The Chemical Analysis of Biodiesel.

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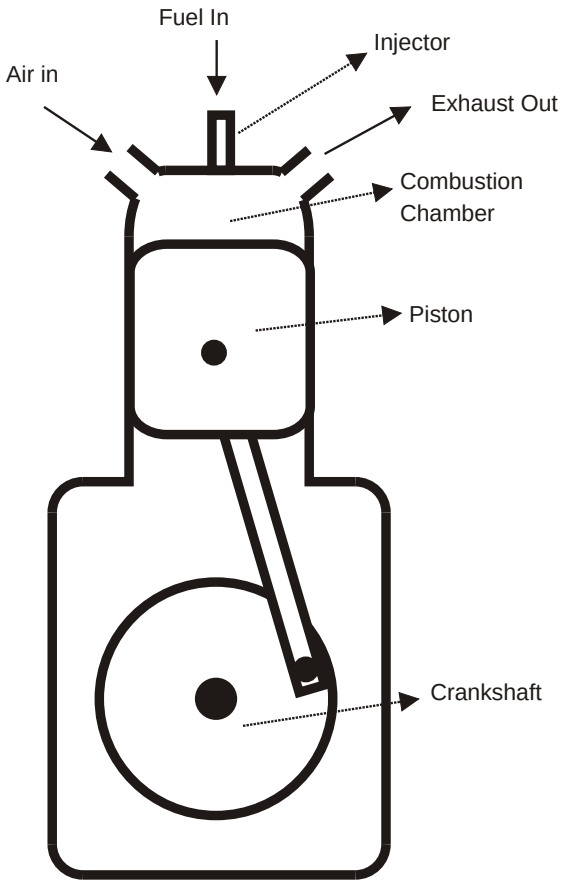
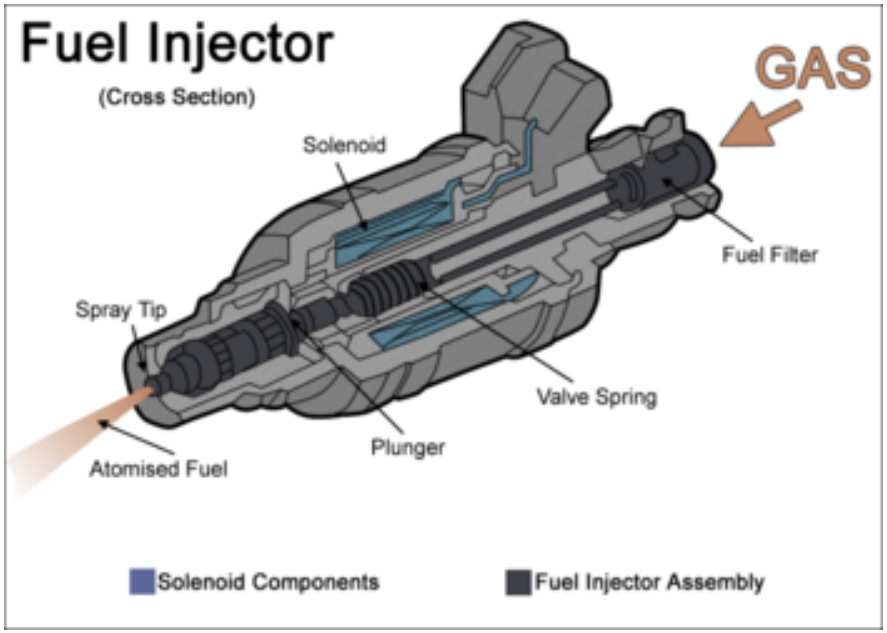
The Diesel Engine

- Diesel engine: A reciprocating internal-combustion engine driven by compression ignition of fuel in air.
- Engine: A device that turns chemical energy into kinetic energy by pressure from a combustion process.
- Internal Combustion: The combustion of the fuel takes place inside the engine.
- Reciprocating: Piston moving in a cylinder drives a crankshaft to give rotary motion
- Compression Ignition: Fuel ignites due to high air temperature achieved through adiabatic compression.

Diesel Engine



Diesel Injector[11]



- Injects fuel into combustion chamber
- Between 1 and 70 μl
- Injection lasts 1.5 ms
- Operates at 180 MPa

Diesel Fuel: Conventional diesel fuel

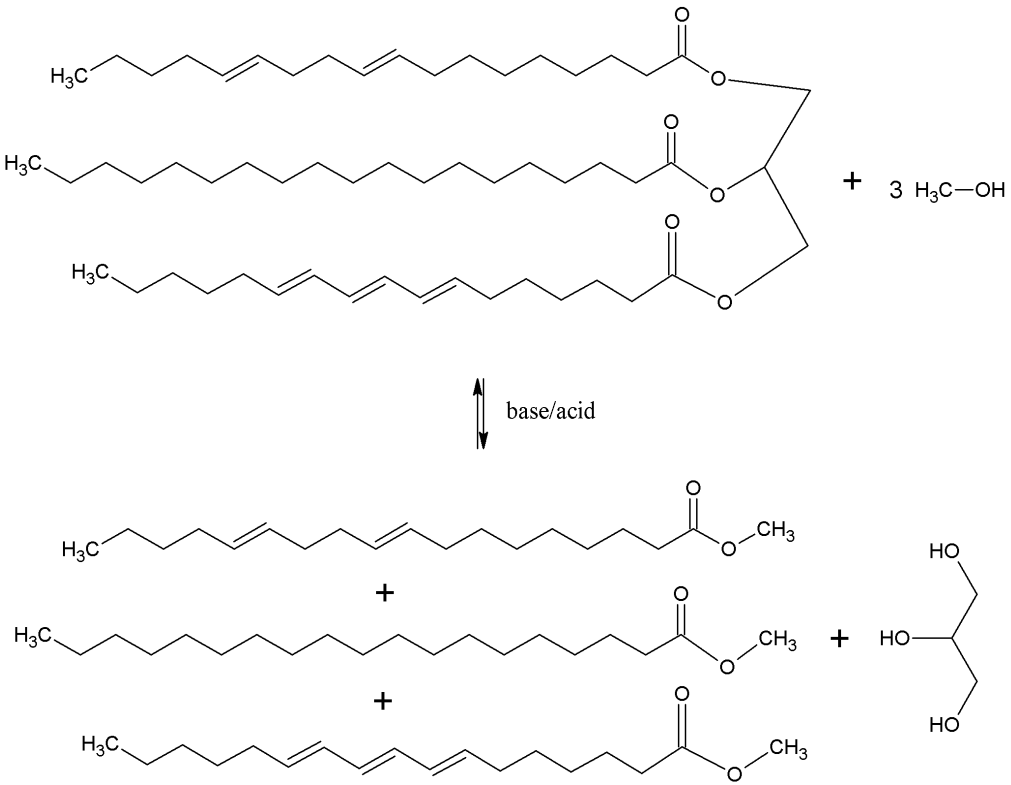
- Diesel engines can be fuelled by a wide variety of fuels.
- Petrodiesel: Conventional iesel fuel from crude oil distilled between 180 °Cand 380 °C[9]
- Ether/kerosene mixture for model aircraft[13]
- Heavy oil for marine engines[12]
- Jet fuel for diesel aircraft engines.[1]
- Engine and fuel forms a single system

Diesel Fuel: Why biodiesel?

- Biodiesel is a renewable resource.
- Biodiesel from soybeans produces 93% excess energy[3].
- Biodiesel compatible with petrodiesel.

Diesel Fuel: Biodiesel production

Definition: a fuel comprised of methyl esters of long chain fatty acids derived from vegetable oils.
Produced by transesterification of vegetable oils.



Diesel Fuel: Biodiesel sources[6]

- Canola
- Sunflower
- Soybean
- Palm
- *Jatropha*
- Recycled frying oil.

Biodiesel: Standards

- USA: ASTM D 6751
- Europe: EN 14214
- South Africa: SANS 1935

Biodiesel: Physical properties

Density at 15 °C[1],[2]: 860 – 900 kg/m^3

Kinematic viscosity at 40 °C[3]: 3,5 – 5,0, mm^2/s Lower than petrodiesel

Depends on the degree of unsaturation

Injector efficiency

[1]ISO 3675, Crude petroleum and liquid petroleum products – Laboratory determination of density or relative density – Hydrometer method.

[2]ISO 12185, Crude petroleum and petroleum products — Determination of density — Oscillating U-tube method.

[3]ISO 3104, Petroleum products — Transparent and opaque liquids — Determination of kinematicviscosity and calculation of dynamic viscosity.

Biodiesel: Physical properties

Flash point[4]: 120 °C, min Limits unreacted alcohol
Higher than petrodiesel
Safety

Cold Filter Plugging Point (CFPP)[5] Winter, −4 °Cmax
Summer, +3 °Cmax

[4]ISO 3679, Determination of flash point — Rapid equilibrium closed cup method.

[5]EN 116, Diesel and domestic heating fuels — Determination of cold filter plugging point.

Biodiesel: Diesel engine suitability

Cetane Number[6]: 51,0 min

Saturated FAMEs has higher cetane number than unsatured.

[6] ISO 5165, Petroleum — Diesel fuels — Determination of the ignition quality of diesel fuels — Cetane engine method.

Biodiesel: Deposition material

Carbon residue[7]: 0,3 mass fraction max

Sulfated ash content[8]: 0,02 % mass fraction max

Inorganic component

Abrasive

Forms deposits

Total contamination[9]: 24 mg/kg max Insoluble material on 8 μm filter

[7] ISO 10370, Petroleum products — Determination of carbon residue — Micro method.

[8] ISO 3987, Petroleum products — Lubricating oils and additives — Determination of sulfated ash.

[9] EN 12662, Liquid petroleum products — Determination of contamination in middle distillates.

Biodiesel: Water content

Water content[10]: 0,05 % mass fraction max Promotes biological growth
Hydrolysis
Corrosion
Problem in blends

[10]ISO 12937: Petroleum products — Determination of water — Coulometric Karl Fischer titration metod

Biodiesel: Inorganic compounds

Group I metals (total of Na and K)[11],[12]: 5,0 mg/kg max

Group II metals (total of Ca and Mg)[13]: 5,0 mg/kg max

[11] EN 14108, Fat and oil derivatives — Fatty acid methyl esters (FAME) — Determination of sodium content by atomic absorption spectrometry.

[12] EN 14109, Fat and oil derivatives — Fatty acid methyl esters (FAME) — Determination of potassium content by atomic absorption spectrometry.

[13] prEN 14538, Fat and oil derivatives — Fatty acid methyl ester (FAME) — Determination of Ca and Mg content by optical emission spectral analysis with inductively coupled plasma (ICP OES).

Biodiesel: Inorganic compounds

Phosphorus content[14]:10,0 mg/kg max Phosphorus damages catalytic converters.
Not a problem

Sulfur content[15]: 10,0 mg/kg max Biodiesel is naturally sulfur free

[14] EN 14107, Fat and oil derivatives — Fatty acid methyl esters (FAME) — Determination of phosphorus content by inductively coupled plasma (ICP) emission spectrometry.

[15] ISO 20884, Petroleum products — Determination of sulfur content of automotive fuels — Wavelengths-dispersive X-ray fluorescence spectrometry.

Biodiesel: Corrosiveness

Copper strip corrosion [16]: rating max Class 1

(3 h at 50 °C)

Indicates possible corrosion.

Acid value [17]: 0,5 mg KOH/g max

Titration

Possible corrosion

Fuel system deposits

Indication of quality

Both free fatty acids and mineral acids contribute

[16] ISO 2160, Petroleum products — Corrosiveness to copper — Copper strip test.

[17] EN 14104, Fat and oil derivatives — Fatty acid methyl esters (FAME) — Determination of acid value.

Biodiesel: Stability

Oxidative stability[18]: min 6 h at 110 °C Rancimat — measures tertiary breakdown products at elevated temperatures.[2]

Thermal stability and storage stability not yet specified.[7]

[18] EN 14112, Fat and oil derivatives — Fatty acid methyl esters (FAME) — Determination of oxidation stability (Accelerated oxidation test).

Biodiesel: Methanol

Methanol content[19]: 0,2 % mass fraction max Headspace GC

[19] EN 14110, Fat and oil derivatives — Fatty acid methyl esters (FAME) — Determination of methanol content.

Biodiesel: Fuel content

Ester contents[20]: 96,5 % mass fraction, min

GC method

Limits total contaminants.

Ensures the biogenic origin of biodiesel.

[20] EN 14103, Fat and oil derivatives — Fatty acid methyl esters (FAME) — Determination of ester and linolenic acid methyl ester contents.

Biodiesel: Free glycerol

Free glycerol[21]: 0,02% mass fraction max

GC of aqueous extract

Separate Phase: Attracts water, soaps

Injector deposits

Collects in tanks

[21] EN 14106, Fat and oil derivatives — Fatty acid methyl esters (FAME) — Determination of free glycerol content.

Biodiesel: Total glycerol

Monoglyceride content[22]: 0,8 % mass fraction max

Diglyceride content: 0,2 % mass fraction max

Triglyceride content: 0,2 % mass fraction max

Total glycerol: 0,25 % mass fraction max

GC of trimethylsilyl derivatives on non-polar columns[8]

A measure of transmethylation completeness

[22] EN 14105, Fat and oil derivatives — Fatty acid methyl esters (FAME) — Determination of free and total glycerol and mono-, di- and triglyceride content (Reference method).

Biodiesel: Degree of saturation

An important measure of oxidative stability
Type of unsaturation probably also important[5].

Iodine value[23]:140 g of iodine/100 g of FAME max

European standard: max 120 g/100 g

Can also be caluclated from ester content data

Linolenic acid methyl ester[24]: 12 % mass fraction max Three conjugated double bonds

Polyunsaturated methyl esters: 1% mass fraction max

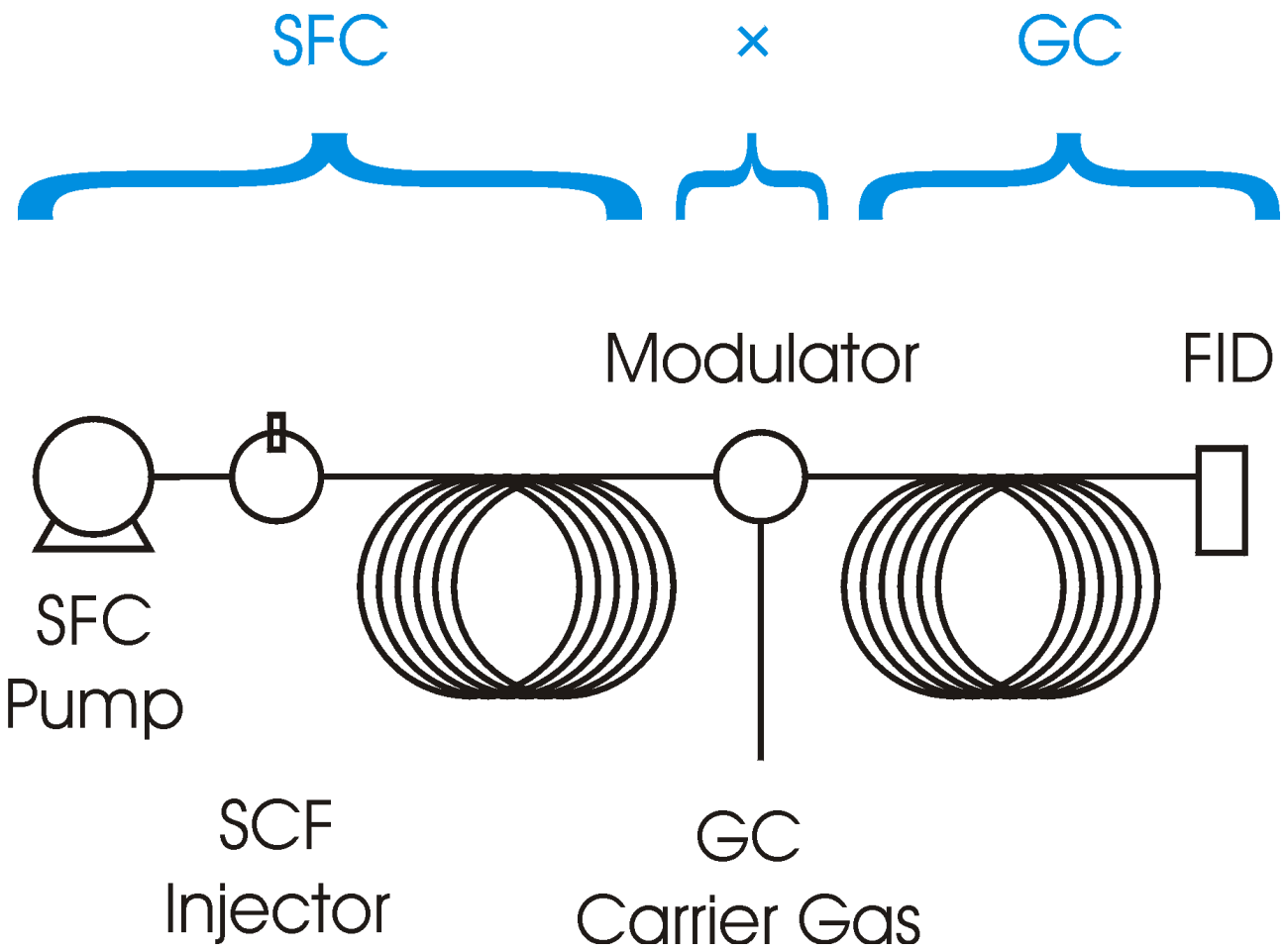
Four or more double bonds

Method under development

[23] EN 14111, Fat and oil derivatives — Fatty acid methyl esters (FAME) — Determination of iodine value.

[24] EN 14103, Fat and oil derivatives — Fatty acid methyl esters (FAME) — Determination of ester and linolenic acid methyl ester contents.

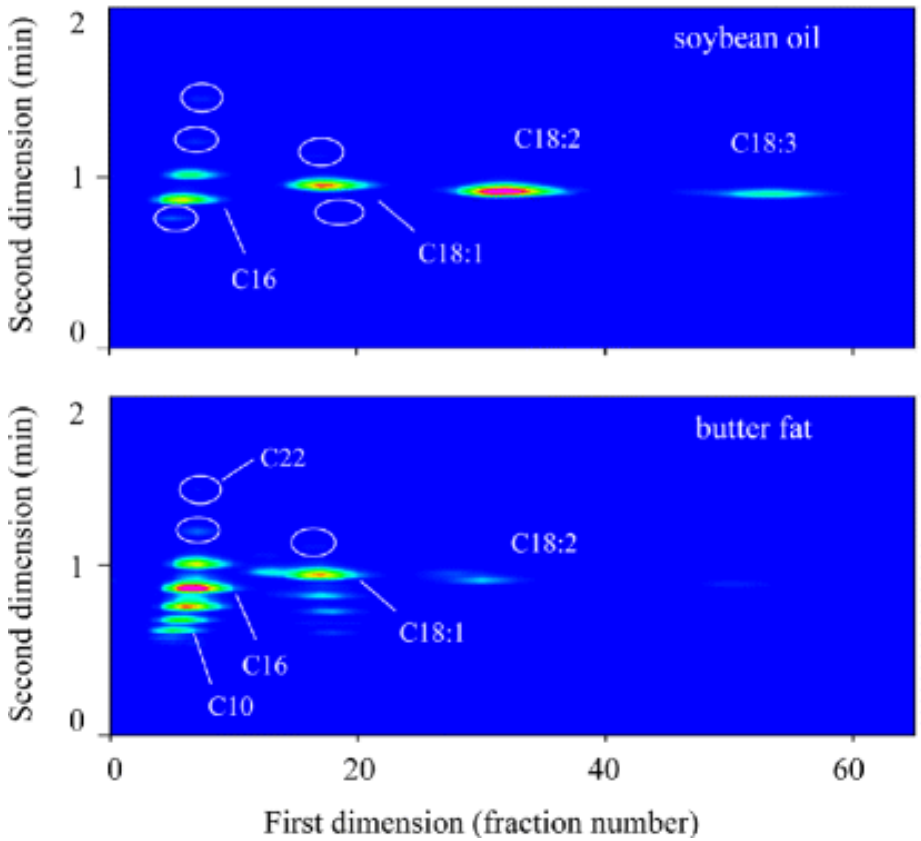
Biodiesel: SFCxGC Principles



Biodiesel: Application of SFCxGC

- SFC of FAME on silica separates according to number of double bonds.[10]
- GC of FAME on ODS separates according to chain length.

Biodiesel: Application of SFCxGC



Packed columns using CO_2 as carrier[4]

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