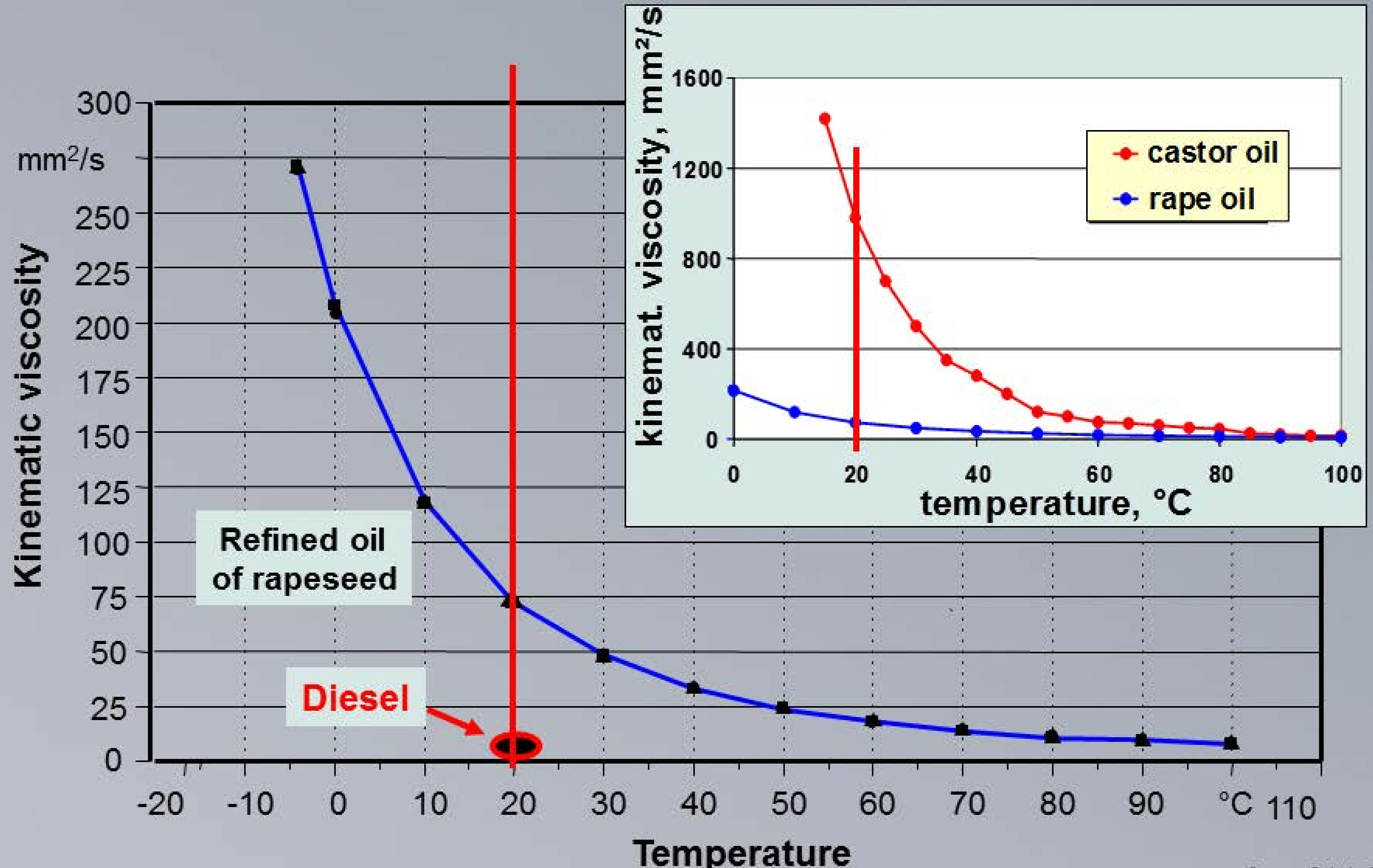
Fuel parameters of vegetable oils
used in in engines (3)

Other fuel characteristics:

Phosphatidics, Turbid substances. They swell with the presence of water, **clogs filters** and promote microbial **breakdown** of oil. Phosphatidics crystallize in the cylinder and accelerate the **wear** of the engine.

- ✓ Free fatty acids FFA (determined by the index of acidity) reduce the ignition point and **viscosity**, but increase the corrosion and **wear** of the engine.
- ✓ Oxidation stability
- ✓ Amount of sulfur
- ✓ Amount of phosphorus (see phosphatidic)
- ✓ Total amount of Mg and Ca
- ✓ Quantity of ash
- ✓ Water content (Humidity)
- ✓ Amount of carbon residues
- ✓ Amount of impurities (dirt) total

Viscosity
A very important parameter

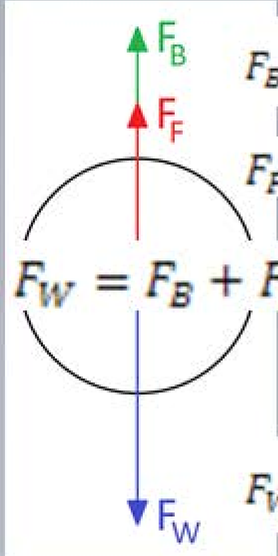


Source: Scholz, 2005

Viscosity
How to measure

Viscosity is a measure of the **resistance of a fluid** which is being deformed by either shear or tensile stress.

Dynamic viscosity $\eta_{(dyn)}$ in kg/(m s) or Poise.
Kinematic viscosity $\nu_{(kin)}$ in mm²/s or Stokes.
The latter is mostly used for liquid fuels.



$$F_B = \frac{4}{3}\pi \cdot r^3 \cdot \rho_L \cdot g$$

$$F_F = 6\pi \cdot \eta \cdot r \cdot v$$

$$F_W = F_B + F_F$$

$$F_W = \frac{4}{3}\pi \cdot r^3 \cdot \rho_B \cdot g$$

- Weight force F_W
- Frictional force F_F
- Buoyancy force F_B (= lifting force)

$$\eta_{(dyn)} = \frac{2}{9} \cdot \frac{r^2 \cdot g}{v} \cdot (\rho_B - \rho_L)$$

$$\upsilon_{(kin)} = \frac{\eta_{dyn}}{\rho_L}$$

r… Radius of the ball (mm)
v … Velocity of the ball (m/s)
g… Gravitational acceleration (9.81 m/s²)
ρ_B… Density of ball (kg/m³)
ρ_L… Density of liquid (kg/m³)

A liquids' viscosity can be measured using the **law of Stokes**:
"Three forces act on a dropping ball"

Weight force (F_w) accelerates the ball, frictional force (F_F) and buoyancy force (F_B) act in the opposite direction. The density of the ball (ρ_B)determines weight force (F_w) and buoyancy force (F_B), whereas frictional force (F_F) depends on the ball's velocity (v). When dropped with v_{start} = 0, the ball accelerates and reaches a steady speed. Dropping at steady speed, the three forces are in equilibrium.

Source: Schneider, Renac (2011)

Fuel characteristics
of selected vegetable oils (1)

	Density (15° C) kg/dm³	LHV MJ/kg	Kin. Visco-sity (20°C) mm²/s	Cetan number -	Pour point °C	Flash point °C	Number of iodine -	Index of acidity mg KOH/g
Diesel	0,84	42,7	4....6	50	-	80	-	-
Castor oil	0,95[2)]	37,2	297	42	-10...-18	229	82...89	175...187
Rapeseed oil	0,92	37,6	74	40	0....-3	317	94...113	167...180
Sunflower oil	0,93	37,1	66	35,5	-16...-18	316	118...144	186...194
Soybean oil	0,93	37,1	63,5	38,5	-8....-18	350	114...138	188...195
Linseed oil	0,93	37	51	(52)	-18...-27	-	169...192	187...197
Olive oil	0,92	37,8	83,8	37,1	-5....-9	-	76...90	186...196
Cotton oil	0,93	36,8	89,4	41	-6....-14	320	90...117	189...198
Jatropha oil	0,91	37,2	71	(51)	-	340	(103)	(138)
Coco oil	0,87	35,3	21,7 [1)]	-	14....25		7...10	246...268
Palm oil	0,92	37	29,4 [1)]	42	27....43	267	34...61	195...206
P. kernel oil	-	35,5	21,5 [1)]	-	20....24	-	14...22	245...255

1) Kinematic viscosity for 50 °C
2) Temperatur not stated

the most different values from Diesel

Source: Scholz, 2005

Fuel characteristics
of selected vegetable oils (2)

Vegetable oil	Visc.[a] mm²/s	Cetane[b] No.	HHV kJ/kg	Cloud point °C	Pour point °C	Flash point °C	Density kg/l	Water & sed. %v	Carbon residue %w	Ash %w	Sulphur %w	Copper Corros.	Induction period h
Castor	297	?	37274	none	-31.7	260	0.9537	trace	0.22	<0.01	0.01	1a	95.0
Corn	34.9	37.6	39500	-1.1	-40.0	277	0.9095	trace	0.24	0.01	0.01	1a	9.3
Cottonseed	33.5	41.8	39468	1.7	-15.0	234	0.9148	0.04	0.24	0.01	0.01	1a	7.3
Crambe	53.6	44.6	40482	10.0	-12.2	274	0.9044	0.2	0.23	0.05	0.01	1a	9.0
Linseed	27.2	34.6	39307	1.7	-15.0	241	0.9236	trace	0.22	<0.01	0.01	1a	2.9
Peanut	39.6	41.8	39782	12.8	-6.7	271	0.9026	trace	0.24	0.005	0.01	1a	6.4
Rapeseed	37.0	37.6	39709	-3.9	-31.7	246	0.9115	trace	0.30	0.054	0.01	1a	10.0
Safflower	31.3	41.3	39519	18.3	-6.7	260	0.9144	trace	0.25	0.006	0.01	1a	3.1
H.O. Safflower	41.2	49.1	39516	-12.2	-20.6	293	0.9021	trace	0.24	<0.001	0.02	1a	9.8
Sesame	35.5	40.2	39349	-3.9	-9.4	260	0.9133	trace	0.25	<0.01	0.01	1a	8.7
Soybean	32.6	37.9	39623	-3.9	-12.2	254	0.9138	trace	0.27	<0.01	0.01	1a	7.4
Sunflower	33.9	37.1	39575	7.2	-15.0	274	0.9161	trace	0.23	<0.01	0.01	1a	5.4
Diesel[c]	2.7	47	45343	-15.0	-33.0	52	0.8400	<0.05	<0.35	<0.01	<0.01	3	<150

a measured at 38° C
b measured using a modified form of ASTM D613 in which ignition delays were observed visually
c Typical No.2

Source: CIGR Handbook of Agricultural Engineering, Vol. 5, 1999

Fuel characteristics
of selected vegetable oils (3)

	Cetan number	Iodine value	LHV	Flash point
	-	-	MJ/kg	°C
Sun flower oil	36	109-120	37,1	316
Soy bean oil	39	114-138	37,1	350
Cottonseed oil	41	103-115	34,2	320
Jatropha oil	51	99-105	37	240
Palm oil	42	34-61	34	267
Rapeseed oil	40	94-113	36	317

... and further reasons for regulating/controlling the biofuels:

- **Climate change**
  - Biofuels as an important part to contribute to GHG emission reductions
  - → Policies to promote the production and the usage of biofuels.
- **Feedstock**
  - Sustainability → The feedstock is not to harm the environment.
- **Usage of biofuels in engines**
  - Fuel quality → Car manufacturers demand for quality standards.

Quality norm of straight vegetable oil
for use as transport fuel

go green ltd.

German standard DIN 51 605:2010-10 Part 1 for rapeseed oil

Parameter	Value		Unit
	min.	max.	
Visual Inspection	Limpid, no free water visible, no contaminations visible		
Density at 15 °C	910	925	kg/m3
Viscosity at 40 °C	-	36	mm2/s
Calorific Value, lower	36	-	MJ/kg
Iodine Value	-	125	g Iod/100g
Acid Value	-	2	mg KOH/g
Flash Point	101	-	°C
Ignition Quality (DCN)	40	-	-
Oxidation Stability at 110 °C	6	-	h
Sulfur Content	-	10	mg/kg
Phosphorous Content	-	3	mg/kg
Ca Content	-	1	mg/kg
Mg Content	-	1	mg/kg
Water Content	-	750	mg/kg

Source: renac

Use of straight vegetable oil
in engines

Vegetable oils are different from diesel:
- Many triglycerides and diglycerides
- High **viscosity** and **pour point**
- High **flash point**

→ Need of high pressure
→ Need of pre-heating

Options:
- ~~**Unmodified diesel engines**~~
- ~~**Blending with diesel**~~
- **Special SVO engines**
- **Modified diesel engines (kit)**
- **Transesterification !!!**

Vegetable oil can be **principally used** in some **older diesel engines** that do not use common rail or unit injection electronic diesel injection systems. However, only a handful of drivers have experienced **limited success.**
With unmodified engines some unfavorable effects may be reduced by **blending, or "cutting", the SVO/PPO with diesel fuel**. However, **opinions vary (!)** as to the efficacy of this.

Several companies like Elsbett have developed **special SVO-engines** . (Indirect injection (pre-chamber), high pressure, good mixing with air, and pre-heating of oil are favorable)

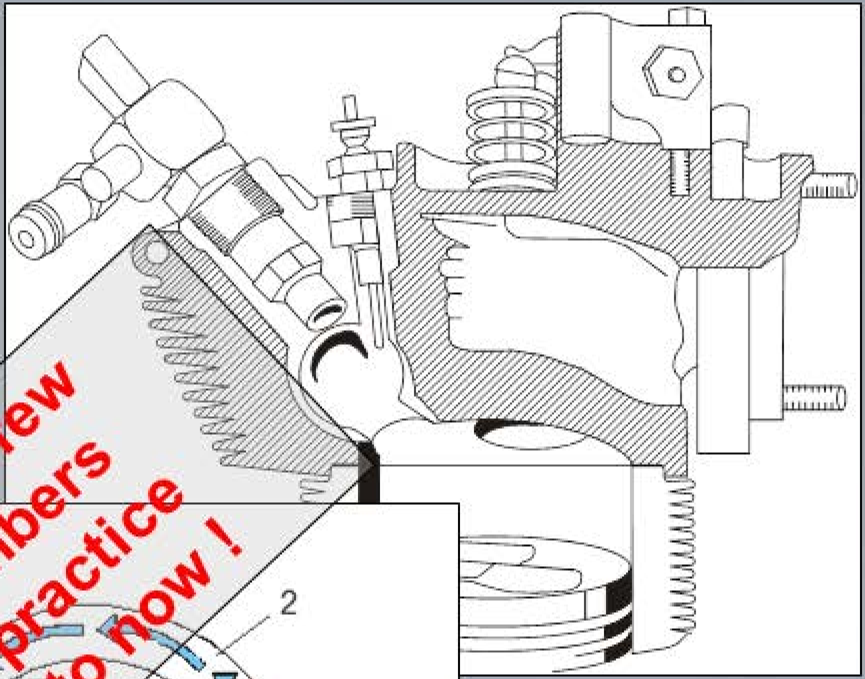
Later on were developed various **conversion kits** and installed hundreds of them over the last decades (see following slides).

Mixing of fuels not advisable:
- Different fuels have different properties
- Binding of moisture (rape seed oil is hygroscopic, palm oil is not)
- Different pour points → different pre-heating
- Chemical reactions after mixing → corrosion
- Injection system properties not as flexible as viscosity of fuels
- Separation effects after mixing

Source: renac

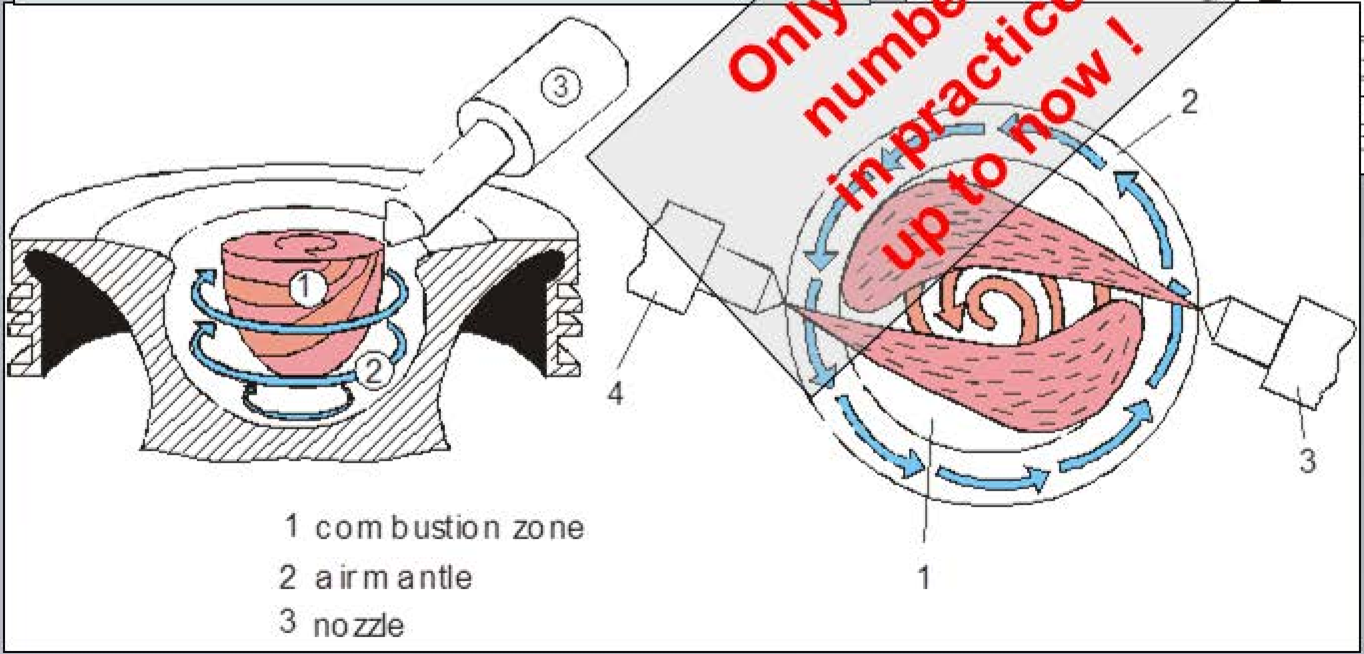
Principles of special motors
for straight vegetable oil

Principle of an engine with centrifugal pre-chamber (KHD Engine FL-912W)



Indirect injection (pre-chamber), high pressure, good mixing with air, and pre-heating of oil are favourable!

Only a few numbers in practice up to now !



Principle of Elsbett Engine (Duotherm system)

Source: renac

Previous experiences
of use of straight rapeseed oil

in diesel engines with different kit types

- ✓ The results significantly depend on the **type of engine** and **kit.**
- ✓ The **conditions** of use are important. E.g. many dead points (no load) cause a dilution of motor oil by vegetable oil.
- ✓ **Two tanks** (diesel + vegetable oil) facilitate the system and are more secure.
- ✓ The **power** is on average as **the diesel engine** (± 10%), but during operation with low load power is lower.
- ✓ The **emission** values are **similar**. NOx is slightly higher, but much lower phosphorus.
- ✓ The oil enters in motor oil, so the **oil changes intervals** should not exceed more than **200-250 hours**.
- ✓ The **durability of the fuel filter is decreased**. The ranges of exchange of the filters should be half of the conventional diesel engines.
- ✓ The **quality of oil** has a great influence. The most important parameters are the **impurities** (particles < 1µm), the amount of **phosphorus** (10 to 15 ppm) and **the number of neutralization** (e.g. because of bad storage).

Only a few applications in practice up to now !

The main kit components are:

- Controller
- Additional fuel tank (optional)
- Electric switching unit
- Electric fuel preheater
- Heat exchanger
- Control electronics
- Pre-assembled cable loom
- ATG Controller
- Additional fuel tank (optional)

>2000 €

Source: renac

Use of straight vegetable oil
in trucks, busses and tractors

Examples:

40 busses and trucks operated with vegetable oil
Operator: Omnibusverkehr Bühler GmbH & Co.
9 Mio kms with 2 Mil. Liters of vegetable oil

Rare Examples!

Source: northseabioenergy.org

Some manufacturers start operation tests of rapeseed adapted tractors fullfilling the strong German emission limits (step IIIB and later step IV)

The better option is biodiesel!!!

Source: renac

Use of straight vegetable oil
in (combined heat) power plants

Example:

- Operator of the plant: ItalGreen Energy
- Engine supplier: Wärtsilä
- Power output: **24 MW (el.)**
- Fuel: vegetable oils
- World largest bio-oil fuelled CHP- plant
- Start of operation: 2004
- Operation closed: 2013 due to permitting issues

CHP-engine-suppliers for vegetable oil:

Well experienced:

- Wärtsilä
- MAN B&W
- ABC

Less experienced:

- Lindenberg
- Caterpillar (MAK)

A few large CHP projects in operation for years, but some of them were stopped because of technical and sustainability reasons.

Biodiesel

- Definition and benefits
- Basics and technologies of transesterification
- Characteristics of biodiesel
- Biodiesel standards
- Exhaust emissions
- Examples

Definition and benefits
of biodiesel

Biodiesel (**FAME** = Fatty Acid Methyl Ester) refers to a **vegetable oil-** or **animal fat-based diesel fuel** consisting of long-chain alkyl (methyl, propyl or ethyl) esters. Biodiesel is typically made by chemically reacting lipids (e.g., vegetable oil, animal fat (tallow)) **with an alcohol**.
Biodiesel is meant to be used in **standard diesel engines** and is thus distinct from the vegetable and waste oils used to fuel converted diesel engines. Biodiesel can be **used alone**, or **blended** with petrodiesel, e.g. 7% biodiesel (B7). Biodiesel can also be used as a low carbon alternative to **heating oil**.

Biodiesel provides several benefits:

- **reducing the** risk of **explosion**,
- **no groundwater pollution** in the case of leakages,
- **no need** of **adaptation** of engines for low percentages, e.g. B7.

Highly blended petrodiesel (>B7) and pure biodiesel need an authorization from the manufacturer of the engine!!!
And it is recommended to change oil and fuel filter more often.

Source: http://en.wikipedia.org/wiki/Biodiesel

Largest biodiesel producers
by feedstock and country

Feedstock	Countries
Rapeseed	Canada, China, India, Germany, France, Australia
Soy Bean	China, USA, Argentina, Brazil
Oil Palm	Indonesia, Malaysia (85% of global production of palm oil)
Coconut	Philippines, Indonesia, India
Olives	Spain, Italy, Greece, Syria, Morocco, Turkey
Cotton Seed	China, India, Pakistan, Brazil, USA
Used cooking & frying oil	Japan, Switzerland, UAE, Germany
Beef Tallow	USA, Ireland
Sunflower seeds	Ukraine, Russian Fed., Argentina

Source: United States Department of Agriculture, 2014, www.indexmundi.com

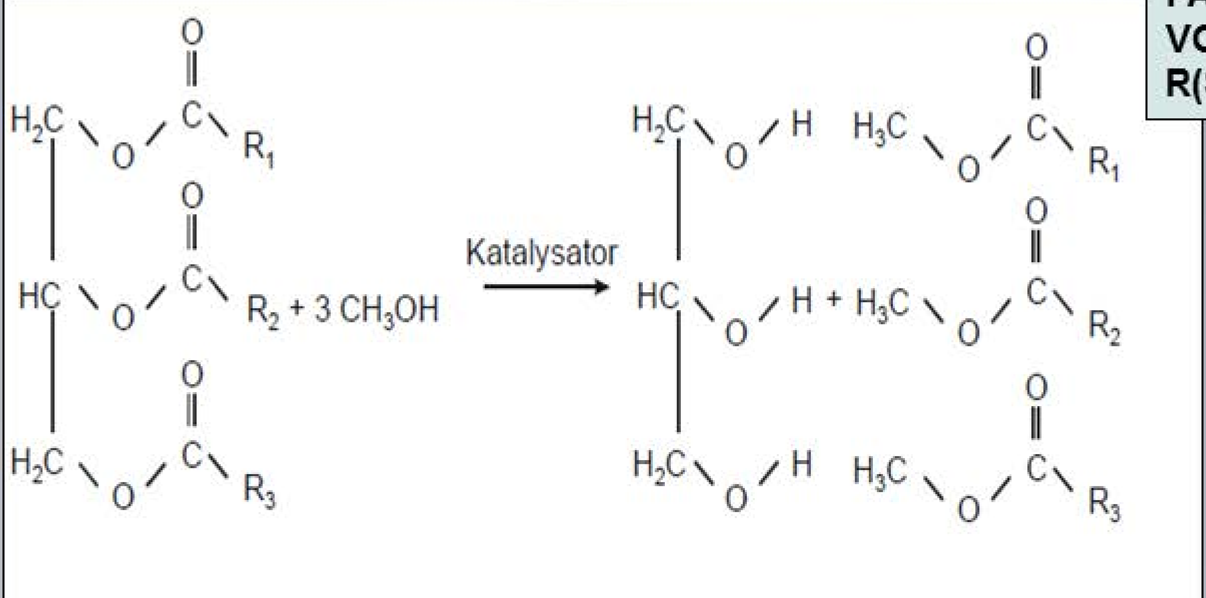
Basics of transesterification
of vegetable oil (1)

The limitations of the use of vegetable oils in engines are related to various characteristics, such as **high viscosity**, **fatty acid** composition in the presence of **free fatty acids** as well as the trend showing the formation of **gum** by the processes of oxidation and **polymerization**, either during its **storage** or **combustion.**

The undesirable properties of vegetable oils can be transferred by transesterification to biodiesel.

Other terms of biodiesel:

FAME	Fatty Acid Methyl Ester
FAMAE	Fatty Acid Mono Alkyl Ester
FAEE	Fatty Acid Ethyl Ester
VOME	Vegetable Oil Methyl Ester
R(S)ME	Rape Seed Methyl Ester



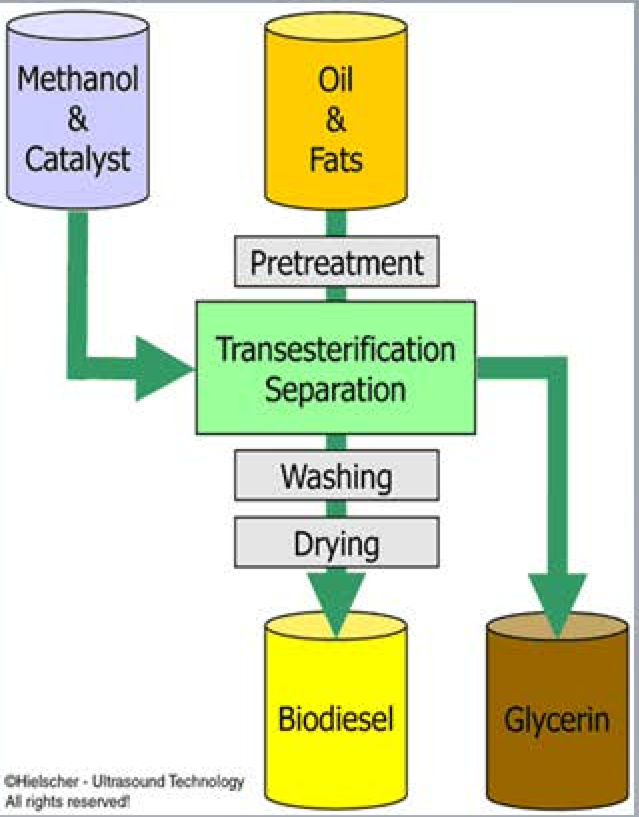
Triglyceride + 3 Methanol → 1 Gycerin + 3 Fatty acid methyl ester

Transesterification of triglycerides by methanol

Source: renac

Basics of transesterification
of vegetable oil (2)

go green ltd.



Reaction
Esterification or transesterification reaction.
FA molecules break away from glycerol and esterify an alkyl coming from alcohol molecule.

Alcohol
Either **methanol** or **ethanol.**
Reaction with methanol is faster, but costs of raw material should be considered

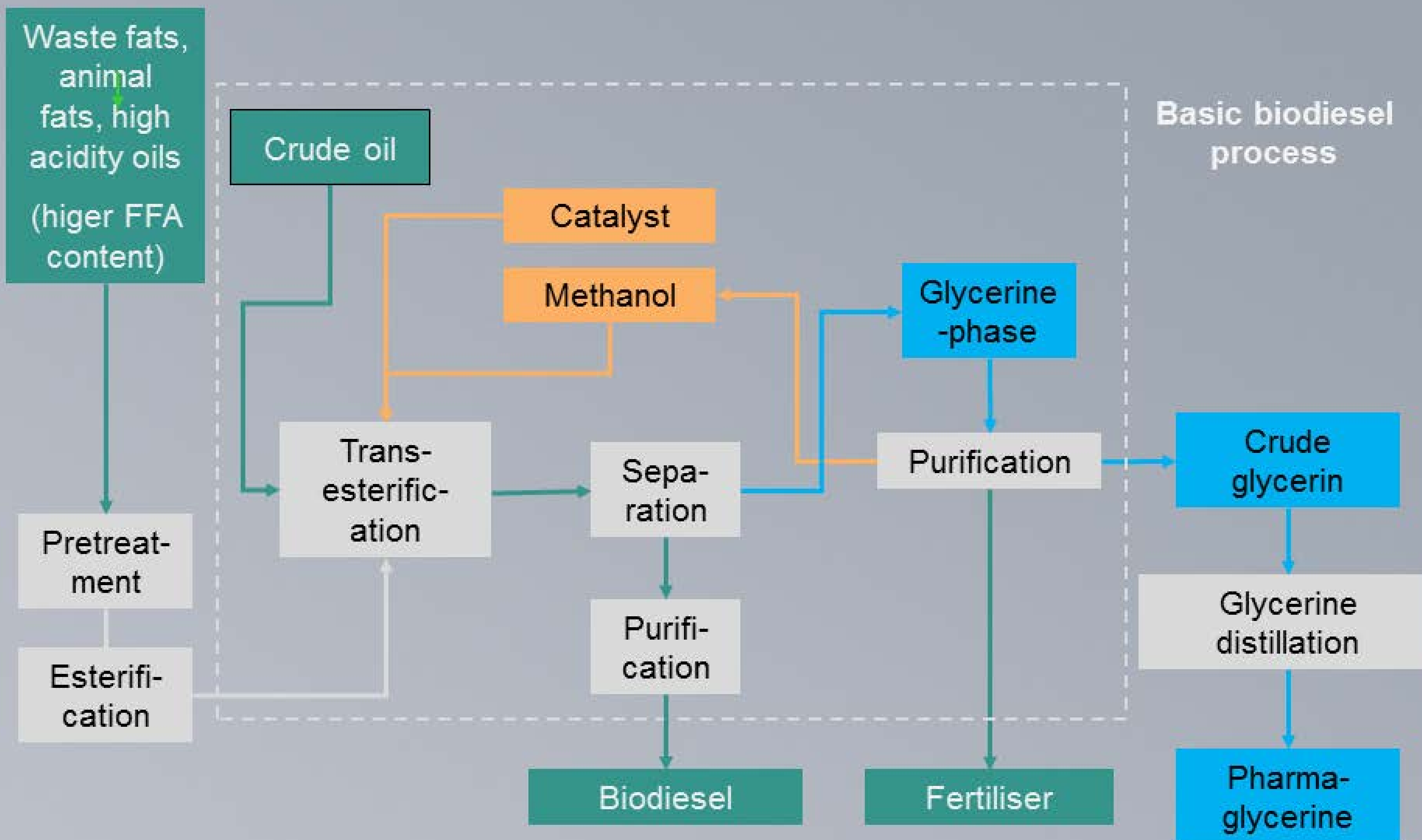
Catalysts
Reduce the temperature and duration of reaction.
Sodium hydroxide, sodium methoxide and potassium hydroxide.
Sodium metoxide prevents any **saponification** reaction.

Temperature
Medium-high temperature or **room temperature** process
Continuous (and pressurized) process.

In research: Transesterification *in sito*
A transesterification in the uncrushed seed grain with methanol or ethanol and acid between 30 °C and 70 °C also seems to be possible.

Source: renac

Technology of transesterification
of vegetable oils, waste and animal fats



Source: renac

Mass balance
of biodiesel production by transesterification

1002 kg	Vegetable oil
113 kg	Methanol
14 kg	KOH (base)
12 kg	H_2SO_4 (acid)

21 kg	Water
32 m^3	Cooling water
390 kg	Steam
62 kWh	Electricity

Example Rapeseed

Products

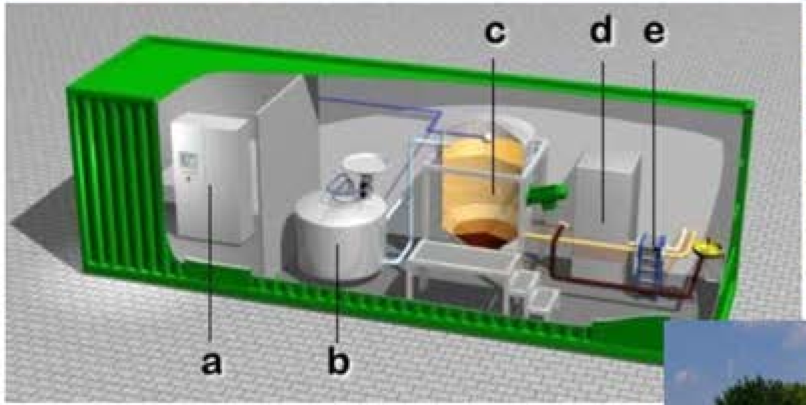
1000 kg	**Biodiesel**
118 kg	**Glycerine**
22 kg	**Fertilizer**

Source: Energea

Biodiesel production
in commercial scale

Large-scale suppliers (>100‘000 t/a):

- Evonik Industries AG (Germany)
- DeSmet Ballestra (Italy)
- GEA Westfalia (Germany)
- MAN Ferrostaal (Germany)
- AT Agrartechnik (Germany)
- CPM SKET GmbH (Germany)
- Axens, IFP Group (France)
- JJ-Lurgi (Malaysia)
- BDI Biodiesel (Austria)
- Biodiesel Technologies (Czech Rep.)
- Pacific Biodiesel (US)



a ... Steuerung
b ... Anmischstation
c ... Reaktor
d ... Pufferspeicher
e ... Wärmetauscher

Decentralized production in a container unit
Capacity: 900 t/y
Price: 250 000 Euro

More details, types, manufacturers and prices in: Scholz, V.: Prospects and Limits of the Energetic Use of Castor Oil. Bornimer Agrartechnische Berichte, Heft 52, 2005

Biodiesel production
by DIY method (do it yourself)

go green ltd.

<u>Here's what you need:</u>

- 1 litre of new vegetable oil, fresh, uncooked
- 200 ml of methanol, 99+% pure
- lye catalyst, either potassium hydroxide (KOH) or sodium hydroxide (NaOH) can be used, but we recommend KOH, especially for beginners -- KOH is easier to use and it gives better results
- blender or preferably a mini-processor
- scales accurate to 0.1 grams, preferably less – 0.01 grams is best
- measuring beakers for methanol and oil
- half-litre translucent white HDPE container with bung and screw-on cap
- 2 funnels to fit the HDPE container, one for methanol, the other for lye
- 2-litre PET bottle (water or soft-drinks bottle) for settling two 2-litre PET bottles for washing
- duct tape
- thermometer

Source: journeytoforever.org/biodiesel_make.html#biodnew

Specifications of biodiesel
compared with SVO and diesel

Characteristic	Unit	Diesel fuel	Raw oil	Refined oil	Methyl ester
Density	kg/dm^3	0,82-0,85	0,915	0,910	0,86-0,90
Kin. viscosity at 40°C	cSt	2-3	32	30	3,5-5,0
Net calorific value	MJ/kg	42-43	39,4	40,2	40,0
Filtration limit point	°C	–18	-6	-1	-9-24
Cetane number		49,2	40	40	48-49
Distillation range	°C	180-360	359-893	350-890	300-360
Flash point	°C	74	300	300	>100
Ashes	% in peso	0,002	0,1	0,01	<0,01
Total acidity	mg KOH/g	–	2,8	<1	<0,5-0,8
Saponification numb.	mg KOH/g	–	190,3	180-190	<170
Iodine number	$gI_2/100g$	–	110-130	110-130	110-125
Phosphorous content	ppm	–	180	<10	10-20
Water content	ppm	–	1000	<500	300-700

Source: Riva, Sisoor

... and environmental friendly!

Biodiesel standards
in EU and USA (1)

Properties	EN 14214		ASTM D 6751	
	Unit	Limits	Unit	Limits
Ester content	% (m/m)	96.5	-	-
Density at 15 °C	kg/m³	860 - 900	-	-
Viscosity at 40 °C	mm²/s	3.50 – 5.00	mm.²/sec	1.9-6.0
Flash point	°C	120 min	°C	130 min
Sulfur content	mg/kg	10.0 max	% mass	0.05 max
Carbon residue	% (m/m)	0.30 max	% mass	0.050 max
Cetane number		51.0 min		47 min
Sulfated ash	% (m/m)	0.02 max	% mass	0.02 max
Water content	mg/kg	500 max	% volume Water/sediment	0.050 max
Total contamination	mg/kg	24 max	-	-

Source: renac

Biodiesel standards
in EU and USA (2)

Properties	EN 14214		ASTM D 6751	
	Unit	Limit	Unit	Limit
Copper strip corrosion	rating	class 1		No. 3 max
Cloud point	-	*)	°C	Report
Oxidation stability	hours	6.0 min	-	-
Acid value	mg KOH/g	0.5 max	Mg KOH/g	0.8 max
Iodine value	g/100g	120 max	-	-
Free glycerol	% (m/m)	0.02 max	% mass	0.02
Total glycerol	% (m/m)	0.25 max	% mass	0.24
Group I metals (Na+K) Group II metals (Ca+Mg)	mg/kg mg/kg	5.0 max 5.0 max	-	-
Phosphorus content	mg/kg	10.0 max	% mass	0.001 max
Distillation temp. 90%	-	-	o C	360 max

Source: renac

Comparison of biodiesel standards
and some fuel characteristics

	Cetan number	Iodine value	Acid value
	-	g/100 g	mg KOH/g
Straight rapeseed oil	36- 51	34-138	<20
Biodiesel	48-55	95-125	<0.5-0.8
Vegetable waste oil	38-85	10-130	<150
US Standard	> 47	-	<0.8
EU Standard	>51	<120	<0.5

100% soybean or sunflower no problem

A mixture of e.g. 60% rapeseed 0-40% palm 0-20% soybean

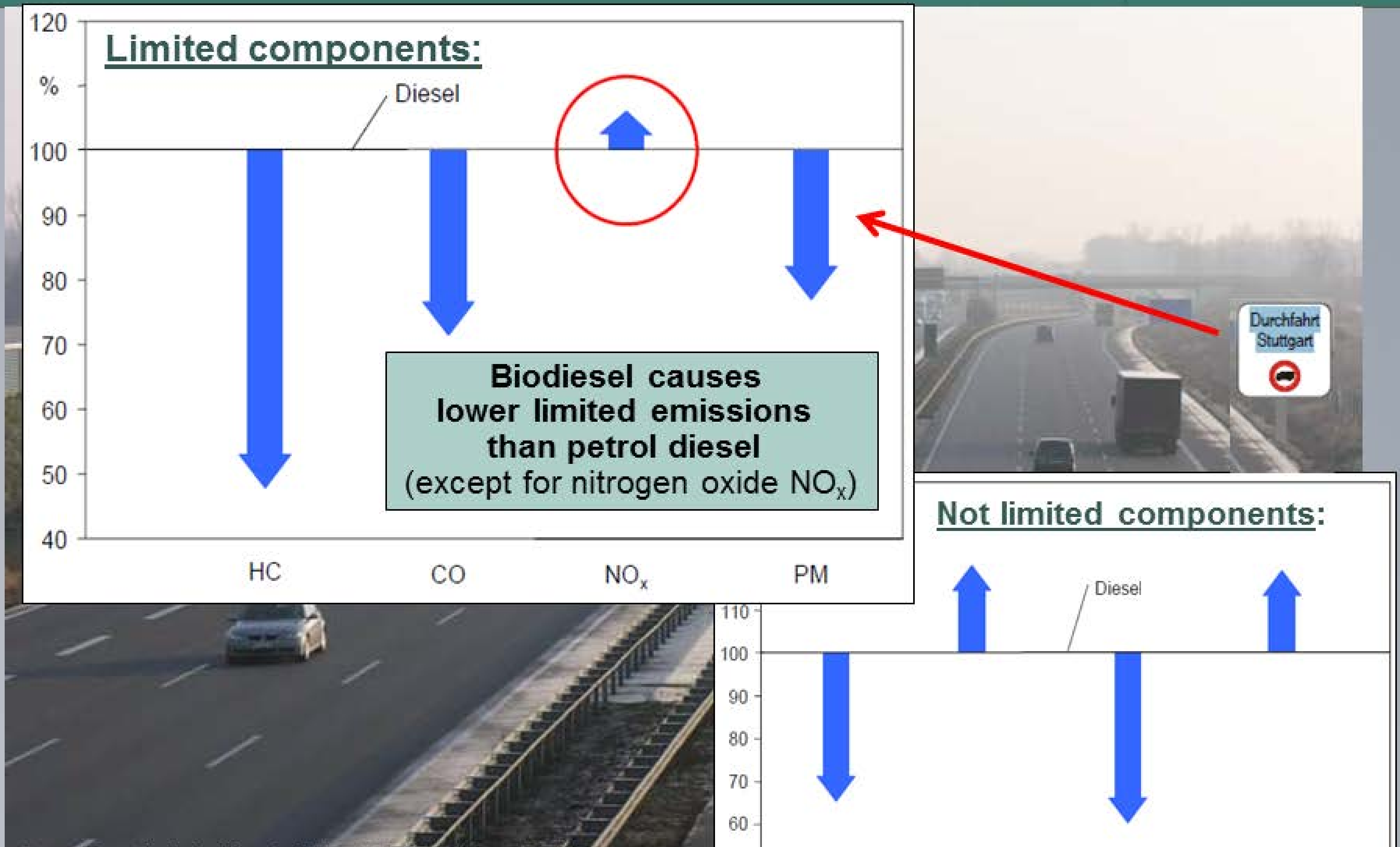
- **Feedstock relates directly to the product quality.** For example **Iodine value**
  - Not influenced by any process: iodine in = iodine out
  - Sunflower and soy bean have high iodine
  - Cheaper feedstock often have lower Iodine number (animal fats)
- **Free fatty acids (acid value)**
  - Vegetable oils: 1-2% FFA
  - Animal fats: FFA > 5%
  - Destroys alkali catalyst
  - Removal through acid esterification before transesterification

From some oils an EN14214 product cannot be made!

important for export

Source: renac

Exhaust emissions
of biodiesel compared to diesel



Source: Jürgen Krahl; Axel Munack: Biodiesel - Ein Meilenstein auf dem Weg zur nachhaltigen Mobilität. Lecture, TU Braunschweig 2007 In: http://www.tu-braunschweig.de/Medien-DB/presse/ringvorlesung-krahl.pdf

Use of pure and blended biodiesel
as a transport fuel

<u>Use of B100</u> <u>(100% biodiesel)</u>
Transport companies (trucks, buses, some trains) (In Austria due to the tax exemption, biodiesel is cheaper than fossil diesel)

<u>Use of B7</u> <u>(7% biodiesel in petrodiesel)</u>
Standard diesel at gas stations in Germany provide up to 7% blended biodiesel. The mixture of fossil diesel and biodiesel has increased continuously.

May be the better way!

Source: northseabioenergy.org

… and rearly (!) for CHP production

Combined heat and power unit

- Operator: Moreco/Iran
- Investor: Rampco group
- Capacity: 6 MW_{el}
- Fuel: biodiesel B100
- Year of implementation: 2012

Source: renac

Thank you

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