Biodiesel Cost Optimizer ®
Least Cost Biodiesel Composition Calculation

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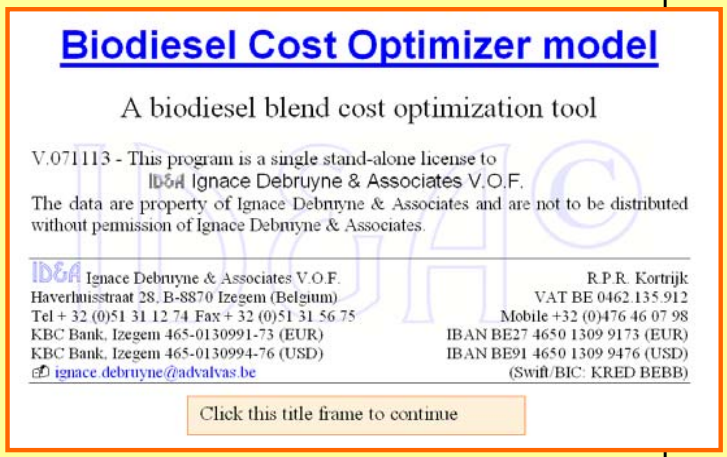

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Standards:
Raw material or Process (1)

	ASTM D-6751-07a	EN 14214:2003	Units
Application	FAMAE	FAME	
Density at 15°C	-	0.86 -0.90	g/cm³
Viscos. 40°C	1.9-6.0	3.5-5.0	mm²/sec.
Distillat.Temperature, AET, 95%	90% @ 360°C	-	°C
Flash Point	>130 (150 av.) or methanol <0.20 %mass	>120	°C
Flash Point (closed cup)	>93	-	°C
CFPP	-	*country specific	°C
Pour point	-	-	°C
Cloud point	report customer	-	°C

Raw material dependent
Process dependent

Standards:

Raw material or Process (2)

	ASTM D-6751-07a	EN 14214:2003	Units
Application	FAMAE	FAME	
Sulfur	<0.0015 (S15), <0.05 (S500)	<10 mg/kg	% mass
CCR 100%	-	-	% mass
10% dist. resid.	-	<0.3	% mass
Sulfated ash	<0.02	<0.02	% mass
(Oxid) Ash	-	-	% mass
Water mg/kg	<0.050% vol. (water & sediment)	<500	mg/kg
Total contam. mg/kg	-	<24	mg/kg
Cu-Corros. 3h/50°C	<No.3	1	
Oxidation stability hrs;110°C	3 hours min	6 hours min	h
Cetane No.	>47	>51	
Neutral. No. (Acid Value)	<0.50	<0.50	mg KOH/g

Raw material dependent
Process dependent

Standards:

Raw material or Process (3)

	ASTM D-6751-07a	EN 14214:2003	Units
Application	FAMAE	FAME	
Methanol	<0.20 or Flash Point 130 min	<0.20	% mass
Ester content	-	>96.5	% mass
Monoglyceride	-	<0.8	% mass
Diglyceride	-	<0.2	% mass
Triglyceride	-	<0.2	% mass
Free glycerol	<0.020	<0.02	% mass
Total glycerol	<0.240	<0.25	% mass
Iodine No.	-	<120	
Linolenic acid ME	-	<12	% mass
C18:3 and high. unsat.acids	-	-	% mass
C(x:4) & greater unsaturated esters	-	<1	% mass
Phosphor	<0.001% mass	<10	mg/kg
Ramsbottom carbon residue	<0.050	-	% mass
Carbon residue	<0.050% by mass	-	
Gp I metals (Na,K) mg/kg	<5	<5	mg/kg
Gp II metals (Ca,Mg) mg/kg	<5	<5	mg/kg
Alkalinity mg/kg	-	-	mg/kg

Raw material dependent
Process dependent

Standards (Summary)

- Some Specifications are exclusively related to the Process, incl. Downstream or Upstream Treatment:
  - Presence of contaminants or residual raw material (fractions)
- Other Specifications are Primarily Determined by the Raw Material Choice
  - Density, Viscosity, Cold Flow properties
  - Sulfur, Phoshorus, FAC, and Ester content
  - Iodine Value, Oxidation Stability, Cetane Number
  - Heat of Combustion, Emissions

Biodiesel Fuel Blend Modeling

Calculation of

- Cetane Number
- Density
- Viscosity
- Combustion energy

Estimates for

- CFPP = Cold flow behavior
- OSI = Oxidation Stability

Always at the lowest cost

Critical Aspects

- Lower energy content: higher consumption
- Lower oxidation stability
- Higher viscosity at lower temperature
- Risk of crystallization and filter plugging

Why are vegetable oil derivatives suitable as diesel fuel?

- Conventional diesel fuel
  - Boiling range: 180-340°C
  - Composition: n-alkanes, cycloalkanes, alkylbenzenes, polyaromatic compounds
  - Quality: Cetane Number (CN) range 40-100
  - **The Cetane Number indicates which oils could be suitable as alternative diesel**

Cetane Number (CN) is based on a linear set of blends of cetane in α-methyl naphtalene

Cetane or hexadecane ($C_{16}H_{34}$ = fast ignition)	CN 100
α-Methyl naphtalene ($C_{11}H_{10}$ = ignition delay)	CN 0

Iodine Value calculation

Methyl ester of the following acids	Percentage % m/m	Factor	Contribution
Myristic C14:0	0,3	0	0
Palmitic C16:0	4,0	0	0
Palmitoleic C16:1	1,1	0,950	1,0
Stearic C18:0	2,0	0	0
Oleic C18:1	60,5	0,860	52,0
Linoleic C18:2	19,8	1,732	34,3
Linolenic C18:3	9,4	2,616	24,6
Eicosanoic C20:0	0,4	0	0
Eicosenoic C20:1	0,7	0,785	0,6
Docosanoic C22:0	0,7	0	0
Docosenoic C22:1	1,1	0,723	0,8
		Calculated Iodine Value	113,3

Based on AOCS Cd 1c-85; FAME ≈ TAG

Oxidation stability modeling

- FAME oxidation stability is directly linked to origin of raw materials, i.e. FAC and presence of natural antioxidants
  - PUFA FAME have a much lower oxidation stability than MUFA or SAFA FAME
  - Distilled FAME = low oxidation stability, since all natural antioxidants are removed
- Problems:
  - Oxidation is not a linear reaction
  - Natural [or added] antioxidants have limited capacity

How to predict Oxidative Stability?

OCL VOL 3 N° 5 SEPTEMBRE/OCTOBRE 1996

Interpreting the oil stability index*

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Abstract: *It has been found that the Oil Stability Index (OSI) as determined with a Rancimat apparatus on blends of triglyceride oils and fats can be expressed as :*

$$R = \frac{\sum_i x_i a_i}{\sum_i x_i v_i}$$

wherein R = *OSI value of the blend*
x_i = *mass fraction of component i*
a_i = *net anti oxidative property of component i*
v_i = *rate of oxidation of component i*

v_i oxidation rate = different for saturated, mono-, di- and tri-unsaturated fatty acids

a_i antioxidant factor = different for different raw materials

CFPP Cold Filter Plugging Point

EN14214; only when used as B100

Temperate climates

Property	Unit	Limits						Test method [a]
		Grade A	Grade B	Grade C	Grade D	Grade E	Grade F	
CFPP	°C, max.	+5	0	-5	-10	-15	-20	EN 116

[a] See also 5.5.1.

Arctic climates

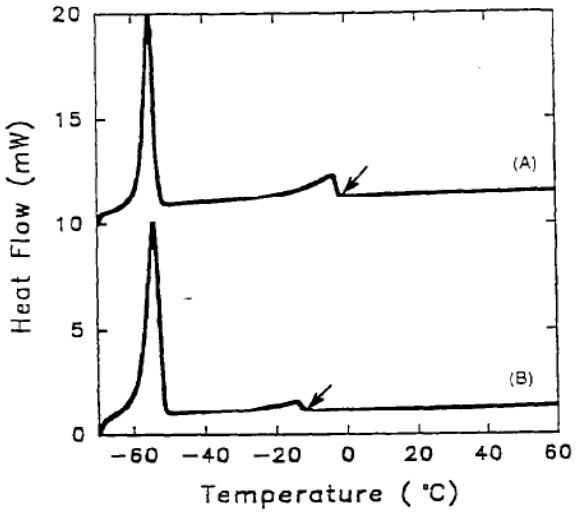
Property	Units	Limits					Test method [a]
		class 0	class 1	class 2	class 3	class 4	
CFPP	°C, max.	-20	-26	-32	-38	-44	EN 116

[a] See also 5.5.1.

The market evolves to two types of B100 Biodiesel to be used in (B2-B30) blends with fossil diesel having the required CFPP after additivation

- **B100 for blends with CFPP = 0°C in Summer**
- **B100 for blends with CFPP = -10°C for Winter**

How much saturates are acceptable to prevent crystallization?



LEFT: SME Winterization on lab scale in hexane to remove SAFA methyl esters [is not used in daily practice because of the poor yield]

BELOW: Winterization in hexane shows that around 10% SAFA from SME is close to the acceptable limit for stability at –20°C

Source: Reducing the Crystallization Temperature of Biodiesel by Winterizing Methyl Soyate Inmok Lee, Lawrence A. Johnson, and Earl C. Hammond, IAOCS. Vol. 73. no. 5 (1996)

TABLE 6
Fatty Acid Compositions of Fractions from Methyl Esters of Normal Soy Oil Winterized in Hexane

Winterization step	Fraction	Temperature (°C) of winterization	Fatty acid (%) 16:0	18:0	18:1	18:2	18:3	Saturates
	Unfractionated		10.5	4.1	23.0	54.0	7.6	14.6
1	Liquid	−21.5	8.5	2.7	24.5	56.3	8.0	11.2
2	Liquid	−25.0	5.8	1.6	25.5	58.8	8.4	7.4
3	Liquid	−28.4	4.8	1.2	25.9	59.6	8.4	6.0
1	Crystals	−21.5	31.8	14.8	15.7	33.2	4.5	46.6
2	Crystals	−25.0	30.3	11.9	16.5	36.2	5.1	42.2
3	Crystals	−28.4	25.0	8.1	18.8	42.2	6.0	33.1
LSD[a]			0.2	0.1				0.2

[a]Least significant difference at $P < 0.05$.

Crystallization Modeling Issues

- Crystallization is a thermodynamic process driven by basic physical characteristics of FAME present
- Nucleation onset is very difficult to predict
- Presence of high melting minor components can severely affect crystallization onset and kinetics
  - Saturated MG
  - Sterol Glycosides (SG)

  ➔ Haze formation
  - Combination of high melting FAME, Sterol Glucosides (SG), bound glycerine, and free sterols

Possible Strategies:

1. **Apply a pragmatic approach: e.g. SAFA+TFA limit**
2. **Fine-tuning possible for specific blend ranges using multivariate model predicting CFPP based on the FAME composition**

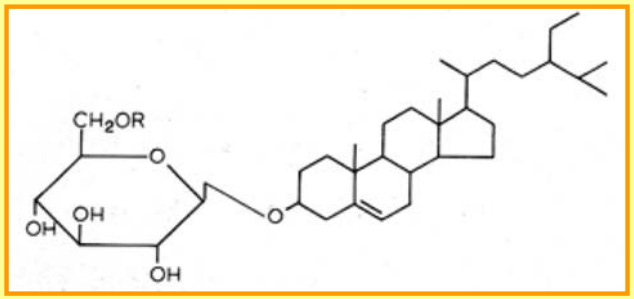
The Effect of Minor Components can at best be Studied, not Predicted

TABLE 1
Combinations of components added to distilled soy biodiesel vs. cloud points and filter times obtained [a]

Components added, ppm				Responses	
MG	SG	Soap	Water	CP, °C	Filter time, s
0	40	0	500	1.4	1022
10000	0	40	500	3.6	107
10000	40	20	0	2.1	904
0	0	0	500	0.6	83
10000	20	40	0	2.4	868
0	40	40	0	0.3	1412
0	0	40	0	1.6	488
10000	40	40	500	3.9	3562
5000	40	0	0	0.3	440
10000	0	0	0	1.8	97
10000	20	0	500	2.3	2139
0	20	0	0	0.4	87
10000	40	0	250	2.2	895
5000	0	20	250	1.4	201
0	20	40	500	0.4	1531
5000	20	20	250	0.5	446
5000	20	20	250	0.6	362
5000	20	20	250	0.5	394
7500	10	10	125	1.4	103
2500	30	10	250	0.7	320
7500	30	30	375	2.3	1207
5000	40	40	500	1.3	2431
0	40	0	250	0.8	982
0	0	0	500	1.4	85
10000	20	40	0	2.3	609
0	40	40	0	0.4	1265
0	0	40	0	0.6	558
0	20	40	500	0.5	1497
10000	0	40	500	3.6	105
10000	40	20	0	2.3	889

[a]CP = cloud point; MG = monoglycerides; SG = sterol glucosides.

- **Saturated Monoglycerides** (range 0-1%) have melting point at 78°C
- **Sterol glycosides** (range: 0-40 ppm) formed during alkaline transesterification of Soybean Oil or Palm Oil with Methanol have very ***high melting point*** at 300-310°C (R = H, CH_3) and ***low solubility***



- **Soaps** (range: 0-40 ppm)
- **Water** (range: 0-500 ppm)
- **Acylated Sterol glycosides** (range: up to 3000 ppm) have high melting point (close to 200°C) but also high solubility

Source: Biorenewable Resources N°4
Inform supplement Sept. 2007

Blend calculation: some background data

Fatty Acid	Fatty acid	Mol. wt. FAME	m.p. (°C)	b.p. (°C)	mbar b.p.	Cetane N°.	purity (CN)	Cetane N° (IQT)	Kinematic viscosity at 40°C (mm^2/s)	OSI 70°C	OSI 90°C	ME factor	Heat of Combustion (kg-cal/mole)
8:00	caprylic	158.24	-	193		**33.6**	98.6					0.000	**1313**
10:00	capric	186.30	-	224		**47.7**	98.0		**1.72**			0.000	**1625**
12:00	lauric	214.35	5	266	766	**61.4**	99.1		**2.43**			0.000	**1940**
14:00	myristic	242.41	18.5	295	751	**66.2**	96.5		**3.30**			0.000	**2254**
14:1w5									**2.73**			*1.066*	*2230*
16:00	palmitic	270.46	30.5	415-8	747	**74.5**	93.6	**85.9**	**4.38**			0.000	**2550**
16:1w7	palmitoleic					**45.0**		**51.0**	**3.67**	***90.0***	**22.1**	**0.950**	*2535*
18:00	stearic	298.51	39.1	442-3	747	**86.9**	92.1	**101.0**	**5.85**			0.000	**2859**
18:1w9	oleic	296.49	-20	218.5	20	***55.0***		**59.3**	**4.51**	**55.6**	**10.7**	**0.860**	**2828**
18:2w6	linoleic	294.48	-35	215	20	***36.0***		**38.2**	**3.65**	**4.6**	**1.2**	**1.732**	**2794**
18:3w3	linolenic	292.46	-57	109	0.018	***28.0***			**3.14**	**5.5**	***0.5***	**2.616**	**2750**
20:00	arachidic								***7.80***			0.000	*3165*
20:1w9	gadoleic	352.60	-	221-5		***82.0***			**5.77**	**57.2**	**13.0**	**0.785**	**3454**
20:2w6												*1.570*	*3150*
20:3w6												*2.355*	*3150*
20:4w6	arachidonic											*3.140*	*3150*
20:3w3												*2.355*	*3150*
22:00	behenic											0.000	*3470*
22:1w9	erucic								**7.33**	**59.5**	**13.9**	**0.723**	*3450*
24:00	lignoceric											0.000	*3775*
22:6w3	DHA											*2.169*	*3450*
24:1w9	nervonic											*0.671*	*3800*
TFA (C18:n)									***5.50***				

Data in italic defined by extrapolation

Biodiesel Cost Optimizer ®

Least Cost Biodiesel Composition Calculation

Biodiesel Cost Optimizer model

A biodiesel blend cost optimization tool

V.071113 - This program is a single stand-alone license to
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Blends of SBO, RSO and PaOil

Prices 20 Sep 2007

		$984	$1040	$828			$/MT	$/MT
	SAFA+TFA	SBO	RSO	PaO	IV	CN		Profit
Winter	7.2	0	101.5	0	116.2	50.3	1056	
	8.0	3.4	97.5	0.7	116.4	50.3	1053	3
	9.0	8.6	90.8	2.2	116.4	50.3	1048	8
	10.0	13.8	84.2	3.8	116.3	50.3	1042	14
	12.0	24.3	70.8	6.8	116.2	50.2	1032	24
	14.0	34.7	57.4	9.9	116.1	50.5	1021	35
	16.0	45.2	43.9	13.1	116.0	50.5	1010	46
Summer	19.0	61.0	23.7	17.7	115.9	50.7	994	62
	22.0	76.9	3.3	22.5	115.7	50.8	978	78
	25.0	72.2	0.0	30.8	109.7	52.1	965	91
	30.0	57.6	0.0	45.9	97.8	54.7	946	110

[4.2 parts SBO + 1 part palm oil] behave as RSO

Price benefit is moderate

Blend calculation (+oxidation stability)

	A	B	C	D	E	F	G	N	O	P
1	Fatty Acid	Fatty acid	Mol. wt. FAME	SBO Soybean	RSO Canola Rapeseed Oil	SFO Sun-flower	Palm oil crude	Recycled Oil "G"	BLEND	EN 14214
24	TFA (C18:n)			0.2	0.2	0.2	0.1	*4.0*	2.1	
25			SUM	99.9	99.9	99.1	99.6	100.0	99.8	
26			C16+18+20 + TFA	14.7	7.5	10.0	49.2	22.9	**15.0**	SAFA+TFA=OK
27			FFA, Polymer content & refinery loss	2.0	1.5	1.5	5.0	5.0	3.3	
28			Measured CN	46.2	50.0	46.6	63.0	*53.0*		
29			Measured IV	134.0	116.0	135.0	53.0	100.0		
30	$/MT		CIF/FOB R'dam (crude)	984	1040	1330	828	700	905	-151 $ per MT biodiesel
31			Antioxidant factor	95.4	57.0	53.6	60.0	*60.0*	58.4	
32			Calculated CN	46.9	50.2	46.2	64.5	53.9	52.0	CN = OK
33			Calculated Kinematic Viscosity	3.99	4.22	3.99	4.40	4.30	4.26	Viscosity=OK
34			Calculated Heat of Combustion	2776	2815	2788	2692	2780	2801	100%
35			Calculated IV	134.2	116.0	134.6	52.1	100.4	108.5	IV = OK
36			O.S.I. (estimate)	5.6	6.3	3.0	19.7	7.1	6.7	OSI = OK
37			BLEND		53.4			49.9	103.3	vs.RME
38	price factor (0-100)	C16+18+20 + TFA limit	This cell is minimized	SBO Soybean	RSO Canola Rapeseed Oil	SFO Sun-flower	Palm oil crude	Recycled Oil "G"	BLEND	Solve
39	100%	15.0	-139.4		1	1	1	1		
40				This column is maximized		Light Blue	open for INPUT CHANGE			
41						Green	SOLVER values for CN, Kinematic viscosity,			MT +TFA (
42						Orange	set on ZERO before using SOLVER			
43						INPUT: Copy Raw Material columns directly from "Raw Mateiral Input Data" worksheet, or i				
44										
45	V. 071004 IDB				52.6			47.4		

Blend calculation (+oxidation stability)

	A	B	C	D	E	F	G	N	O	P
1	Fatty Acid	Fatty acid	Mol. wt. FAME	SBO Soybean	RSO Canola Rapeseed Oil	SFO Sun-flower	Palm oil crude	Recycled Oil "G"	BLEND	EN 14214
24	TFA (C18:n)			0.2	0.2	0.2	0.1	*4.0*	0.9	
25			SUM	99.9	99.9	99.1	99.6	100.0	99.7	
26			C16+18+20 + TFA	14.7	7.5	10.0	49.2	22.9	**15.0**	SAFA+TFA=OK
27			FFA, Polymer content & refinery loss	2.0	1.5	1.5	5.0	5.0	2.6	
28			Measured CN	46.2	50.0	46.6	63.0	*53.0*		
29			Measured IV	134.0	116.0	135.0	53.0	~~108.9~~		
30	$/MT		CIF/FOB R'dam (crude)	984	1040	1330	828	700	976	-80 $ per MT biodiesel
31			Antioxidant factor	95.4	57.0	53.6	60.0	*30.0*	52.1	
32			Calculated CN	46.9	50.2	46.2	64.5	53.9	52.5	CN = OK
33			Calculated Kinematic Viscosity	3.99	4.22	3.99	4.40	4.30	4.30	Viscosity=OK
34			Calculated Heat of Combustion	2776	2815	2788	2692	2780	2799	100%
35			Calculated IV	134.2	116.0	134.6	52.1	100.4	106.2	IV = OK
36			O.S.I. (estimate)	5.6	~~6.3~~	3.0	~~19.7~~	3.5	6.3	OSI = OK
37			BLEND	0.0	71.7		11.1	19.9	102.6	vs.RME
38	price factor (0-100)	C16+18+20 + TFA limit	This cell is minimized	SBO Soybean	RSO Canola Rapeseed Oil	SFO Sun-flower	Palm oil crude	Recycled Oil "G"	BLEND	Solve
39	100%	15.0	-65.8		1	1	1	1		
40				This column is maximized		Light Blue	open for INPUT CHANGE			
41						Green	SOLVER values for CN, Kinematic viscosity,			MT A+TFA (
42						Orange	set on ZERO before using SOLVER			
43						INPUT: Copy Raw Material columns directly from "Raw Mateiral Input Data" worksheet, or ir				
44										
45	V. 071004 IDB				70.6		10.5	18.9		

Biodiesel Cost Optimizer

- Biodiesel based on raw material blends can be much more economic than pure RME or pure SME and still comply with EN14214 or ASTM 6751
- In summer conditions almost any raw material can be used for FAME production
- Using low cost components can generate significant price benefits
- Oxidation stability of the final product will affect raw material choice (OSI can be corrected with antioxidants!)
- In winter, CFPP or SAFA+TFA constraint will limit raw material choice, but B2 or B30 allows plenty of flexibility; special additives can generate required Oxidation and Crystallization stability
- ***Always: lowest cost blend of the day***