Optimization of Bioenergy Use

Lecture : Transport Biofuel Basics

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Additional reading

VTT research notes 2426

Nylund, Aakko-Saksa, Sipilä:

"Status and outlook for biofuels, other alternative fuels and new vehicles". VTT 2008

http://www.vtt.fi/inf/pdf/tiedotteet/2008/T2426.pdf

SI Combustion basics

- SI engine = spark ignition engine
- Combustion = turbulent premixed combustion initiated by spark. => flame propagation.
- Stoiciometric combustion.
- Knock = autoignition of fuel during flame propagation resulting in heavy pressure oscillation and uncontrolled combustion.
- SI engine fuels: resistant againts autoignition, Octane Number (ON), fuel should be easily evaporated and mixed with air before combustion.

CI Combustion basics

- CI engine = compression ignition engine
- Combustion = turbulent mixing controlled combustion initiated by autoignition => mixing control combustion.
- Lean combustion. Flame is still close to stoichiometric.
- Fuel injection is the key issue that affects mixing.
- CI engine fuels: easily ignitable, Cetane Number (CN). Fuel should also be easily injected and mixed with air during combustion.

Terms...

- Biofuel?
  - Fuel, whose feedstocks are (short carbon cycle) organic materials
- Renewable fuel?
  - Larger category!
  - A fuel is renewable, if its energy source is replaced by natural processes at a rate comparable or faster than its rate of consumption by humans
    - For instance, hydrogen from water, if the energy to produce the hydrogen is from a renewable source
  - Renewable diesel
- Alternative fuel?

Terms...

- Alternative fuel?
  - A fuel seen as an alternative for traditionally produced (fossil) fuels
  - Not necessarily renewable!
- Biodiesel?
  - Defined by US legistlation: FAME!!!
  - Controversy in literature
  - For more developed diesels: bio-based diesel, renewable diesel, green diesel (another controversy...)

Ethanol

(Bio)Ethanol added to gasoline

- Almost all the world's ethanol from grain is used as gasoline additive
- Previously in Eutope maximum ethanol amount 5%, in the future 10% (E10)
  - Transition: in Finland beginning of 2011, many EU countries (e.g. Sweden) 2012
- 5 % => no fuel consumption changes, 10 % => increase
- Increase of gasoline vaporization and vaporized emissions
  - E5 ... 10 => old car carburetor adjusted to richer, new cars (~ < 15 years) ok
  - 10 - 25 % ethanol => changes to fuel injection system (seals, tanks...)
- Ethanol must be 99,7 % pure!
  - Special process needed for water removal
  - Fuel logistics: clean, no water!

Ethanol

E85, FFV (Flexible Fuel Vehicle)

- E85 = 85 % ethanol + 15 % gasoline
  - gasoline needed for cold starts (25% in very cold conditions)
- Injection lenghts, ignition advance etc. automatically controlled
- Differences:
  - fuel tanks, fuel hoses, seals, nozzles, engine control, valve sockets
  - oil change twice as often
  - E85: 40 % greater fuel consumption
- Otto engine efficiency less than for diesel, for instance:
  - Ford Focus FFV; with E85 10 l / 100 km
  - with gasoline 7 l / 100 km
  - TDI with biodiesel 5 l / 100 km

Ethanol

- Mainly because of the cultivation cycle emissions grain ethanol is quite inefficient in decreasing GHG!
  – Fertilizer industry emissions; carbon dioxide (CO_2), nitrous oxide (N_2O)
  – Cultivation CO_2, N_2O (whitewash)
  – Grain drying
- VTT, MTT 2006: negative grain ethanol GHG balance
  – **The presumptions and boundary conditions have a huge impact on the life cycle analysis' results!**
- Cellulose –based ethanol production
  – technically in development stage
  – high investment and operation costs (enzymes etc.)

Biogas and natural gas

- Mainly methane: in end use, chemically the same!
  - colourless, non-toxic, weight ~ half of air
- Need to be cleaned before use in transport
  - Biogas: CO_2, N_2
  - Natural gas: water, oil, mud, CO_2 , H_2S, mercury.
- Fits well to Otto-cycle engines
  - logistics, fuel injection differences!
- Dual-fuel: diesel –gas engine, diesel fuel ignition
  - energy mainly from (cars 90%, ships 99%) from gas
- Bifuel: otto engine able to use both gasoline and gas
  - (cold) start often with gasoline
- Heavy duty gas engines mainly modified diesel engines
  - spark + compression ratio decrease => efficiency decrease

CNG, LNG and LPG

- CNG: compressed natural gas
  - compressed to less than 1% of the volume at standard atmospheric pressure.
  - stored and distributed in hard containers at a pressure of 200–248 bar
- LNG: liquefied natural gas
  - Takes up about 1/600th the volume of natural gas in the gaseous state.
  - The gas cooled down in stages until it is liquefied.
    - close to atmospheric pressure (maximum transport pressure set at around 25 kPa)
    - approximately −162 °C.
  - The reduction in volume:
    - cost efficient to transport over long distances.
    - specially designed cryogenic sea vessels (LNG carriers) or cryogenic road tankers.
- LPG: liquefied petroleum gas
  - propane, butane, or both propane and butane
  - Synthesised by refining petroleum or "wet" natural gas
    - manufactured during the refining of crude oil, or extracted from oil or gas streams as they emerge from the ground
  - Gaseous in atmospheric T and p;
    - vapour pressures: 2.2 bar butane at 20 °C (68 °F), 22 bar for propane at 55 °C
    - LPG is heavier than air, and thus will flow along floors and tend to settle in low spots, such as basements. This can cause ignition or suffocation hazards if not dealt with

Renewable diesel fuels

Term ”biodiesel” in legistlation: ”traditional” fatty acid ester diesels

- FAME = fatty acid methyl ester

Synthetic diesel: paraffinic hydrocarbons

- Produced from any carbon-based combustable matter
- Fischer-Tropsch (FT) –diesel
  - Biomass-to-liquids BTL
  - Gas-to-liquids GTL
  - Coal-to-liquids CTL

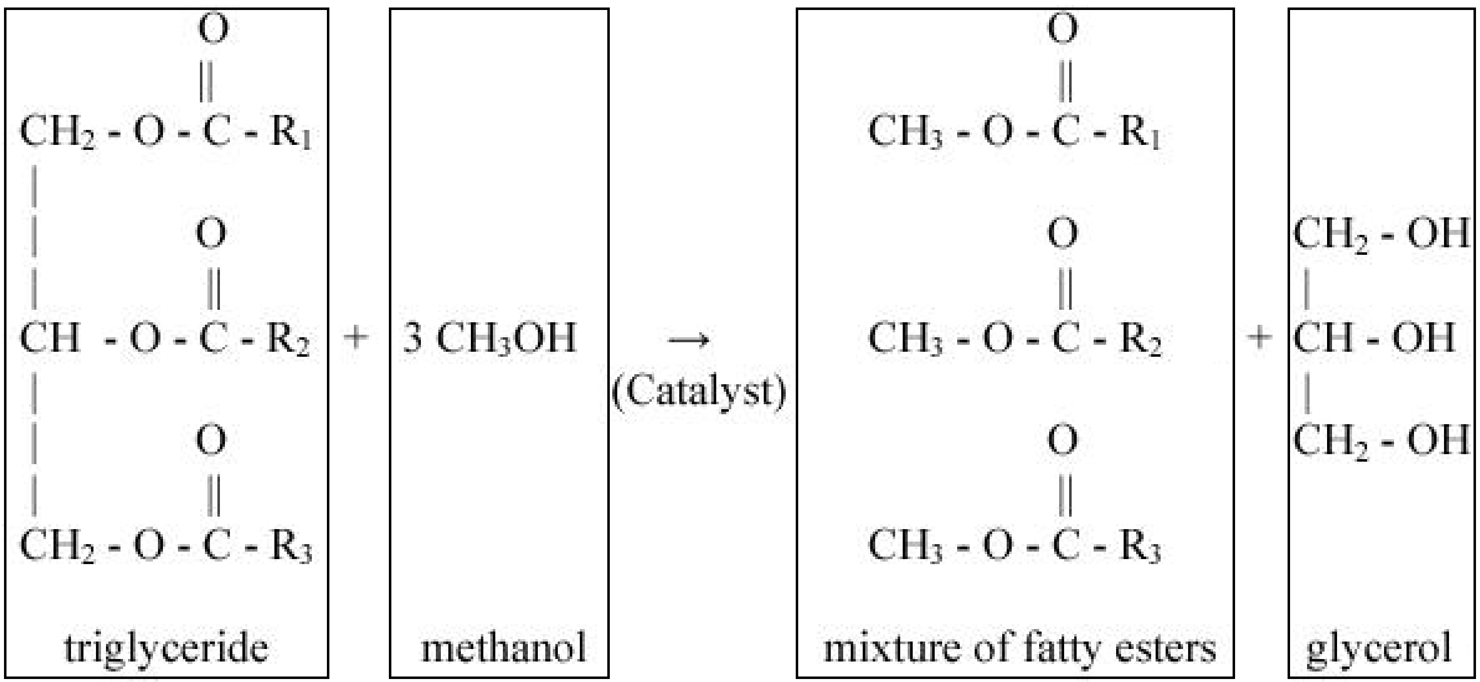
Hydrotreated vegetable oil (HVO)

- Feedstocks like FAME, end-product like synthetic diesel

Trad biodiesel = FAME

fatty acid methyl ester

– non-toxic biodegradable, simple and easy process



Trad biodiesel = FAME

- Less emissions than with regular diesel
  - particulate matter (PM), HC, CO;
    - oxygen content important!
- ...but
  - life cycle analysis' (LCA): CO_2 not necessarily decreased
  - NO_x –increase in most cases
  - oil plant cultivation: competition with food production
  - in engines: cold property problems, engine oil deterioration, rubber part embrittlement, corrosion, carbon deposits
  - storage problems (biodegradable, water...)
  - standards (EU): max. 7% in any diesel

Trad biodiesel = FAME

– Thermodynamically ~ trad. diesel

– Blended with other diesel fuels: lubricity improver

– High density, viscosity, low compressibility

$\Rightarrow$ Faster and bigger p-changes, higher max p in fuel injection system, faster start of injection

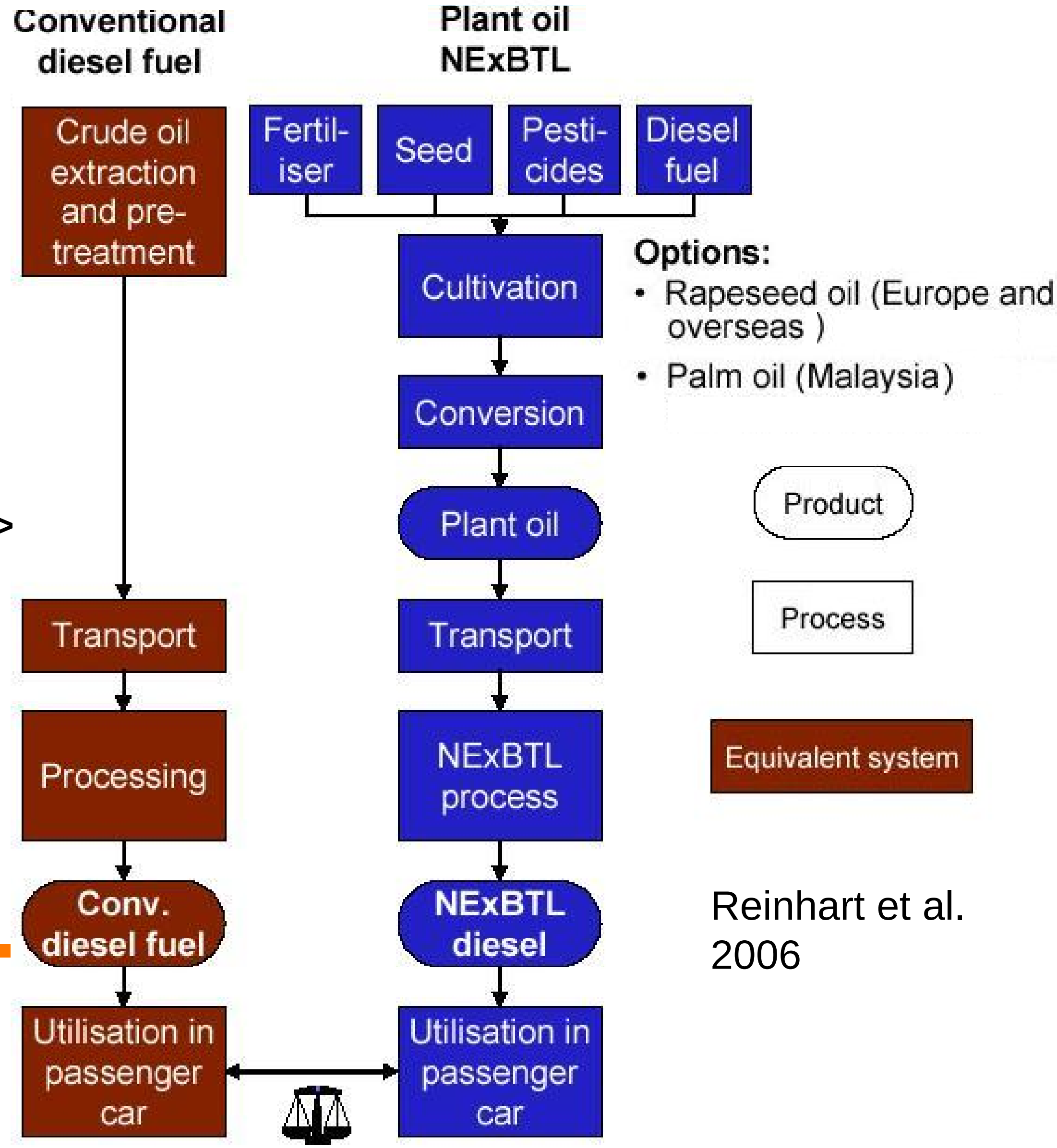
$\Rightarrow$ Bigger droplets, narrower opening angle, longer penetration, decreased mixing in fuel sprays

– chemical properties: as such problematic for fuel injection systems, may require material changes

- seals, rubber parts
- small amounts (according to EN 590) should be ok

Hydrotreated vegetable oil: HVO

– Neste oil: NExBTL
  - ”As an anwer to the demand for high quality renewable diesel produced at refinery volumes”
  - Production integrated with a trad. oil refinery => hydrogen, heat, infrastructure



Reinhart et al. 2006

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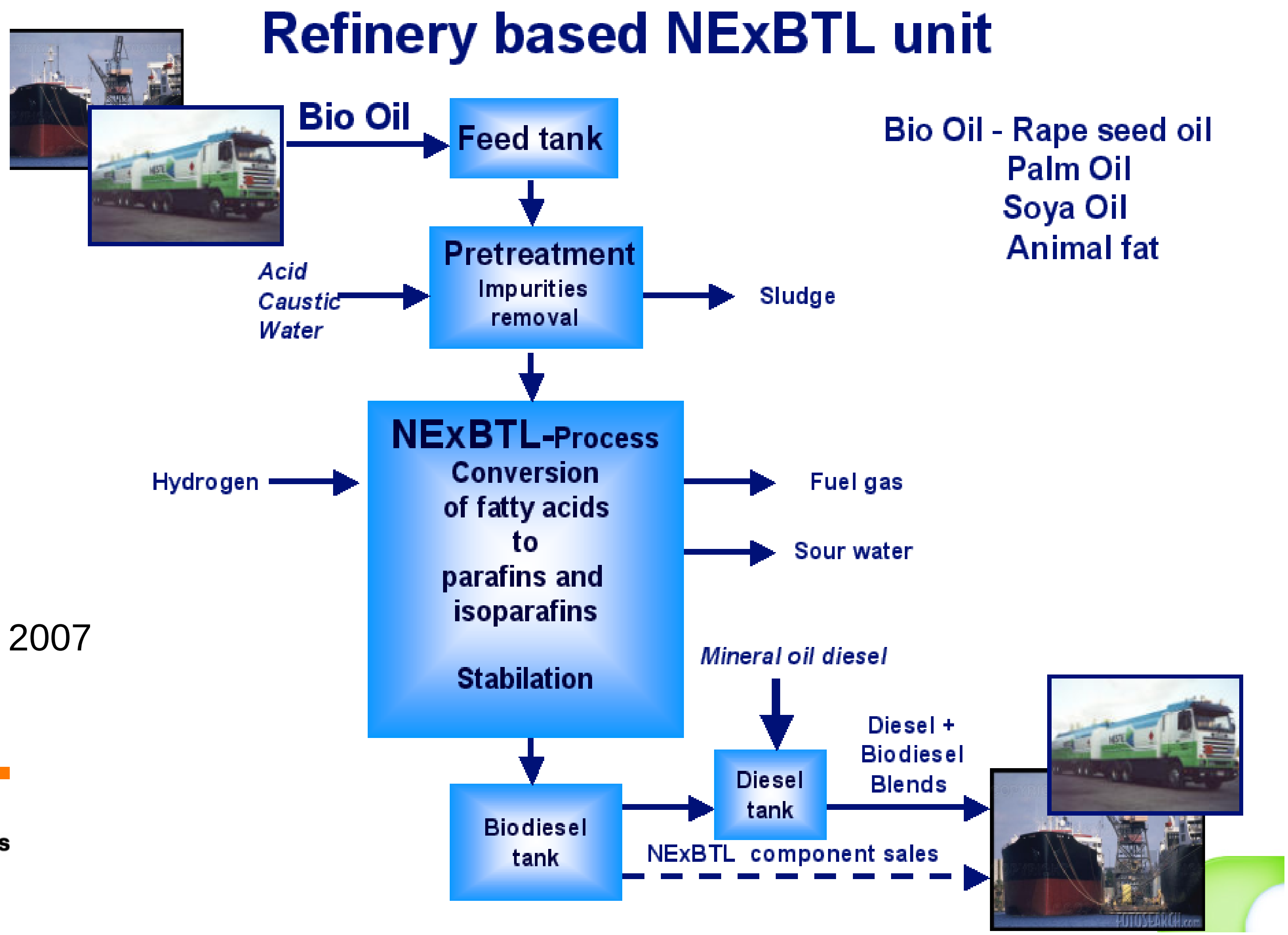
Hydrotreated vegetable oil: HVO

Production: oil/fat pretreatment => fatty acid hydrotreatment => paraffin-HC => isomerisation



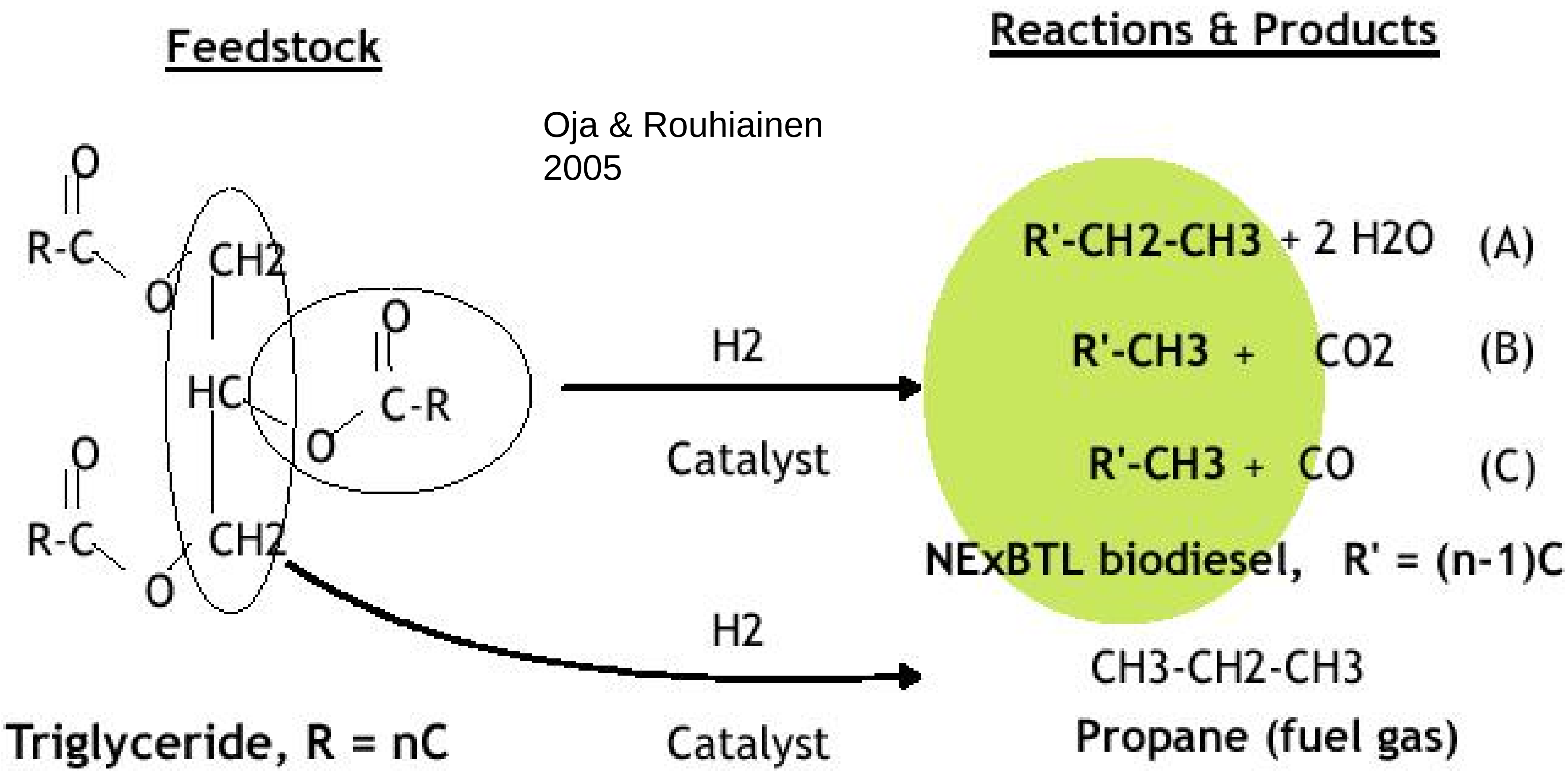
Mikkonen, 2007

Aalto Univers

Hydrotreated vegetable oil: HVO

– T, p control => chain length, isomerization => properties
  - Catalysts e.g. $NiMo/Al_2O_3$, $CoMo/Al_2O_3$

Oja & Rouhiainen 2005



Hydrotreated vegetable oil: HVO

– Lower density, more compressible => injection later (especially in older engines)
– HC chain length and branching (= cold properties) adjustable (process T ja p => isomerization)
– Low lubricity => need of additives (as usual)
– Chemistry: combustion, ignition easier => Less PM
– Paraffinic HC => high CN

⇒ possibilities to decrease NOx with technologies lowering T and worsening combustion conditions (EGR, Miller)

– lower density, viscosity, faster vaporization

⇒ increased spray angle, decreased penetration, smaller droplets

⇒ good mixing, no wall interactions => PM, NO, HC –decrease

Hydrotreated vegetable oil: HVO

– LCA's: CO_2 –emissions -33%...-80%
  - indirect land-use changes (deforestation) hard to calculate, not taken into account!
  - palm oil => deforestation? => ??

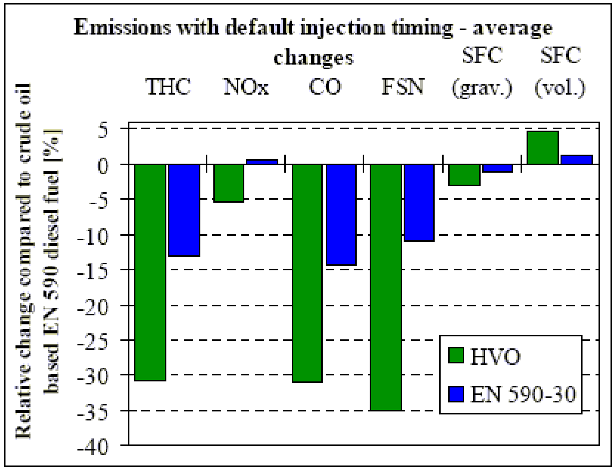
– Feedstocks oils; competition with food industry;
  - however, wider feedstock possibilities (good quality fuel)

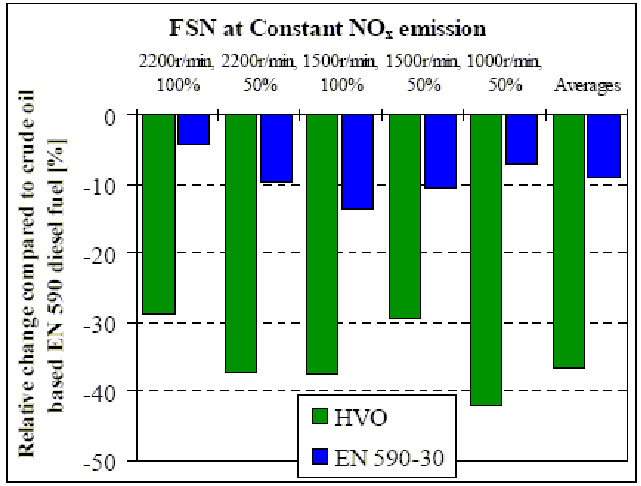
– emission studies (VTT, Scania):
  - standard high –duty engine, no optimization for new properties!

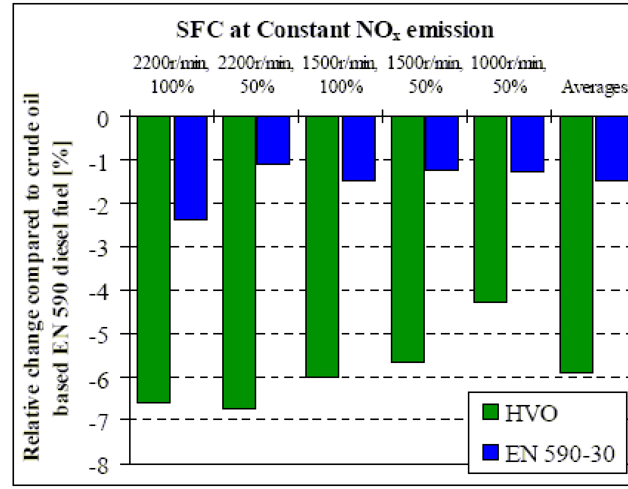
regulated	not regulated
• NOx - 0 ... - 20 %	• Aldehydes - 40 ... - 45 %
• Particles - 17 ... - 30 %	• Benzene - 40 ... - 45 %
• CO - 45 ... - 55 %	• PAH less
• HC - 45 ... -55 %	• Mutagens less

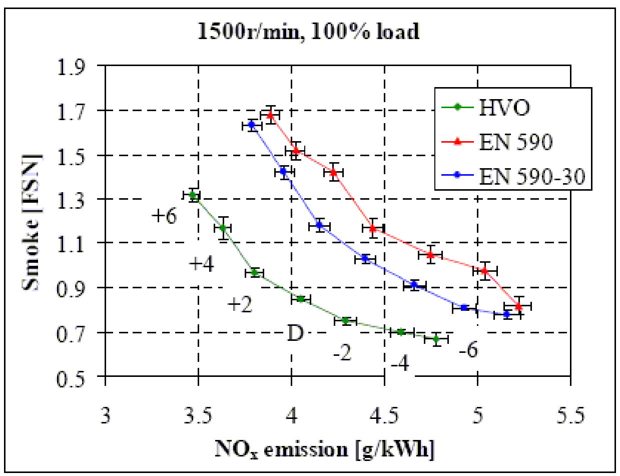
Hydrotreated vegetable oil: HVO

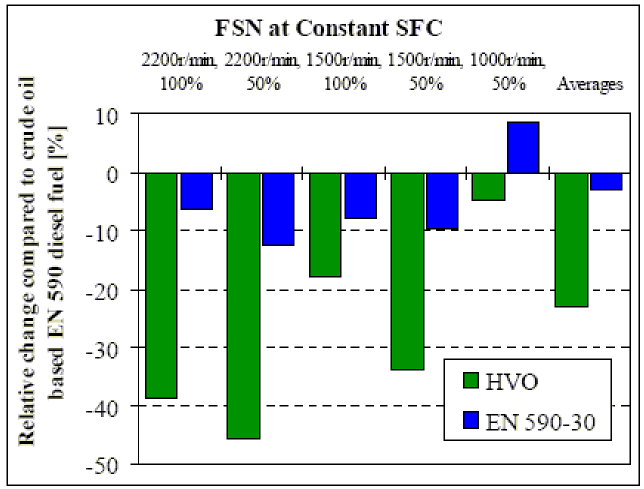
Aatola, 2008

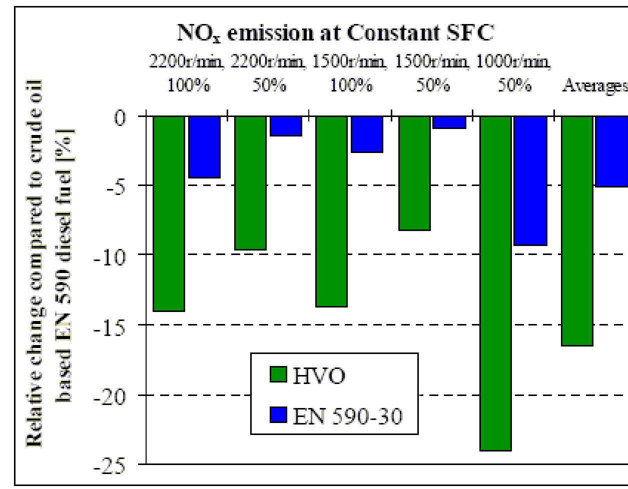










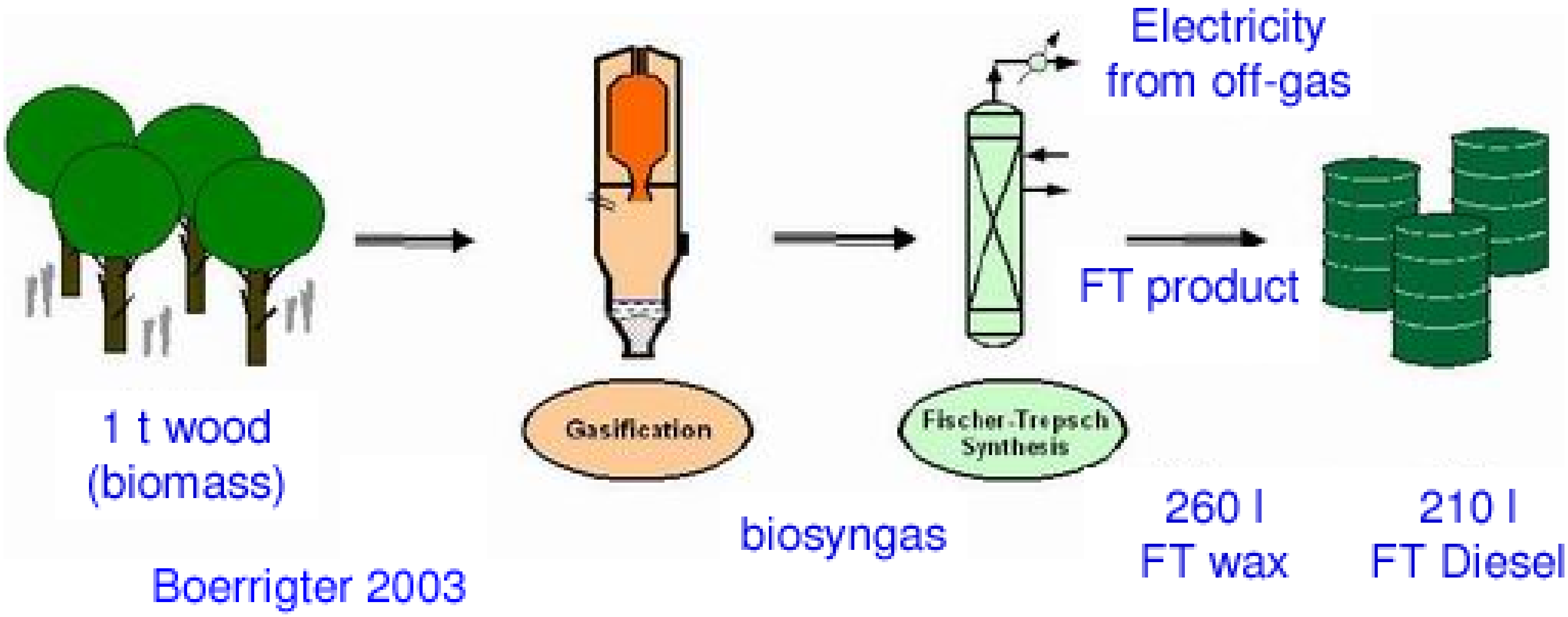


Fischer-Tropsch (FT) -diesel

– Biomass to liquids (BTL), Gas to liduids (GTL), Coal to Liquids (CTL)

= same end-product as HVO, same properties

– raw material gasification => CO ja H_2 (Synthesis gas, ”Syngas”) => FT-process => (iso)paraffinic HC:s



Fischer-Tropsch-diesel

Synthesis gas production, gasification

– $C + H_2O \rightarrow CO + H_2$, ΔH = 135,1 kJ/mol

– $C + 2\ H_2O \rightarrow CO_2 + 2\ H_2$, ΔH = 96,2 kJ/mol

– $C + CO_2 \rightarrow 2\ CO$, ΔH = 173,2 kJ/mol

– $C + ½\ O_2 \rightarrow CO$, ΔH = -110,5 kJ/mol

– $C + O_2 \rightarrow CO_2$, ΔH = -393,7 kJ/mol

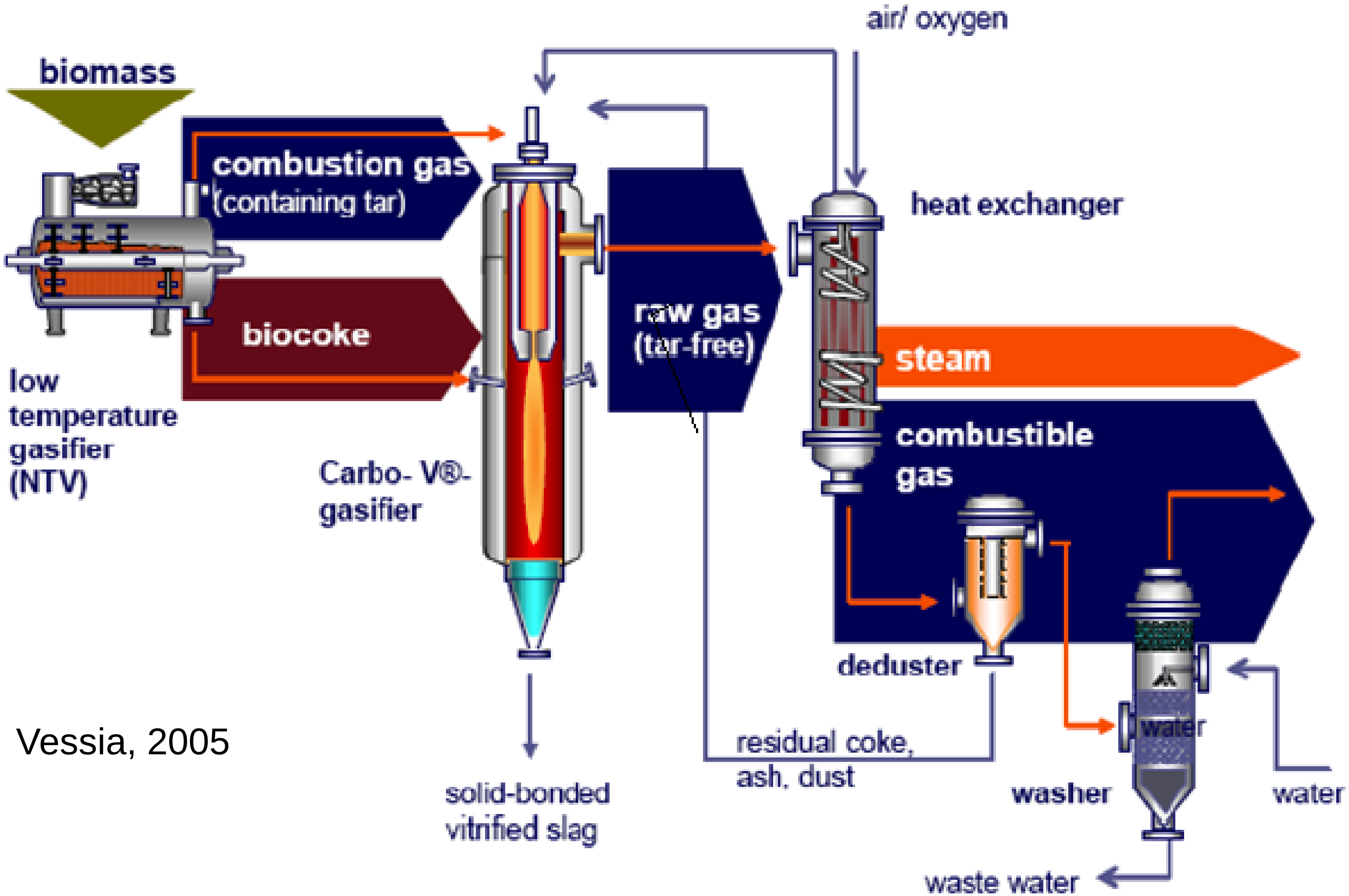
– $CO + H_2O \rightarrow CO_2 + H_2$, ΔH = -42 kJ/mol (Water-Gas Shift)

– $CO + 3\ H_2 \rightarrow CH_4 + H_2O$, ΔH = -217,6 kJ/mol (methane!)

=> Synthesis gas cleaning; e.g. tar problem with BTL

Fischer-Tropsch-diesel

Synthesis gas production



Vessia, 2005

Fischer-Tropsch-diesel

Fischer-Tropsch -synthesis

–473-523 K, 25-60 bar; conditions (T, p) => quality

–Paraffins: $n\ CO + (2n + 1)\ H_2 \rightarrow C_nH_{2n+2} + n\ H_2O$

–Olefins: $n\ CO + (2n)\ H_2 \rightarrow C_nH_{2n} + n\ H_2O$

–Alcohols: $n\ CO + (2n)\ H_2 \rightarrow C_nH_{2n+1}OH + (n-1)\ H_2O$

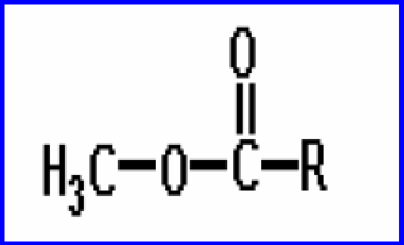
=> polymerization

Fischer-Tropsch-diesel

– High-grade fuel (~HVO), but costs ~ 3x trad diesel
  - Small volumes, raw material production scattered (BTL)
  - Costly technology (catalysts etc.)
  - Energy efficiency?
  - GTL the easiest (cleaning not so difficult)
  - CTL has been in production stage already very long ago (South Africa, WW II germany)

– Research and development ongoing
  - GTL: Sasol, Shell, BTL: Choren, Neste Oil+Stora Enso

Biobased diesel fuel comparison

	1st Generation	2nd Generation	3rd Generation
In	Vegetable oils	Vegetable oils Animal fats	Biomass
	Esterification	Hydrogenation	Gasification Fischer-Tropsch
	FAME	NExBTL	BTL
Out		C_nH_{2n+2}	C_nH_{2n+2}

Juva, 2007

Biobased diesel fuel comparison

	FAME	HVO	BTL
Process route	Transesterification	Hydrotreatment	Gasification, FT
Feed Product	Vegetable oils	Oils, fats	Biomass
Product (type)	Fatty acid methyl esters	Isomerized paraffinic hydrocarbons	Isomerized paraffinic hydrocarbons
Product quality	Consistency and stability issues	High	High
CO_2 emissions (LCA)	1.6-2.3 kg CO_2/kg oil equivalent	0.5-1.5 kg CO_2/kg oil equivalent	0.3-1.5 kg CO_2/kg oil equivalent
Note: Fossil diesel fuel value reported as 3.8 kg CO_2 / kg oil equivalent (Bown D. 2007)			

Aalto University

Biobased diesel fuel comparison

	NExBTL Diesel	GTL FT Typical	FAME (RME) Typical	Typical diesel fuel	EN 590
Density at +15°C (kg/m3)	780 - 785	770- 785	n. 885	n. 835	820-845
Viscosity at +40°C (mm2/s)	3.0 - 3.5	n. 3.2- 4.5	n. 4.5	n. 3.5	2.0-4.5
Cetane number	98 - 99	n. 73 - 81	n. 51	n. 53	>51
10 % distillation (°C)	n. 260- 270	n. 260	n. 340	n. 200	
90 % distillation (°C)	295 - 300	325 - 330	n. 355	n. 350	
Cloud point (°C)	n. - 15	n. 0 ... +3	n. 0 ... - 5	n. - 5	
Heating value (MJ/kg)	n. 44	n. 43	n. 38	n. 43	
Heating value (MJ/l)	n. 34,5	n. 33,8	n. 34	n. 36	
Polyaromatic content (wt-%)	n. 0	n. 0	n. 0	n. 4	<11
Oxygen content (wt-%)	n. 0	n. 0	n. 11	0	
Sulfur content (mg/kg)	< 10	< 10	< 10	< 10	<50

DME – dimethyl ether

- Use as a heating fuel and as an aerosol propellant

⇒ already widespread production!

- Gaseous in normal conditions, needs to be pressurized (like LPG)

⇒ logistical and storage properties: like LPG, infra exists!

- Problems
  - Need of pressurized tanks
  - Low viscosity (=> leaks), incompatible with some materials (elastomers)

  ⇒ need for new materials in fuel injection
  - density, heating value low

  ⇒ need of longer injection for same power
  - High compressibility, vapour pressure => cavitation problem?

DME – dimethyl ether

- **Structurally the simplest ether**
  - one component => more controllable in-cylinder phenomena
- **Compatible to diesel process: high CN**
- **Very low exhaust emissions (comparable with biogas)**
  - No particulate matter (PM); very low NOx; no SOx)
  - Low CO_2 emissions
  - Low engine noise
  - High fuel economy
  - High well-to-wheel efficiency
  - Thermal efficiency equivalent to diesel engine performance
  - Ignition characteristics equivalent to diesel engine performance

DME – dimethyl ether

Property	DME	Propane	Butane
Boiling Point, ºC	-24.9	-42.1	-0.5
Vapor Pressure @ 20 ºC, bar	5.1	8.4	2.1
Liquid Density, @ 20 ºC , kg/m3	668	501	610
Specific density, gas	1.59	1.52	2.01
Lower Heating Value, kJ/kg	28,430	46,360	45,740
Auto Ignition Temperature @ 1 atm, ºC	235-350	470	365
Explosion/Flammability Limit in air, vol %	3.4-17	2.1-9.4	1.9-8.4

	LNG(as CH_4)	LPG(as C_3H_8)	DME	Diesel
Boiling point °C	-161.5	-42	-25.1	180 -360
Low heating value (kcal/kg)	12,000	11,100	6,900	10,200
Specific gravity (liquid)	-	0.49	0.7	0.84
Ignition point (deg. C)	632	504	350	250
Explosion limit (%)	5 ~ 15	2.1 ~ 9.4	3.4 ~ 17	0.6 ~ 7.5
Cetane number	-	5	55 - 60	40 - 55

DME – dimethyl ether

Production:

- **straight synthesis from methanol (exothermic reactions)...**
  - **CO_2+ 3 H_2 => CH_3OH + H_2O**
  - **H_2O + CO => H_2 + CO_2**
  - **2 CH_3OH => CH_3OCH_3 + H_2O**
- **...or synthesis gas and synthesis**
  - **3 CO + 3 H_2 => CH_3OCH_3 + CO_2**
  - **2 CO + 4 H_2 => CH_3OCH_3 + H_2O**
  - **2 CO + 4 H_2 => 2 CH_3OH + CO_2**
  - **2 CH_3OH => CH_3OCH_3 + H_2O**
- **Life cycle GHG–emissions very low, when production wholly biomass -based (studies e.g. Volvo+Chalmers)**

Bio-based diesels, in short

- FAME
  - Production: oil+alcohol => fatty acid ester (+glycerol)
  - ☺ simple production, low emissions
  - ☹ quality, food vs. fuel, enough feedstocks? NOx?
- HVO
  - oils/fats + hydrotreatment => paraffin HC
  - ☺ quality, emissions low, production at refinery levels
  - ☹ food vs. fuel, enough feedstocks?, deforestration, price?
- BTL
  - Biomass => gasification => syngas (CO +H2) => (Fischer –Tropsch synthesis) => paraffin HC
  - ☺ quality, emissions, any biomass ok!
  - ☹ price, development stage, difficult process, small production scale so far
- DME
  - From syngas or direct synthesis from methanol
  - ☺ quality, emissions, any biomass ok, existing production, no new logistics solutions (vs. LPG)!
  - ☹ Logistics and production in a new scale, requires pressurized systems, engine adaptation requirement, difficult process

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Thank you!

Trad diesel vs. synthetic diesel

Lähde: ASFE 2006