Properties of Biodiesel and Other Biogenic Fuels

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Background

- Energy security
  - Reduce dependence on petroleum-derived fuels
  - Derived from renewable resources
- Enhance domestic (agricultural) economy
- “Green” benefits: Biodegradability, reduced exhaust emissions

Historical Background

Biofuels are not a recent concept.

- Considerable research and use in the early 1900's.
- "Age of petroleum" approximately from 1945 to the 1970's.
- Renewed interest in alternative fuels in the 1970's due to energy crises.

Historical Background

- Vegetable oil-based fuels
  - First demonstration at the 1900 World Exposition
  - Interest through the early 1940's
  - Late 1940's / early 1950's some work at Ohio State U and Georgia Institute of Technology
  - First biodiesel described in 1937 Belgian Patent 422,877

- Ethanol
  - Use and interest as blends / antiknock agent with gasoline through the 1930's.
  - Tetraethyl lead as antiknock agent discovered in 1920's

Petroleum-Based Fuels

Hydrocarbons:

- Gasoline: "Lighter" branched hydrocarbons
  - Exemplified by 2,2,4-trimethylpentane (iso-octane)
- Diesel fuel: Long straight-chain hydrocarbons
  - Exemplified by hexadecane (cetane)
- Jet fuel: "Light" diesel fuel

Biogenic Fuels / Biofuels

- Most common biogenic fuels are oxygenated:
  - Alcohols (ethanol, butanol): By fermentation of carbohydrates
    - Gasoline replacement
  - Fatty acid methyl (alkyl) esters: By transesterification of triacylglycerol-containing materials
    - Diesel fuel replacement
  - Other biofuels include DME, biomethanol, biohydtrogen
- More recently, hydrocarbon fuels from biofeedstocks (renewable diesel, biogasoline) simulating petrofuels developed

Biodiesel and Renewable Diesel

Biodiesel	Renewable Diesel
Methyl (alkyl) esters	Hydrocarbons
By transesterification	By hydrodeoxygenation
Positive energy balance	Energy balance?
No/ low sulfur and aromatics	
Regulated exhaust emissions reduced compared to conventional petrodiesel	
Exception: NOx	
Cold flow problematic	Cold flow varies /"adjustable" "Lighter" form": aviation fuel
Oxidative stability problematic	High oxidative stability
High lubricity	Low lubricity
Biodegradable	Biodegradability likely similar to conventional petrodiesel
Higher flash point	Flash point likely closer to petrodiesel
Feedstock availability and costs problematic	
Well-researched	Other issues?

Fuel Suitability of Fatty Acid Methyl (Alkyl) Esters

- Long-chain, unbranched alkanes are "ideal" petrodiesel fuels.
  - At least in terms of combustion.
  - Branched compounds and aromatics have low CNs

- Structural similarity of long-chain, unbranched alkanes shows suitability of fatty esters as diesel fuels.
  - Long-chain fatty compounds such as methyl palmitate and methyl stearate have CN comparable to hexadecane

- Minimum CN in biodiesel standards > than in petrodiesel standards.
  - 47 in ASTM D6751 (biodiesel) vs. 40 in ASTM D975 (petrodiesel).
  - 51 in EN 14214 (biodiesel) vs. 51 in EN 590 (petrodiesel)

Why biodiesel and not the neat oil?

Vegetable Oil (Triacylglycerol)		Alcohol		Vegetable Oil Alkyl Esters (Biodiesel)		Glycerol
CH_2-OOCR^1				R′OOCR^1		CH_2OH
|			Catalyst			|
CH-OOCR^2	+	3 R′OH	→	R′OOCR^2	+	CHOH
|						|
CH_2-OOCR^3				R′OOCR^3		CH_2OH

Vegetable Oil (Triacylglycerol) Alcohol Vegetable Oil Alkyl Esters (Biodiesel) Glycerol

Viscosity!

27-35 mm^2/sec 4-5 mm^2/sec

Kinematic viscosity of petrodiesel fuels usually ≈ 1.8-3.0 mm^2/sec.

Biodiesel and Alcohols

- Biodiesel
  - Properties can vary considerably depending on the feedstock
  - Feedstocks can have widely varying fatty acid profiles
    - "Conventional" oils, i.e. classical commodity oils and many "alternative" oils contain mainly palmitic, stearic, oleic, linoleic and linolenic acids.
    - Other oils may contain shorter or longer chain acids
      - Many algal oils contain highly polyunsaturated fatty acids.

- Alcohol fuels
  - Same product independent of the feedstock

Some Fuel and Physical Properties of Ethanol and Butanol

	Ethanol	Butanol
Octane number (RON/MON*)	107-112 / 88-90	92-96 / 71-79
Melting point (°C)	-114	-88.6
Boiling point (°C)	78.3	117.7
Heating value [MJ/kg], [MJ/l]	29, 23	37, 30

* RON = research octane number, MON = motor octane number

- Suitability of alcohols as fuel (component) demonstrated by high octane number similar to cetane number of biodiesel.

Biodiesel Standard ASTM D6751

Property	Test method	Limits	Units
Flash point (closed cup)	D 93	93 min	°C
Alcohol control. One of the following must be met:			
1. Methanol content	EN 14110	0.2 max	% volume
2. Flash point	D 93	130 min	130 min
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity, 40 °C	D 445	1.9-6.0	mm^2 / s
Sulfated ash	D 874	0.020 max	% mass
Sulfur	D5453	0.05 or 0.0015 max [a)]	% mass
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report	°C
Carbon residue	D 4530	0.050 max	% mass
Acid number	D 664	0.50 max	mg KOH / g
Free glycerin	D 6584	0.020	% mass
Total glycerin	D 6584	0.240	% mass
Phosphorus content	D 4951	0.001 max	% mass
Distillation temperature, Atmospheric equivalent temperature, 90% recovered	D 1160	360 max	°C
Sodium and potassium, combined	EN 14538	5 max	ppm (µg/g)
Calcium and magnesium, comb.	EN 14538	5 max	ppm (µg/g)
Oxidation stability	EN 15751	3 min	hours
Cold soak filterability	D7501	360 max	sec

a) The limits are for Grade S15 and Grade S500 biodiesel, respectively. S15 and S500 refer to maximum sulfur specifications (ppm).

Biodiesel Standard EN 14214

Property	Test method	Limits	Units
Ester content	EN 14103	96.5 min	% (m/m)
Density; 15°C	EN ISO 3675, 12185	860-900	kg/m^3
Viscosity, 40 °C	EN ISO 3104, ISO 3105	3.5-5.0	mm^2/s
Flash point	EN ISO 2719, 3679	101 min	°C
Sulfur content	EN ISO 20846, 20884	10.0 max	mg/kg
Carbon residue (10% dist. res.)	EN ISO 10370	0.30 max	% (m/m)
Cetane number	EN ISO 5165	51 min	
Sulfated ash	ISO 3987	0.02 max	% (m/m)
Water content	EN ISO 12937	500 max	mg/kg
Total contamination	EN 12662	24 max	mg/kg
Copper strip corrosion (3h, 50°C)	EN ISO 2160	1	
Oxidative stability, 110 °C	EN 14112, 15751	8.0 min	h
Acid value	EN 14104	0.50 max	mg KOH / g
Iodine value	EN 14111	120 max	g iodine /100g
Linolenic acid content	EN 14103	12 max	%(m/m)
Content of FAME with ≥ 4 double bonds		1 max	% (m/m)
Methanol content	EN 14110	0.20 max	% (m/m)
Monoglyceride content	EN 14105	0.80 max	% (m/m)
Diglyceride content	EN 14105	0.20 max	% (m/m)
Triglyceride content	EN 14105	0.20 max	%(m/m)
Free glycerine	EN 14105, 14106	0.02 max	%(m/m)
Total glycerine	EN 14105	0.25max	%(m/m)
Alkali metals (Na + K)	EN 14108, 14109, 14538	5.0 max	mg/kg
Earth alkali metals (Ca + Mg)	prEN 14538	5.0 max	mg/kg
Phosphorus content	EN 14107	4.0 max	mg/kg

Major Ester Components of Most Biodiesel Fuels

Fatty esters in from common vegetable oils (palm, soybean, canola/rapeseed, sunflower, etc):

- Methyl palmitate (C16:0): $CH_3OOC\text{-}(CH_2)_{14}\text{-}CH_3$
- Methyl stearate (C18:0): $CH_3OOC\text{-}(CH_2)_{16}\text{-}CH_3$
- Methyl oleate (C18:1, Δ9*c*): $CH_3OOC\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CH_3$
- Methyl linoleate (C18:2; all *cis*):
  $CH_3OOC\text{-}(CH_2)_7\text{-}(CH{=}CH\text{-}CH_2)_2\text{-}(CH_2)_3\text{-}CH_3$
- Methyl linolenate (C18:3; all *cis*):
  $CH_3OOC\text{-}(CH_2)_7\text{-}(CH{=}CH\text{-}CH_2\text{-})_3\text{-}CH_3$

From other oils:

- Methyl laurate (C12:0): $CH_3OOC\text{-}(CH_2)_{10}\text{-}CH_3$
- Methyl ricinoleate (C18:1, 12-OH; *cis*):
  $CH_3OOC\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}CH_2\text{-}CHOH\text{-}(CH_2)_5\text{-}CH_3$

Properties of Methyl Esters

	Cetane Number	M.P. (°C)	Kin. Visc. (40°C; mm^2/s)	Oxid. Stab. (h)	Heat of Comb. (kJ/kg)
C12:0	67	4.5	2.43	> 24	37968
C16:0	85	28.5	4.38	> 24	39449
C18:0	100	38	5.85	> 24	40099
C18:1	58	-20	4.51	2.79	40092
C18:2	38	-43	3.65	0.94	39698
C18:3	23	-52	3.14	0	39342
C18:1 12-OH	37	-5	15.29	0.67	
ASTM 6751	47 min	CP	1.9-6.0	3 min	-
EN 14214	51 min	CFPP	3.5-5.0	8 min	-

G. Knothe; *Energy & Fuels* 22, 1358-1364 (2008).

Some Fatty Acid Profiles

Vegetable Oil	C16:0	C18:0	C18:1	C18:2	C18:3
Rapeseed / Canola	3-4	1-3	58-62	20-22	9-12
Soy	8-13	2-6	18-30	49-57	2-10
Sunflower	6-7	3-5	21-29	58-67	
Jatropha	13-15	7-8	34-44	31-43	

Properties of Vegetable Oil Esters

Methyl Ester	Cloud Point (°C)	Cetane Number	Kin. Visc. (40°C; mm^2/s)
Rapeseed / Canola	-3	52-55	4.5
Soy	0	48-52	4.1
Sunflower	0	≈ 55	4.4
Jatropha	4-5		

Oxidative stability: usually antioxidants required to meet standard specifications

Property Trade-off

Increasing chain length:

- Higher melting point (-)
- Higher cetane number (+)

Increasing unsaturation:

- Lower melting point (+)
- Decreasing oxidative stability (-)
- Lower cetane number (-)

Influence of Alcohol Moiety

Branched and longer-chain esters:

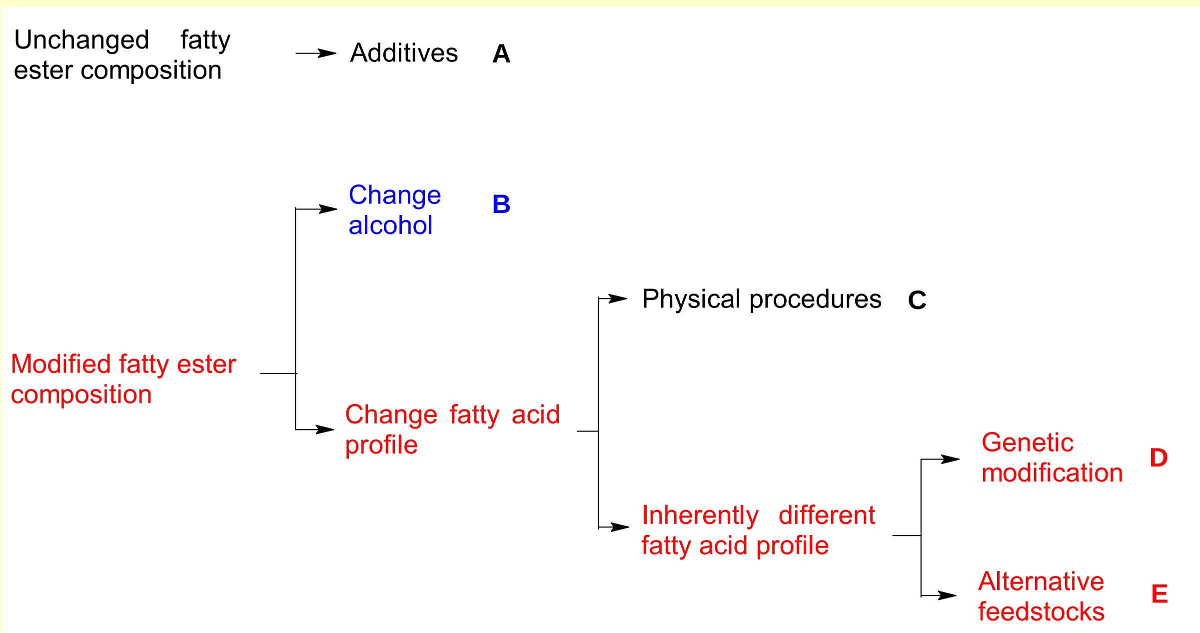
- Lower melting points, similar cetane numbers compared to methyl esters

Ester	M.P. (°C)	CN	Ester	M.P. (°C)	CN
C16:0 Methyl	28.5	85.9	C18:0 Me	37.7	101
C16:0 Ethyl	23.2	93.1	C18:0 Et	33.0	97.7
C16:0 Propyl	20.3	85.0	C18:0 Pr	28.1	90.0
C16:0 *iso*-Propyl	13-14	82.6	C18:0 i-Pr		96.5
C18:1 Methyl	-20.2	59.3	C18:2 Me	-43.1	38.2
C18:1 Ethyl	-20.3	67.8	C18:2 Et	-56.7	39.6
C18:1 Propyl	-30.5	58.8	C18:2 Pr		44.0
C18:1 *iso*-Propyl		86.6			

- Disadvantage: Higher costs of alcohols

Source: *Handbook of Chemistry and Physics*; *The Lipid Handbook,* various publications.

Five Approaches to Improving Biodiesel Fuel Properties

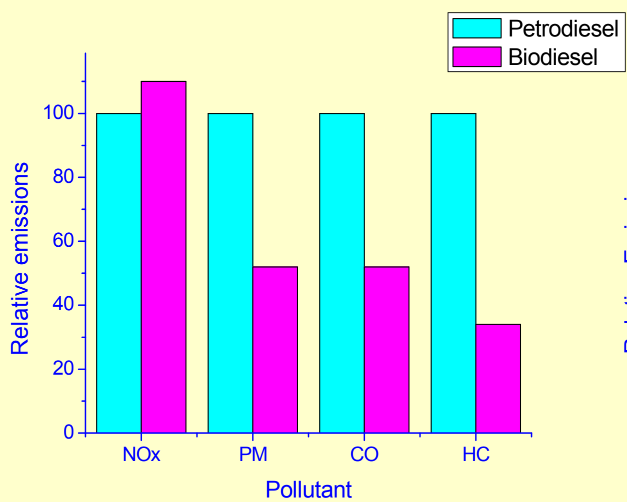


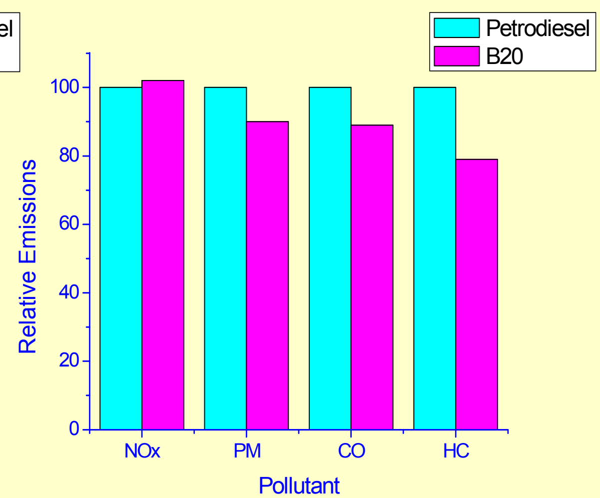
G. Knothe; *Energy & Environmental Science*, 2, 759-766 (2009).

Exhaust Emissions Studies

Average effect of biodiesel and B20 vs. petrodiesel on regulated emissions

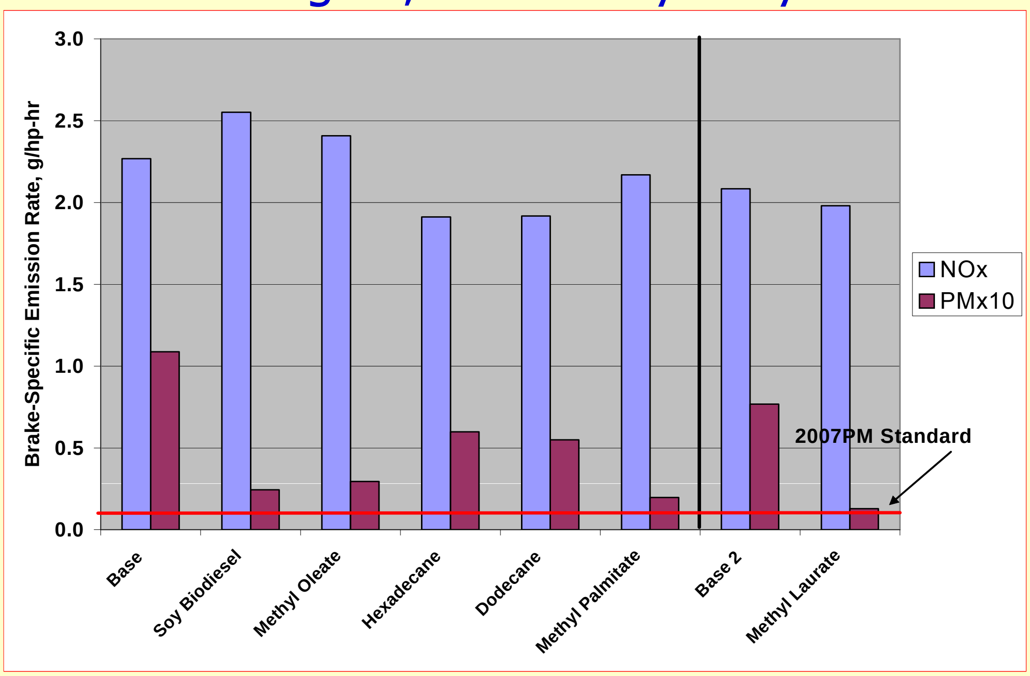
(Source: USEPA report 420-P-02-001)





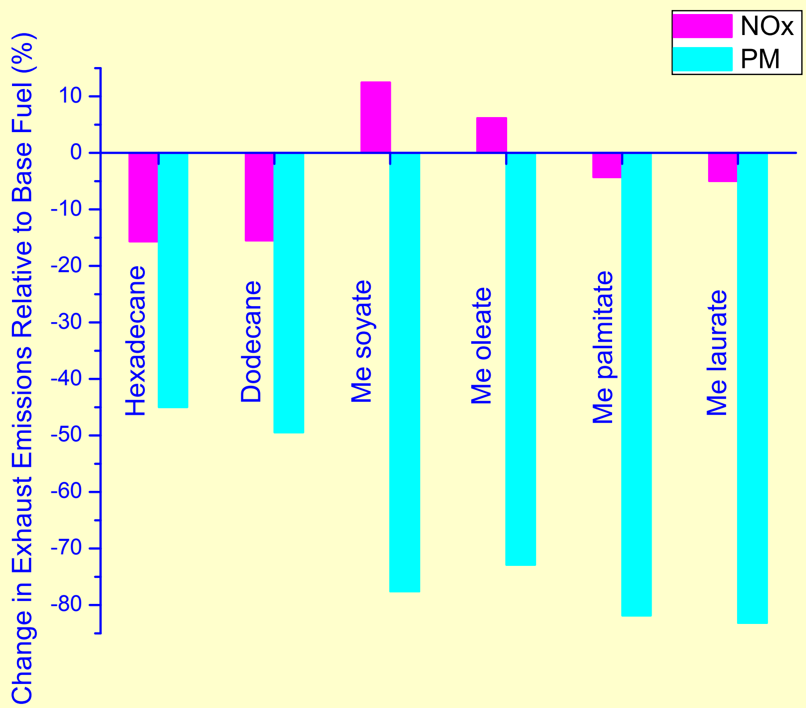
NO_x and PM Exhaust Emissions of Petrodiesel, Biodiesel, Their Components

2003 Engine; EPA Heavy Duty Test



G. Knothe, C.A Sharp, T.W. Ryan III, *Energy & Fuels* 20, 403-408 (2006).

Change in NO_x and PM vs. petrodiesel



Biodiesel and Lubricity

- Neat biodiesel has excellent lubricity as do neat methyl esters.

- Not included in biodiesel standards.

- Low-level blends (~ 2% biodiesel in petrodiesel = B2):
  - Lubricity benefits through biodiesel with (ultra-)low sulfur petrodiesel fuels which do not possess inherent lubricity compared to non-desulfurized petrodiesel fuels.
  - Marginal cost impact.

- High-frequency reciprocating rig (HFRR) tester (ASTM D6079; ISO 12156) in ASTM and EN petrodiesel standards.
  - Maximum wear scars of 520 (ASTM) and 460 μm (EN).

Biodiesel and Lubricity

Lubricity of low-level blends of biodiesel with petrodiesel to a great extent determined by:

- Contaminants (minor components), especially free fatty acids and monoacylglycerols.
  - In the neat form, even better lubricity than methyl esters.
  - Disproportionately affect lubricity of low-level blends.
  - Glycerol has limited effect (insolubility in petrodiesel).

Example (HFRR wear scars):

- ULSD: 651, 636 µm
  - w. 1% methyl oleate: 597, 515 µm
  - 1% oleic acid in methyl oleate, then 1% thereof in ULSD: 356, 344 µm.
  - w. 2% methyl oleate: 384, 368 µm

G. Knothe, K.R. Steidley; *Energy & Fuels* 19, 1192-1200 (2005).

Water in Biofuels

- Oxygenated nature of biofuels causes some differences in properties compared to hydrocarbons as well as some similarities between the biofuels.

- Oxygen content causes some affinity for water:
  - Biodiesel can contain 1000-1700 ppm water, petrodiesel 40-114 under same conditions (4-35^{o}C; 300 h equilibration time) (He et al, Appl. Eng. Agric, 2007).
    - Limited in biodiesel standards to 500 ppm.
  - Ethanol is hygroscopic. Limited in ASTM D4806 to 1%.

- Water in biofuels can promote fuel degradation with acid formation.

Ethanol

Ethanol: Formation of acetic acid (pKa = 4.76) with Acetobacter

- ASTM D4806
  - Limited to 0.007 mass % (by ASTM D1613);
  - pHe 6.5-9.0 (by ASTM 6423; for fuels containing nominally $\geq$70 vol % ethanol)
- ASTM D7795: Acidity in Ethanol and Ethanol Blends by Titration;
  - For low levels of acidity:< 200 mg/kg.
- ASTM D7577: Accelerated Iron Corrosion Rating of Denatured Fuel Ethanol and Ethanol Blends.

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Biodiesel

- Formation of free fatty acids through hydrolysis.
- Water can promote microbial growth:
  - Can affect marine applications as seawater is used as ballast in tanks when fuel consumed.
- Free fatty acids addressed by acid number in biodiesel standards of max 0.50 mg KOH / g.

Biodiesel Oxidation

- Biodiesel affected by presence of oxygen in air.
  - Unsaturated fatty acid chains susceptible to oxidative degradation.
  - Acids can be formed by oxidative degradation.
  - Can be monitored by acid value and / or kinematic viscosity.

Properties of Fatty Acids vs. Fatty Acid Methyl Esters

	Oleic acid	Methyl oleate
Melting point (°C)	12.8	-20.2
Kinematic viscosity (40°C; mm^2/s)	19.91	4.51
Lubricity (HFRR test; µm; two tests)	0, 0	290, 342

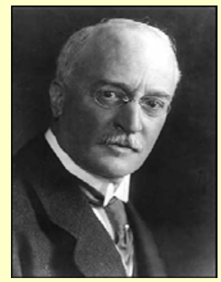
pKa of linoleic acid: 7.6 (Handbook of Chemistry and Physics).

- Free fatty acids also have a benefit: Improve lubricity.

Summary

- Biogenic fuels (biofuels) have a greater affinity for water due to their structure (oxygen content).
    - Can promote the formation of acids.
- For biodiesel, acids also possible by oxidative degradation
- Acids with biodiesel weaker than with ethanol; free fatty acids provide lubricity benefits.
- Biodiesel properties strongly dependent on fatty acid profile.

Parting Thoughts: Rudolf Diesel (1912)



"The fact that fat oils from vegetable sources can be used may seem insignificant to-day, but such oils may perhaps become in course of time of the same importance as some natural mineral oils and the tar products are now. ... In any case, they make it certain that motor-power can still be produced from the heat of the sun, which is always available for agricultural purposes, even when all our natural stores of solid and liquid fuels are exhausted."

R. Diesel, The Diesel Oil-Engine, *Engineering* 93:395–406 (1912). Chem. Abstr. 6:1984 (1912).