The Potential of Biodiesel with Improved Properties to an Alternative Energy Mix

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Some Fuels from Biological Sources (Biomass)

Transportation: spark ignition engines, compression ignition (diesel) engines, turbine (jet) engines

Non-transportation: stationary engines, burners, heaters

Ethanol, butanol: spark-ignition engines

Biodiesel: diesel engines; non-transportation

Renewable diesel: diesel engines; jet engines; non-transportation

Dimethyl ether: diesel engines

Hydrogen

Pyrolysis oils

BTL (Biomass-to-liquid)

Significance of Diesel and Related Fuels

Heavy-duty engines

Light-duty engines

Aviation fuels

Heating oil

United States:

Diesel fuel consumption approximately 200 billion L

Jet fuel consumption approximately 50 billion L

Gasoline (petrol) generally used only for light-duty engines

Focus on Triacylglycerol Feedstocks

Biodiesel, renewable diesel, pyrolysis oils from:

- Vegetable oils
  - Classical (edible) commodity oils (palm, rapeseed / canola, soybean, etc.)
  - "Alternative" (inedible) oils (jatropha, karanja, etc.)
- Animal fats
- Used cooking oils
- "Alternative" feedstocks
  - Algae

Why Triacylglycerol Feedstocks?

Alkanes are "ideal" diesel fuels.

- Cetane number: descriptor related to ignition delay time
- Hexadecane high-quality reference compound on the cetane scale (CN = 100)
- Branched compounds and aromatics have low cetane numbers

Structural similarity responsible for suitability of fatty esters as diesel fuels.

- Compounds such as methyl palmitate and methyl stearate have CN, comparable to hexadecane

Why biodiesel and not the neat oil?

CH_2-OOCR^1				R′OOCR^1		CH_2OH
|			Catalyst			|
CH-OOCR^2	+	3 R′OH	$\rightarrow$	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 is usually ≈ 1.8-3.0 mm^2/sec.

Advantages of Biodiesel

- Renewable fuel of domestic origin
  - Largely CO_2 neutral
- Technically competitive with petrodiesel
  - Miscible with petrodiesel in all ratios
- Largely compatible with the existing infrastructure
- Environmental benefits
  - Biodegradability
  - Most regulated exhaust emissions reduced
- Safer handling (higher flash point)
- Inherent lubricity
- Low or no sulfur / aromatics
- Positive energy balance (> 4:1)

Major Ester Components of Most Biodiesel Fuels

Fatty esters derived 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*): $CH_3OOC\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CH_3$
- Methyl linolenate (C18:3; all *cis*): $CH_3OOC\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3$

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	6 min	-

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

Properties of Vegetable Oil Esters

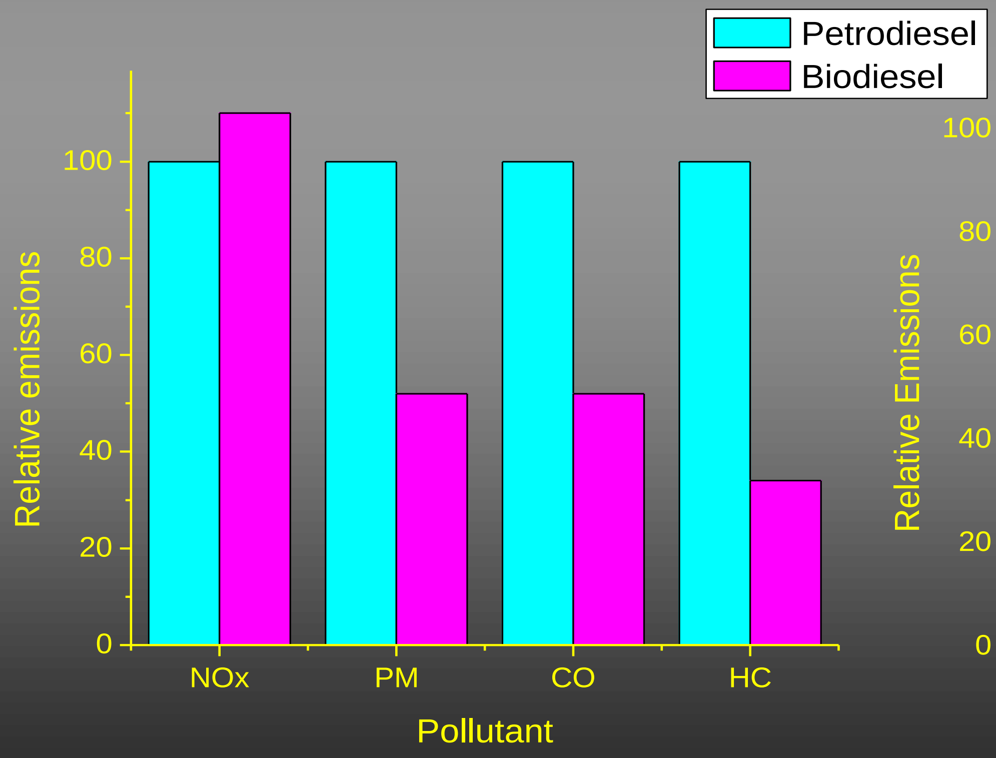
Methyl Ester	Cloud Point (° C)	Cetane Number	Kin. Visc. (40° C; mm^2/s)
Rapeseed / Canola	-3	53-55	4.6
Soy	0	48-52	4.1
Sunflower	0	≈ 55	4.4

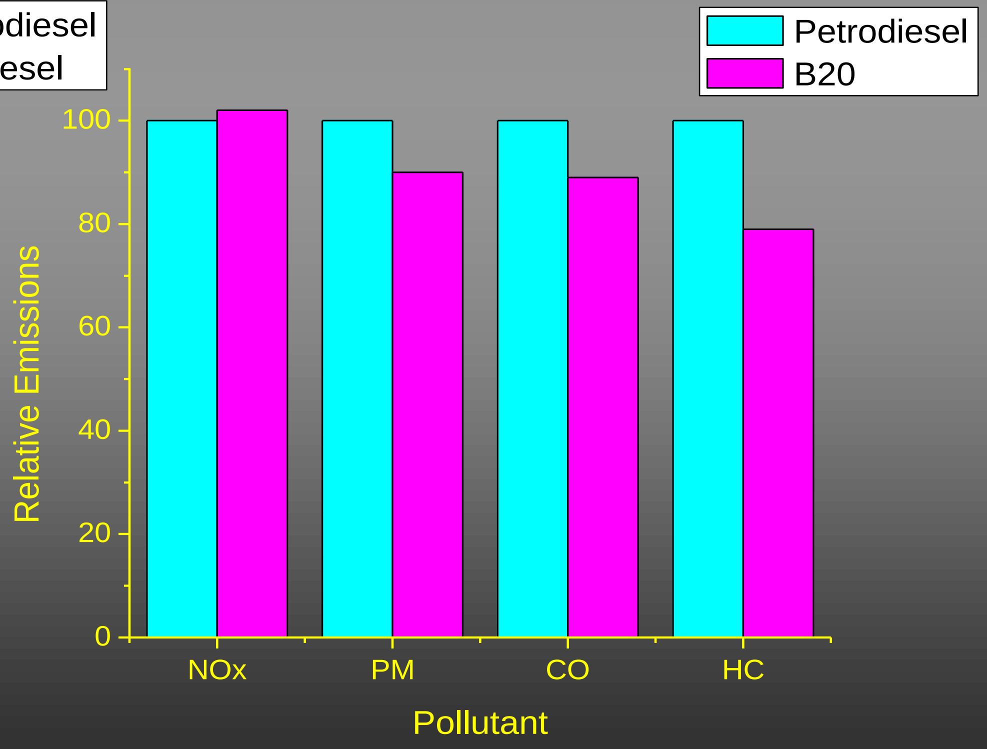
Oxidative stability: usually antioxidants required to meet standard specifications

Exhaust Emissions Studies

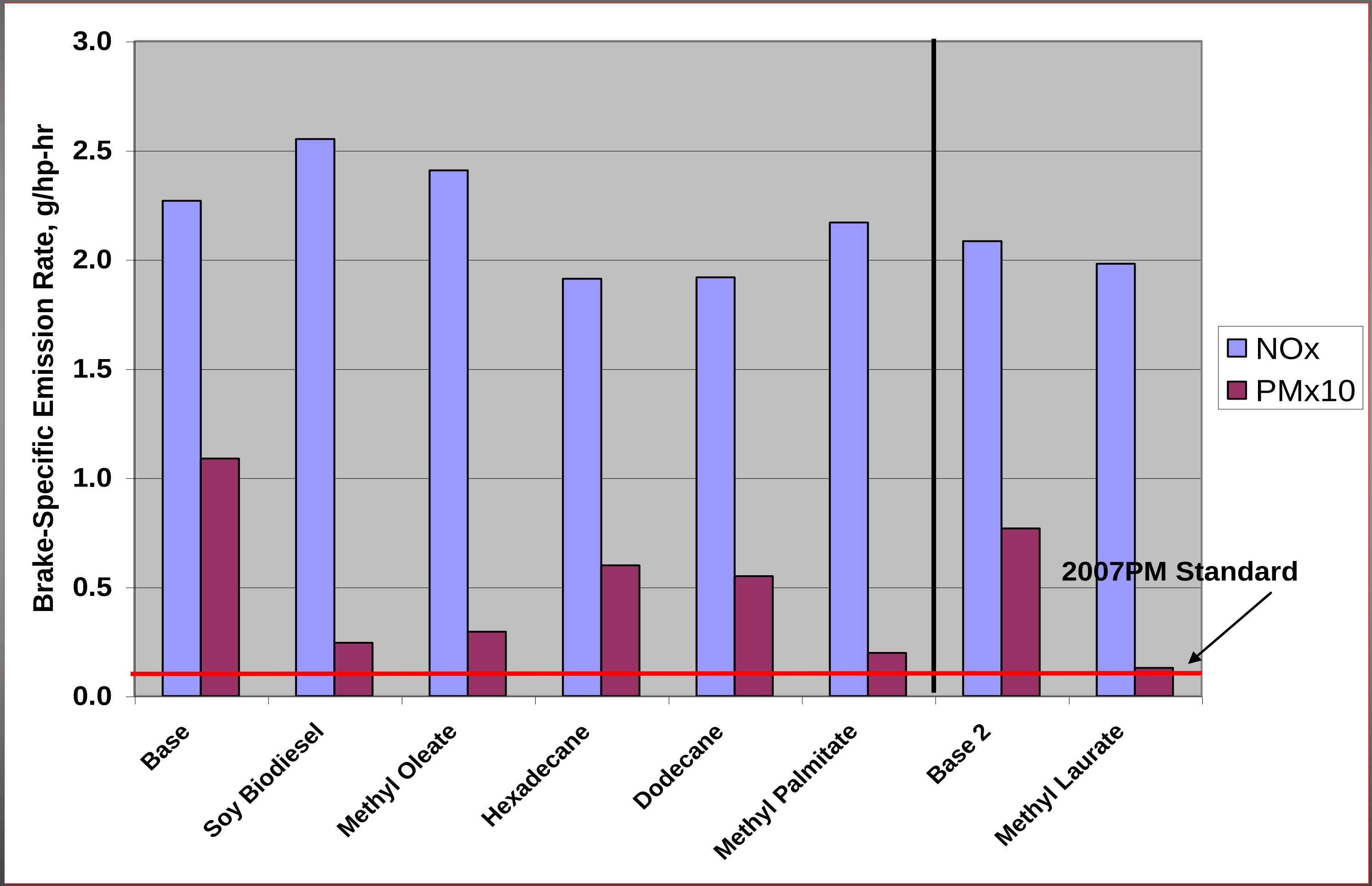
Average effect of biodiesel and B20 vs. petrodiesel on regulated emissions

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



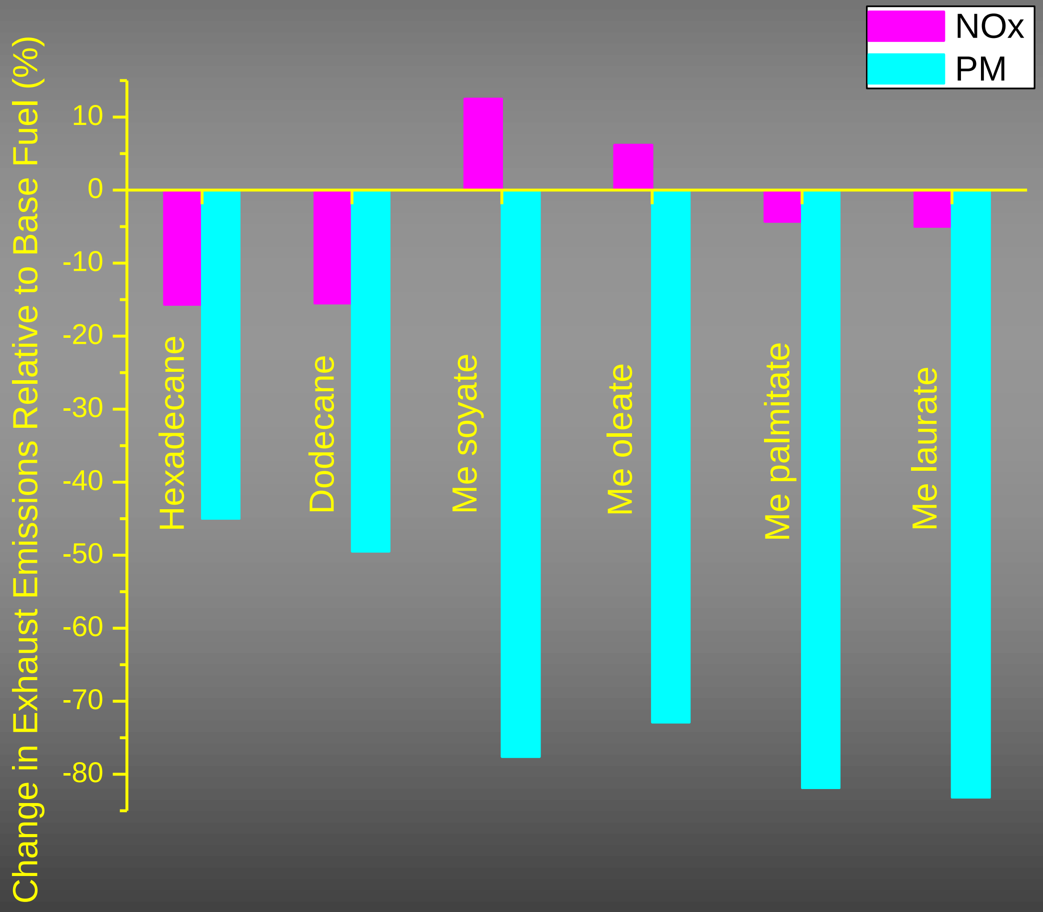


NO_x and PM Exhaust Emissions of Petrodiesel, Biodiesel, Their Components

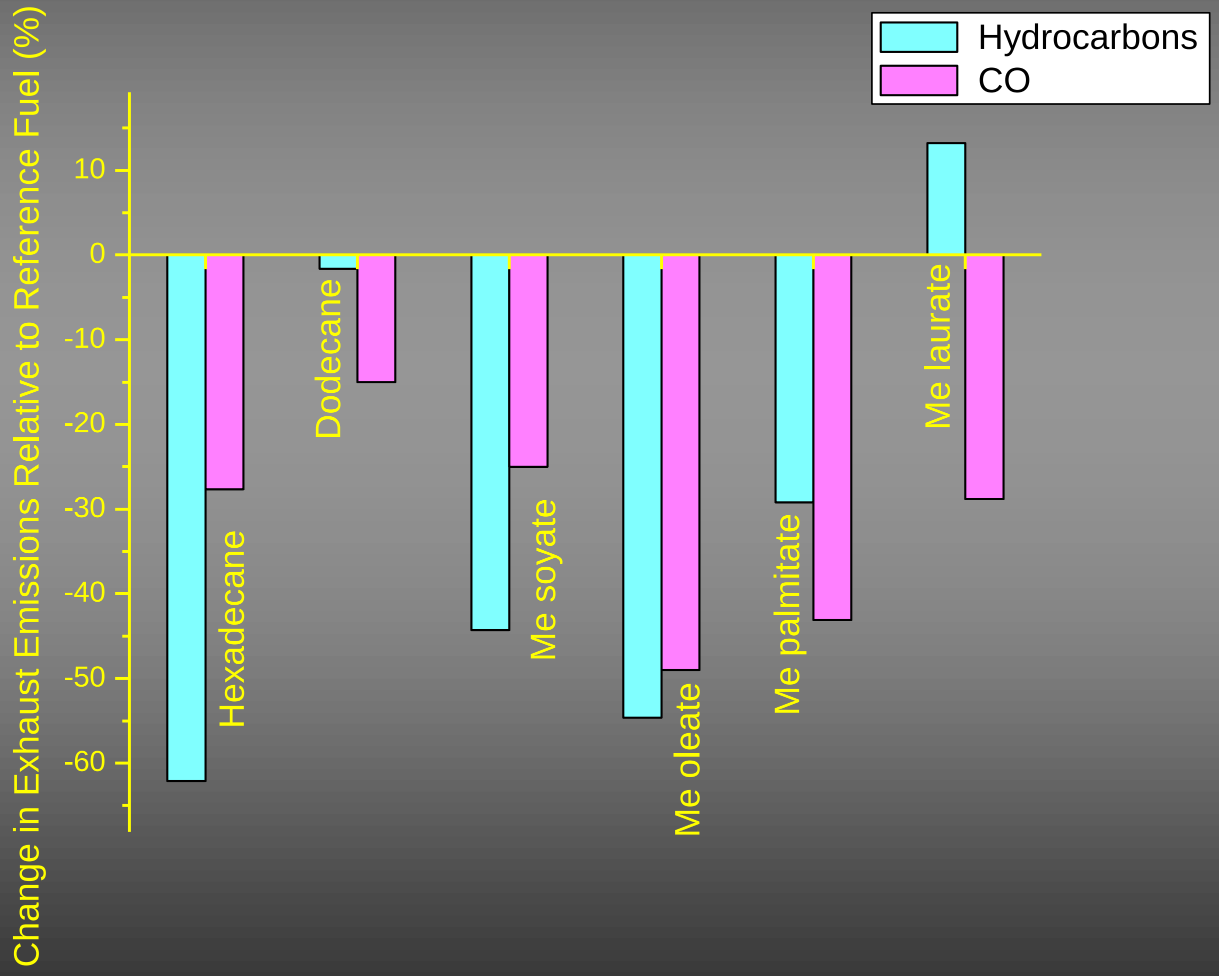


G. Knothe, C.A Sharp, T.W. Ryan III, *Energy & Fuels* 20, 403-408 (2006).

Change in NO_x and PM vs. petrodiesel



Change in HC and CO vs. petrodiesel



Effect of Structure on NO_x / PM

NO_x increases with (McCormick *et al*. 2001)

- Unsaturation
- Decreasing chain length increase NO_x
- PM emissions similar if cetane number > 45, density < 0.89.

Present work:

- Saturated esters NO_x neutral or slight NO_x decrease *vs*. base petrodiesel.
- Change to previous results: Little NO_x /PM dependence on chain length.

R.L. McCormick, M.S. Graboski, T.L. Alleman, A.M. Herring; *Environ. Sci. Technol.* 35, 1742-1747 (2001).

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

Lubricity

Neat biodiesel has excellent lubricity as do neat methyl esters.
Not included in biodiesel standards.

Low-level blends (~ 2% biodiesel in petrodiesel):

- Lubricity imparted to (ultra-)low sulfur petrodiesel fuels
- Marginal cost impact.

Influence of "contaminants" (minor components):

- Neat form: Better lubricity than methyl esters.
- Disproportionately affect lubricity of low-level blends.
- Effect of glycerol limited (poor solubility in petrodiesel).

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

Technical Problems with Biodiesel

- Cold flow
- Oxidative stability
- NO_x exhaust emissions
  - May fade with time due to new exhaust emissions control technologies.
- Other fuel quality issues:
  - Minor components influencing fuel properties.

Property trade-off

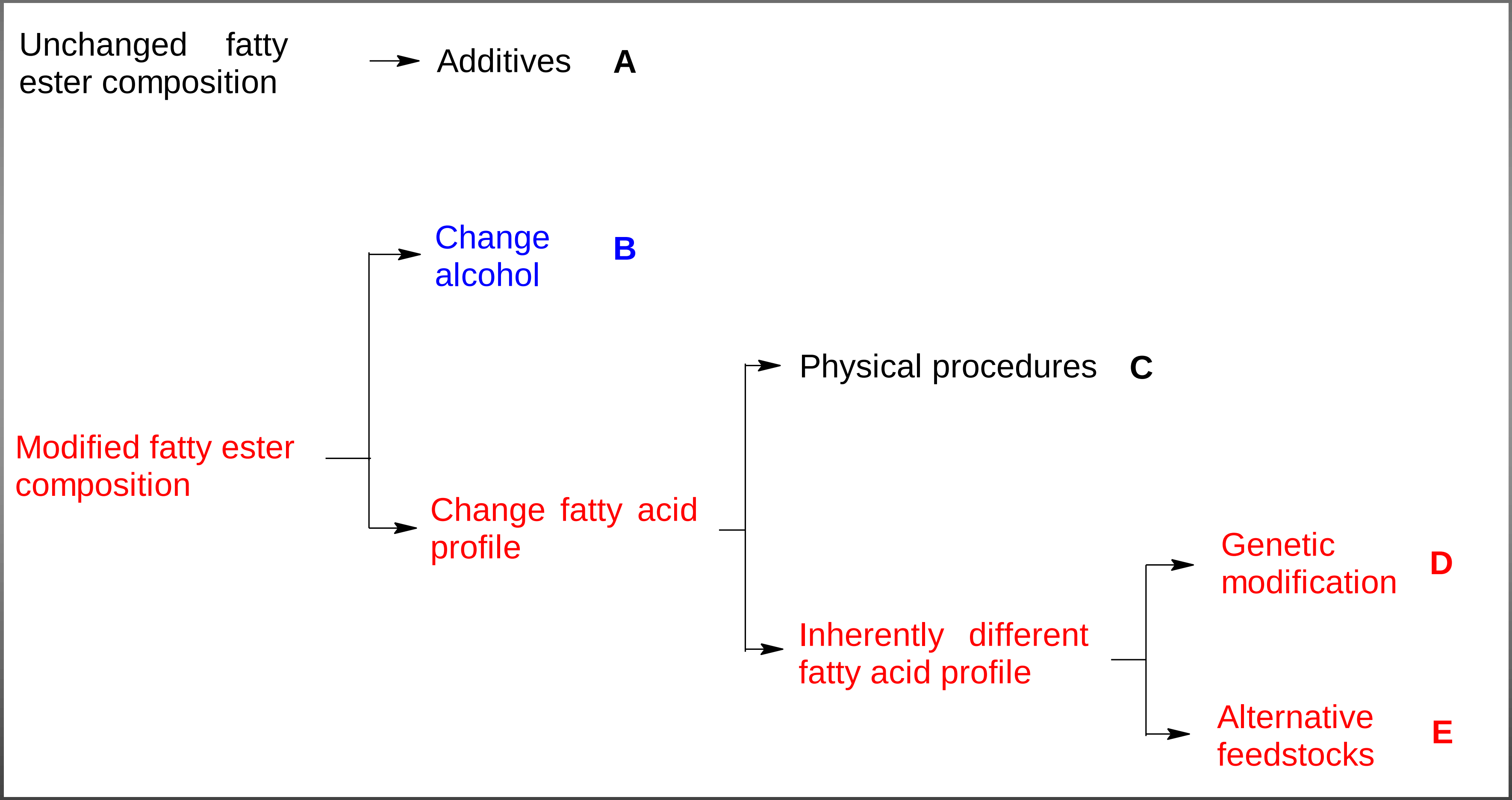
Increasing chain length:

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

Increasing unsaturation:

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

Five Approaches to Improving Biodiesel Fuel Properties



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

Properties to Consider

Two types of specifications in biodiesel standards (ASTM D6751; EN 14214):

Properties inherent to fatty esters

- Cetane number
- Cold flow
- Viscosity
- Oxidative stability

(• Feedstock restrictions: Iodine value, viscosity,specific esters in EN 14214)

Parameters related to production, storage, etc.

- Acid value
- Free and total glycerol
- Na, K, Mg, Ca, P, S
- Water and sediment, sulfated ash, carbon residue

Not in standards: Exhaust emissions, lubricity

Minor Components in Biodiesel

- Mono-, di-, and triacylglycerols
- Alcohol
- Glycerol
- Free fatty acids
- Na, K, Ca, Mg, P, (S)
- Sterol glucosides
- Cold flow problems, stability problems, corrosion, catalyst poisons.

Additives, physical procedures

Additives

- Cold flow improvers

  Do not affect cloud point
- Antioxidants

  Oxidation delayers

Physical procedures

- Winterization for removing saturates to improve cold flow

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.

Fatty Acid Profile: Something "Better" Than Methyl Oleate?

Consider:

- Positional Isomers
  - No major advantages compared to methyl oleate
- Geometric Isomers (*cis*/*trans*)
  - Higher melting points, viscosity of *trans*
- Hydroxylated Chains
  - High viscosity, low cetane number, low oxidative stability
- Shorter Saturated Chains
- Shorter Unsaturated Chains

Shorter-Chain Saturates

	M.P. (° C)	Cetane number	Kin. Visc. (40° C; mm^2/s)	Heat of comb. (kJ/kg)
Methyl octanoate	-37.3	39.7	1.20	34907
Ethyl octanoate	-44.5	42.2	1.32	
Methyl decanoate	-13.1	51.6	1.71	36674
Ethyl decanoate	-19.8	54.5	1.87	
Methyl laurate	4.6	66.7	2.43	37968

High oxidative stability: All > 24 h.

Extrapolation of exhaust emissions for C10 esters:

NOx likely slightly reduced (ca. -5%); PM significantly reduced (80-85%); CO reduced; HC increased

Shorter-Chain Saturates: Cuphea Methyl Esters

Fatty Acid Profile of Cuphea PSR 23 (*C. Viscosissima* × *C. Lanceolata*):

Fatty acid	*Cuphea PSR 23*	Jatropha	Palm	Rapeseed	Soybean	Sunflower
C8:0	0.3					
C10:0	64.7					
C12:0	3.0					
C14:0	4.5					
C16:0	7.0	14.5	44.1	3.6	11	6.4
C18:0	0.9	7.5	4.4	1.5	4	4.5
C18:1	12.2	34-45	39.0	61.6	23.4	24.9
C18:2	6.7	29-44	10.6	21.7	53.2	63.8
C18:3		< 0.5	0.3	9.6	7.8	-

Shorter-Chain Saturates: Cuphea Methyl Esters

Properties of cuphea PSR23 methyl esters:

Cetane number:	55-56
Kinematic viscosity (40° C):	2.38-2.40 mm^2/s
Oxidative stability:	3.1 – 3.5 h
Cloud point:	-9 to -10° C

G. Knothe, S.C. Cermak, R.L. Evangelista; *Energy & Fuels*, 23, 1743-1747 (2009).

Shorter-Chain Monounsaturates

Methyl palmitoleate (C16:1)

- Melting point: -34° C
- Cetane number: 51-56 (ASTM D6890)
- Kinematic viscosity (40° C): 3.67 mm^2/s
- Oxidative stability: 2.11 h
- Extrapolation of exhaust emissions: Effect likely similar to methyl oleate (slight chain-length effect)

Methyl myristoleate (C14:1)

- Melting point: -52° C
- Kinematic viscosity (40° C): 2.73 mm^2/s

Major advantage compared to methyl oleate:

- Improved cold flow, lower kinematic viscosity

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

Shorter-Chain Monounsaturates: An Example

Macadamia nut oil methyl esters:

Two examples:

- 16 and 20 % C16:1;
- 59 and 55% C18:1 Δ9; 4% C18:1 Δ11.

- Cetane number: 57-59
- Oxidative stability: 2 h
- Kinematic Viscosity: 4.5 mm^2/s
- Cloud Point: 7.0 / 4.5 ° C

  but: C16:0 ≈8.5%; C18:0 ≈3.5%; C20:0 ≈ 2.5%; C22:0 ≈ 0.8%.

G. Knothe; *Energy & Fuels* 24, 2098–2103 (2010).

Biodiesel from Algae

- Claimed high production potential
- Avoids food vs. fuel issue
- Problems with growth and harvesting of algae, oil extraction.
- Little to no technical information on biodiesel derived from algal oils.
  - Potential properties need to be estimated from fatty acid profiles.

Biodiesel from Algae: Fatty Acid Profiles

- Many profiles contain high amounts of saturated and polyunsaturated fatty acid chains
- Palmitic acid most common fatty acid (m.p. of methyl ester 28.5° C) in algal oils (and palm oil!)
- Many biodiesel fuels from algae likely possess poor cold flow and poor oxidative stability
- Trade-off likely missing due to relatively low amounts of monounsaturated fatty acid chains
- Some exceptions

Biodiesel: Overview

- Renewable fuel of domestic origin
- Technically competitive and miscible with petrodiesel
- Compatible with the existing fuel distribution infrastructure
- Environmental benefits
  - Biodegradability
  - Most regulated exhaust emissions reduced except NOx (new emissions control technologies lead to reduction lessening of this problem).

Biodiesel: Overview

- Safer handling (higher flash point) than petrodiesel
- Inherent lubricity
- No / low sulfur; no aromatics
- Feedstock availability and costs problematic
- Low-temperature properties problematic
- Oxidative stability varies
- Positive energy balance (up to > 4:1)

Renewable Diesel: Overview

- Similar in composition and properties to (ultra-low sulfur) petrodiesel.
  → Easier acceptance by engine manufacturers.

`
- No / low sulfur
- No / low aromatics
- "Lighter" form: Aviation fuel
- Higher oxidative stability
- Cold flow varies

Renewable Diesel: Overview

- Regulated exhaust emissions reduced compared to "regular" petrodiesel
- Feedstock availability and costs problematic
- Low lubricity
- Energy use / energy balance?
  - Likely less favorable than biodiesel
- Some other technical issues unknown

Biodiesel vs. Renewable Diesel: Mass (and Energy) Balance

Biodiesel - Methyl oleate from triolein:

$C_{57}H_{104}O_6 + 3\ CH_3OH \rightarrow 3\ C_{19}H_{36}O_2 + C_3H_8O_3$

885.45 3 x 296.495 =889.458 = 100.5% mass

≈ 40000 kJ/kg x 1.005 = 40200 kJ

39547 kJ/L

Renewable Diesel - Heptadecane from triolein:

$C_{57}H_{104}O_6 + 6\ H_2 \rightarrow 3\ C_{17}H_{36} + 3\ CO_2 + C_3H_8$

885.453 3 x 240.475 =721.425 = 81.5% mass

≈ 47500 kJ/kg x 0.815 = 38305 kJ

41310 kJ / L

Glycerol and propane not accounted for here.

Biodiesel / Renewable Diesel: An Evaluation

Use each fuel where most appropriate for its properties

- Biodiesel for ground applications?
  - Utilize environmental and other benefits: Reduced exhaust emissions, biodegradability, safer handling
- Renewable diesel (in "lighter" form) for aviation applications due to cold flow?
  - Energy balance may be of less interest here: "Sacrifice" some other energy source(s) in order to have aviation fuel available?
  - No other (realistic) alternative jet fuel.

Biodiesel / Renewable Diesel: An Evaluation

- Consider limited amount of feedstock available.
  - Feedstocks with high yield not (yet) available in sufficient quantities (algae).
  - Fuel property issues.

- Co-products: Renewable glycerol is preferable

- Complex issue: Advantages and disadvantages to both approaches.

Biodiesel with Improved Properties

- Liquid biofuels will be needed, including from triacylglycerol feedstocks

- Biodiesel with improved properties needed to take advantage of its benefits
  - Legislative and regulatory incentives may/do not suffice if properties do not meet market demands

- Feedstocks with high supply potential (algae!) will need to address the issue of fuel properties.

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).