Impact of North Dakota Growing Location On Canola Biodiesel Quality

US Canola Research Conference
Long Beach CA, Nov 2-3, 2010

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BACKGROUND

- 730,000 acres canola harvested in ND, 2009 (90% US production)
- Canola as a feedstock for biodiesel
  - •high monounsaturated (oleic)
  - •low saturated fat
  - (↑ cold flow benefits associated with ↓ saturated fats)
- Cloud point – Temperature wax crystals appear in solution
  - • predictor of cold flow properties
- Biodiesel quality may deteriorate rapidly in storage
  - • improved storage with ↑ oxidative stability index
- **Concerns:** does growing location and/or canola variety impact biodiesel cold flow properties or oxidative stability?

OBJECTIVES

- Characterize variability in canola biodiesel cloud point and oxidative stability among several ND locations and years.
- Two experiments were conducted:

  Exp. 1 - bulked canola varieties sampled across 2003-2009 were processed and evaluated.

  Exp. 2 - One canola variety, Interstate Hyola 357, was evaluated at two locations over four production years.

MATERIALS

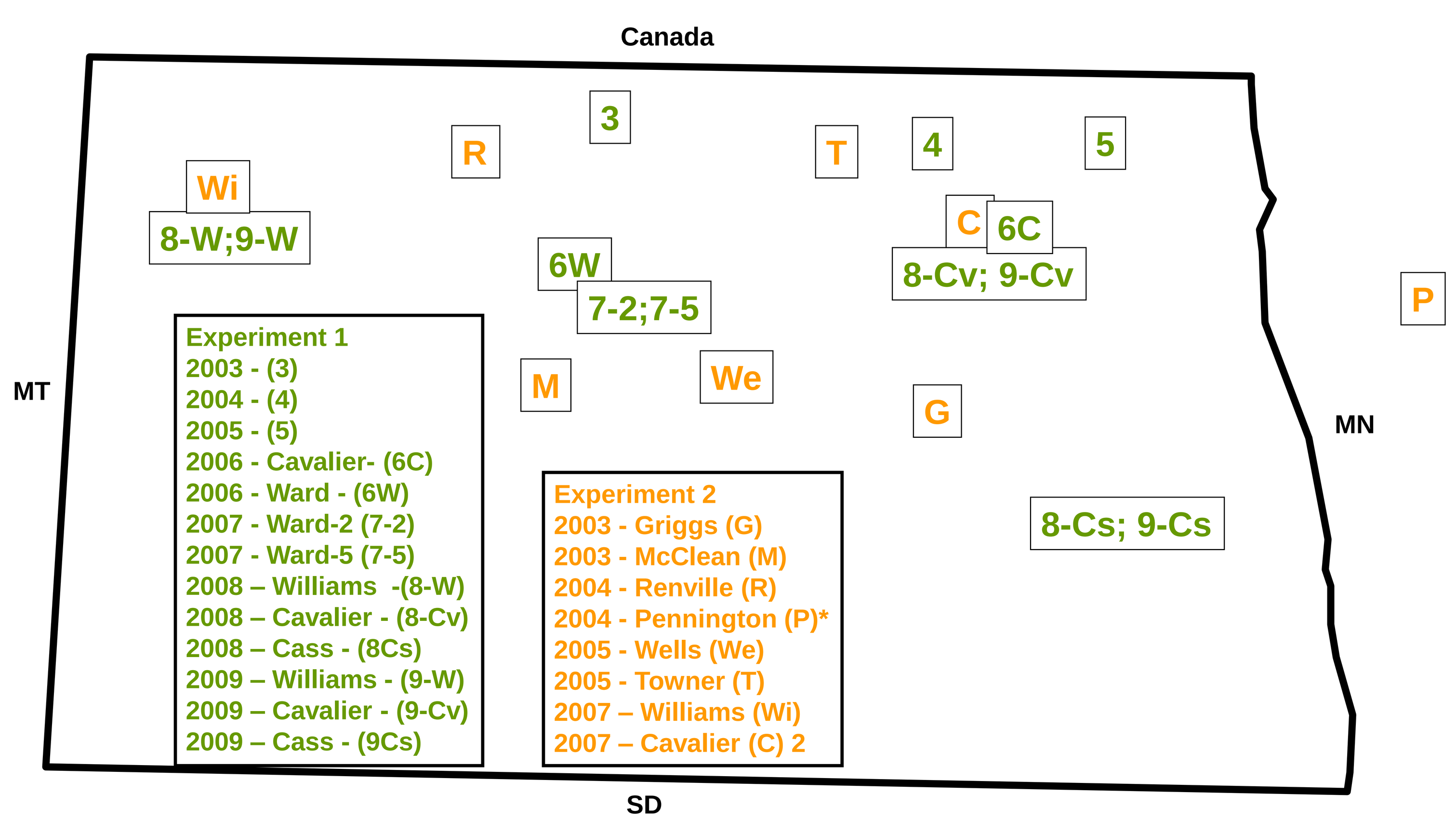

Figure 1. North Dakota canola harvest locations.

Experiment 1:

- Canola varieties were combined from three locations in each of 2003, 2004, and 2005, and analyzed as one bulked sample per year (Fig 1).
- Samples were collected and analyzed separately from two or three locations in 2006, or 2008 and 2009, respectively. In 2007, canola biodiesel was processed from two varieties: Liberty 2663 and InVigor 5550 located in Ward county – (7-2 and 7-5)

Experiment 2:

- Biodiesel was processed from a single variety, Interstate Hyola 357 RR

* P -Pennington county, Minnesota

BIODIESEL PROCESSING AND ANALYSIS

- Seed was cleaned according to USDA-GIPSA methods
- Oil content of intact seed was quantified by NIRS
- Biodiesel was produced from seed via *in situ* alkaline transesterification (TE)
- Seed was coffee ground and flour was dried at 70°C for 3 h or until 1.0% moisture d.b.
- TE was conducted in 500 mL Erlenmeyer flasks, 60°C shaker bath, 200rpm, 6 h
  - • flour equivalent oil wt = 40g
  - • 275:1:1.05 molar ratio of methanol : triacyglyceride : KOH
  - • biodiesel refined with water washing.
  - • biodiesel pooled from duplicated rxn flasks to obtain sufficient volume for analysis
- Fatty acid profiles of canola oil and biodiesel determined by GC according to methods of Haagenson et al. (2010)
- Iodine value (IV) was estimated from the fatty acid composition (AOCS - Cd 1C-85)
- Biodiesel quality (ASTM D6751-09)
  - * kinematic viscosity (40°C)
  - * karl fischer moisture
  - * acid value
  - * total glycerin (SafTest, MP Biomedical)
  - * cloud point
  - * oxidative stability index (Omnion, OSI)
- Experimental design - completely randomized, 3 replicates
- Data were analyzed using ANOVA
- *F*-protected LSD ($P \leq 0.05$) was calculated for mean comparisons

RESULTS

Biodiesel (BD) processing quality

- BD acid number, kinematic viscosity, water, and total glycerin were measured prior to CP and OSI analysis to ensure high quality biodiesel was obtained (Table 1).

Table 1. No Significant differences in process-dependent biodiesel quality factors.

	Acid Number (mg KOH/g)	Kinematic Viscosity (mm^2/s)	Water & Sediment (vol%)	Total Glycerin (wt%)
Experiment 1	0.16	4.6	0.036	0.040
Experiment 2	0.16	4.7	0.035	0.041
ASTM Limits	0.50 max	1.9- 6.0	0.050 max	0.240 max

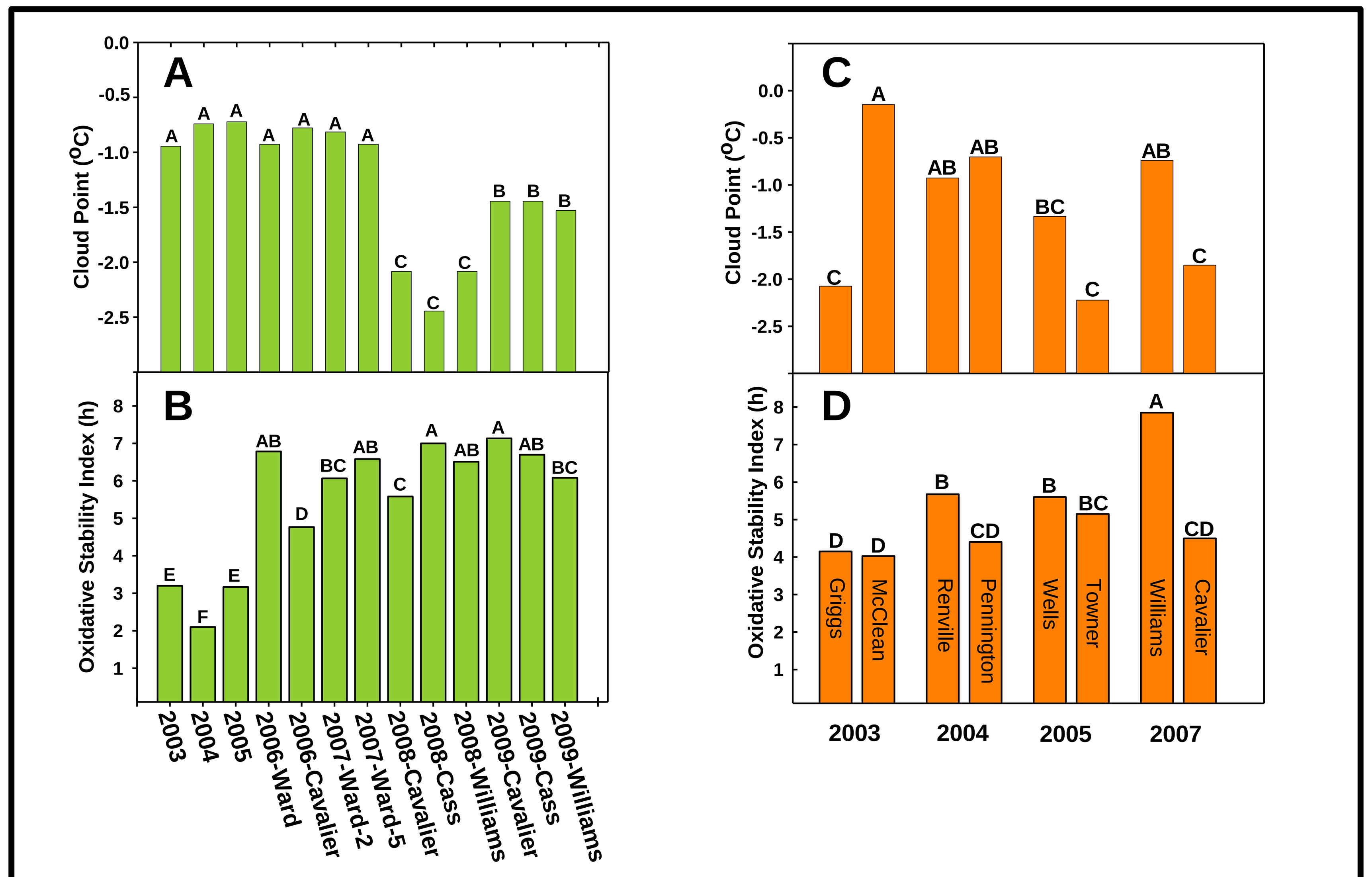

Figure 2. Cloud point and Oxidative Stability from Exp 1 (A, B) and Exp 2 (C, D). n = 3, means followed by the same letter are not significantly different (P<0.05)

Table 2. BD fatty acid composition-mean.

Fatty Acid	wt %
Palmitic (16:0)	5.1
Stearic (18:0)	2.3
Oleic (18:1)	62.5
Linoleic (18:2)	19.1
Linolenic (18:3)	7.6
Arachidic (20:0)	0.6
Gadoleic (20:1)	1.0
Behenic (22:0)	0.3
Lignoceric (24:0)	0.2

Table 3. BD fatty acid saturation.

Exp	Year Location	Biodiesel Saturation	
		Sat	IV
1	2003 – Bulked	8.17	113
	2004 – Bulked	8.41	114
	2005 – Bulked	8.11	114
	2006 – Ward	7.24	115
	2006 – Cavalier	7.25	123
	2007 – Ward – 2	7.71	119
	2007 – Ward – 5	7.07	121
	2008 – Cavalier	7.25	115
	2008 – Cass	7.43	115
	2008 – Williams	7.83	114
	2009 – Cavalier	7.64	117
	2009 – Cass	7.49	115
	2009 – Williams	7.92	115
2	2003 – Griggs	8.17	108
	2003 – McClean	8.41	105
	2004 – Renville	8.11	114
	2004 – Pennington	7.24	114
	2005 – Wells	7.25	118
	2005 – Towner	7.71	111
	2007 – Williams	7.07	106
	2007 – Cavalier	7.25	116

Table 4. Correlation (r) of BD fatty acid saturation and temperature with CP, OSI.

	CP		OSI	
	r	p value	r	p value
Sat[a]	-0.41	0.27	0.65	0.06
IV	0.21	0.58	-0.53	0.14
°C[b]	0.29	0.45	-0.36	0.35

[a] - Weight % of saturates (sat)
[b] - Maximum average temperature (May 1-August 31)

DISCUSSION

- **Cloud point (CP) was impacted by year and location (Fig 2A, 2C) --> CP Temperatures ranged from -0.1 to -2.4°C**
- **Oxidative stability index (OSI) ↓ with ↑ storage, and varied between locations within a year (Fig 2B, D) --> All OSI values met the 3h min standard (3 h), except 2004**
- **No significant difference in biodiesel fatty acid composition among locations or varieties examined in this study.**
- **Variability in biodiesel iodine value was 108 to 123.**
- **(+) relationship between saturation and OSI, and (-) relationship between IV and OSI; although not statistically significant, increasing sample population may increase level of detection**
- **Although variation in fatty acid composition was small, the variability in CP and OSI among ND growing locations and years suggests either differences in minor constituents (antioxidants, waxes) or environmental seed stress.**

ACKNOWLEDGEMENTS, REFERENCES

The authors are thankful for research support from:

- ND Ag Exp Station and ND Center of Excellence for Oilseed Development
- Mukhlesur Rahman, NDSU Plant Science and Barry Coleman, Northern Canola Growers Association for kindly providing canola seed
- Harjot Sidhu and Katherine McKinnon for technical support

Haagenson et al 2010. J Am Oil Chem Soc 87:1351-1358 DOI 10.1007/s11746-010-1607-9