Methods to Improve Oxidative Stability of Biodiesel

Bryan R. Moser

Bio-Oils Research Unit, National Center for Agricultural Utilization Research

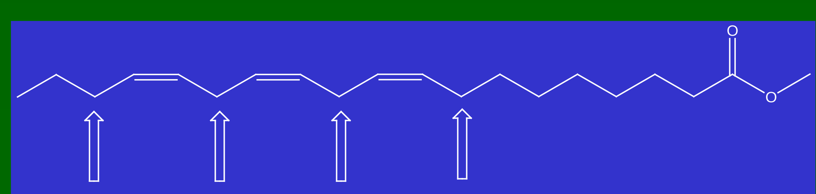
Agricultural Research Service, USDA, 1815 N University St, Peoria IL USA 61604

Bryan.Moser@ars.usda.gov. Tel 1.309.681.6511. Fax 1.309.681.6524.

USDA/ARS NCAUR Improving the Quality of Life

INTRODUCTION

Oxidative stability is one of the most important technical deficiencies of biodiesel versus petrodiesel. Autoxidation of biodiesel primarily occurs at allylic methylene positions found along the hydrocarbon backbone of fatty acid methyl esters:



Allylic positions in methyl linolenate

The more methylene positions a fatty ester contains, the more susceptible it is to oxidative degradation:

FAME	EN 14112 IP, 110 °C, h
18:0	>40
18:1 c9	2.5
18:2 c9, 12	1.0
18:3 c 9, 12, 15	0.2

From: *J Am Oil Chem Soc* 2009, 86, 699-706

Methods to improve oxidative stability of biodiesel include:

1. **Chemical reduction of double bond content**
   - Catalytic partial hydrogenation, e.g.
2. **Physical reduction of double bond content**
   - More stable triglyceride feedstocks, e.g.
3. **Blending**
   - More stable triglyceride feedstocks
   - Petrodiesel
4. **Antioxidants**

The goals of the current study were to explore the impact of each of these methods on oxidative stability of biodiesel.

STANDARDS

Biodiesel	Units	ASTM D6751	EN 14214
Acid value	mg KOH/g	0.50 max	0.50 max
Free glycerol	mass %	0.020 max	0.020 max
Total glycerol	mass %	0.240 max	0.250 max
KV, 40 °C	mm^2/s	1.9-6.0	3.5-5.0
CP	°C	Report	-
CFPP	°C	-	Variable
PP	°C	-	-
Cetane number	-	47 min	51 min
IV	$g\ I_2/100\ g$	-	120 max
IP, 110 °C	**h**	**3.0 min**	**6.0 min**

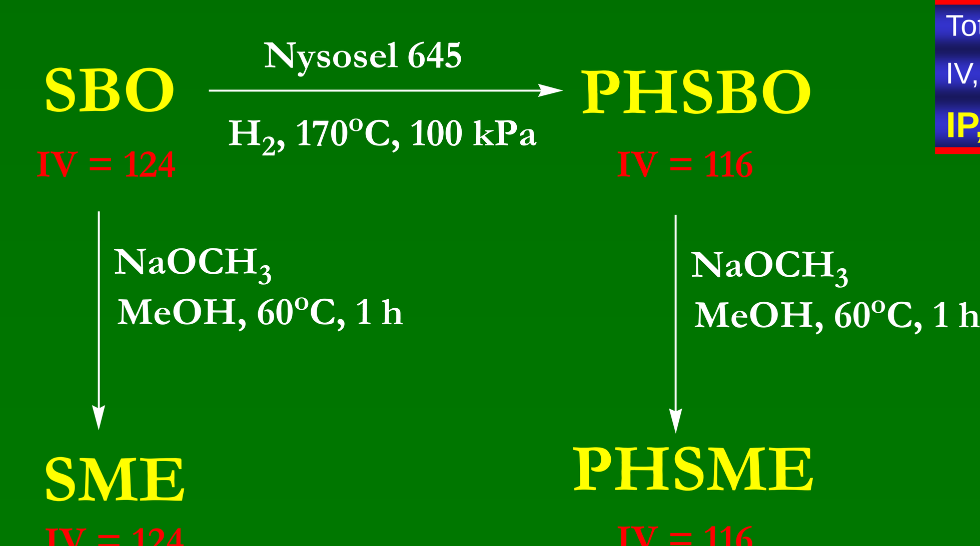
Petrodiesel & Blends	Units	ASTM D975	ASTM D7467	EN 590
Biodiesel	Volume %	0-5	6-20	0-7
Acid value	mg KOH/g	-	0.30 max	-
Sulfur	ppm	15 max	15 max	10 max
Lubricity, 60 °C	µm	520 max	520 max	460 max
KV, 40 °C	mm^2/s	1.9-4.1	1.9-4.1	2.0-4.5
CP	°C	Guidance	Guidance	-
CFPP	°C	Guidance	Guidance	-
PP	°C	-	-	-
Cetane number	-	40 min	40 min	51 min
IP, 110 °C	**h**	**-**	**6.0 min**	**20 min**

Method 1: Chemical Reduction

Soybean oil methyl esters (**SME**) fail the oxidative stability and iodine value (**IV**) specifications of EN 14214 due to the presence of a significant percentage of polyunsaturated fatty acids (**PUFA**; 59.8%):

Area %	SME	PHSME
16:0	10.6	10.3
18:0	5.3	5.1
18:1 c9	23.3	31.7
18:1 t9	0	5.9
18:2 c9, 12	52.6	40.2
18:2 t9, 12	0	1.8
18:3 c9, 12, 15	7.2	3.5
Others	1.0	1.5
Total *trans*-FA	0	7.7
Total PUFA	59.8	44.7

Catalytic partial hydrogenation was therefore explored as a chemical means to reduce double bond content and improve the stability of SME. Soybean oil (**SBO**) with an IV of 124 was hydrogenated to afford partially hydrogenated SBO (**PHSBO**) with a lower IV (116). Both oils were then used to prepare SME and PHSME.



Although the oxidative stability of PHSME (6.2 h) was superior to that of SME (2.3 h), the cold flow properties of PHSME were negatively affected. Introduction of *trans*- constituents (7.7%) upon partial hydrogenation was postulated as the reason for the change in low temperature properties, along with a reduction in polyunsaturated content.

	SME	1:1	PHSME
CP, °C	0	2	3
PP, °C	-2	-1	0
KV, 40 °C, mm^2/s	4.12	4.60	4.93
IP, 110 °C, h	2.3	4.3	6.2

In summary, PHSME:

- Demonstrated that chemical modification can improve oxidative stability, but other properties are affected
- Meets EN 14214 oxidative stability requirement (IP > 6 h)
  - SME was below the minimum limit
- Below EN 14214 IV limit (≤ 120)
  - SME was above maximum limit
- Inferior CP & PP in comparison to SME
- Kinematic viscosity within limits, but higher than SME

Source: *Eur J Lipid Sci Technol* 2007, 109, 17-24
For emissions, see: *Fuel Process Technol* 2009, 90, 1122-1128

Method 2: Physical Reduction

Biodiesel fuels prepared from different feedstocks have different fatty acid compositions. Of course, fatty acid composition strongly influences fuel properties. Therefore, selection of feedstocks with few PUFAs is one method by which oxidative stability can be improved. Furthermore, blending less stable biodiesel fuels with those of higher stability will result in a blend with enhanced resistance to oxidation versus the less stable fuel. Lastly, petrodiesel, which is saturated (or aromatic) and does not contain susceptible allylic methylene positions, is considerably more stable to oxidation than biodiesel. Therefore, biodiesel-petrodiesel blends display enhanced stability versus unblended biodiesel.

Area %	Soybean	Sunflower	Canola	Palm	Meadowfoam	Coriander	Camelina	Cottonseed
16:0	10.5	4.5	4.6	41.9	0.6	5.3	6.8	25.8
18:0	4.1	4.0	2.1	4.6	0.2	3.1	2.7	2.5
18:1 c6						68.5		
18:1 c9	22.5	82.0	64.3	41.2	1.0	7.6	18.6	16.4
18:1 c11	1.6					1.0	1.1	0.8
18:2 c9, 12	53.6	8.0	20.2	10.3	0.9	13.0	19.6	51.5
18:3 c9, 12, 15	7.7	0.2	7.6	0.1			32.6	0.2
20:0		0.3			0.8		1.5	0.3
20:1 c5					64.2			
20:1 c8					0.7			
20:1 c11							12.4	
22:0		1.0			0.2		0.2	0.2
22:1 c13					10.2		2.3	
22:2 c5, 13					18.9			
Others	0	0	1.2	1.9	2.3	1.5	2.2	2.3
Total PUFA	61.3	8.2	27.8	10.4	19.8	13.0	54.3	51.7
IV, $g\ I_2$ 100 g	134	85	110	54	87	89	151	105
IP, 110 °C, h	**5.0**	**6.2**	**6.4**	**10.3**	**66.2**	**14.6**	**2.5**	**5.0**

In summary, oxidative stability of biodiesel can be improved , when practical, by switching to a feedstock with less PUFA. For example, the IP of SME is 5.0 h. If feasible, switching to canola oil methyl esters improves IP to 6.4 h.

Meadowfoam oil methyl esters (**MFME**) have an exceptional IP of 66.2 h due to its unique fatty acid profile. The entire content of PUFAs in MFME does not contain bis-allylic methylene positions, making them less susceptible to oxidation than typical PUFAs.

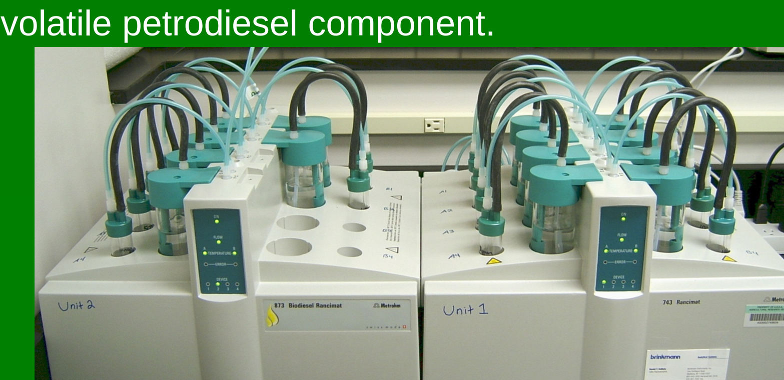
Sources: *Energy & Fuels* 2008, 22, 4301-4306
Energy Environ Sci 2010, 3, 318-327
Biomass Bioenergy 2010, 34, 550-558
Fuel (in preparation)

EN 14112 versus EN 15751

Two oxidative stability test methods utilizing the Rancimat instrument have been developed by the European Committee for Standardization: EN 14112 and EN 15751. Both indirectly measure oxidation by monitoring the change in conductivity of deionized water as volatile oxidative degradation products are transported via air sparge from a vessel containing the sample.

EN 14112: for biodiesel (pictured below)

EN 15751: for biodiesel blends in petrodiesel. The primary difference is that taller sample vessels are required which serve as reflux condensers for the more volatile petrodiesel component.



Method 3: Blending

Biodiesel Blends

Soybean oil methyl esters blended with meadowfoam oil methyl esters:

Blend level	IP (h)	CP (°C)	PP (°C)	KV (mm^2/s)	IV (g/100 g)
0%	5.9	0.1	-2.0	4.05	132
10%	5.8	-0.7	-2.7	4.26	128
20%	6.3	-1.5	-4.0	4.42	123
30%	7.4	-2.4	-5.3	4.60	119
40%	8.3	-3.6	-9.0	4.82	114
50%	9.3	-4.5	-11.7	4.99	110
100%	66.2	-5.8	-10.7	6.15	87

Petrodiesel Blends

Soybean oil methyl ester-petrodiesel blends:

Blend level	IP (h)	CP (°C)	PP (°C)	KV (mm^2/s)	Lubricity (µm)
B0	> 24	-18	-23	2.30	571
B2	> 24	-18	-22	2.31	271
B5	> 24	-16	-22	2.37	198
B10	> 24	-14	-21	2.41	154
B20	17.1	-12	-17	2.54	143

Camelina oil methyl ester-petodiesel blends:

Blend level	IP (h)	CP (°C)	PP (°C)	KV (mm^2/s)	Lubricity (µm)
B0	> 24	-18	-23	2.30	571
B2	> 24	-16	-23	2.33	248
B5	> 24	-14	-23	2.38	147
B10	16.6	-13	-22	2.42	142
B20	8.9	-11	-20	2.58	136

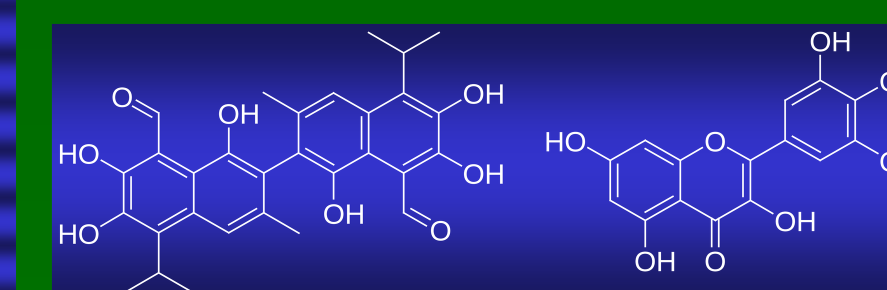
Sources: *Energy & Fuels* 2008, 22, 4301-4306
Energy Environ Sci 2010, 3, 318-327
Bioresource Technol 2010, 101, 646-653
Energy Environ Sci (in press) DOI: 10.1039/C1EE01047F

Method 4: Antioxidants

Synthetic antioxidants such as TBHQ, BHT, BHA and others are known to positively impact oxidative stability of biodiesel. Natural antioxidants, such as the tocopherols, also improve oxidative stability but generally to a lesser extent.

Myricetin is a naturally occurring flavonol found in a variety of foods, including grapes, berries, fruits, vegetables, herbs and other plants. It possesses anti-oxidant behavior, as demonstrated by others previously in sunflower, palm, and canola oils.

Gossypol is a polyphenolic aldehyde possessing antioxidant properties isolated from cottonseed. Because gossypol is toxic, it must be removed from cottonseed oil and meal prior to their uses as in food applications or as animal feed.



Gossypol **Myricetin**

Both myricetin and gossypol were investigated as potential exogenous antioxidants in SME after both 0 and 90 days of storage utilizing the Rancimat method (EN 14112). Below is IP data (110 °C):

Myricetin	SME 0 days	SME 90 days
0 ppm	6.6	4.5
100 ppm	10.1	8.7
500 ppm	14.7	12.7
1000 ppm	15.4	13.1

Gossypol	SME 0 days	SME 90 days
0 ppm	5.5	4.9
250 ppm	7.2	6.6
500 ppm	8.5	7.7

C_f = (IP w/ additive at X d) / (IP w/o additive at X d)

	C_f 0 days	C_f 90 days
Myricetin:		
100 ppm	1.6	1.8
500 ppm	2.2	2.6
1000 ppm	2.3	2.7
Gossypol:		
250 ppm	1.3	1.4
500 ppm	1.5	1.6

In summary:

- Both gossypol and myricetin exhibited antioxidant behavior in SME.
- Myricetin was more effective than gossypol, as indicated by higher comparison factor (C_f) values at similar concentration.

Sources: *Eur J Lipid Sci Technol* 2008, 110, 1167-1174
Eur J Lipid Sci Technol 2010, 112, 802-809
Renewable Energy (submitted for publication)