ORIGINAL PAPER

Impact of the North Dakota Growing Location on Canola Biodiesel Quality

Darrin M. Haagenson · Dennis P. Wiesenborn

Received: 22 December 2010/Revised: 18 February 2011/Accepted: 24 February 2011/Published online: 27 March 2011 © AOCS 2011

Abstract Canola biodiesel (fatty acid methyl esters, FAME) may have superior cold flow properties when compared to other biodiesel feedstocks, which is attributed to canola's high unsaturated and low saturated fat content. The objective of this study was to evaluate canola biodiesel fatty acid composition, cloud point (CP) and oil stability index (OSI) among several ND locations and production years. In Experiment 1, bulked canola varieties from seven growing seasons (2003-2009) were analyzed and in Experiment 2 a single canola variety (Interstate Hyola 357RR) harvested at two locations (2003–2005, and 2007) were analyzed. FAME was produced directly from seed via in situ alkaline transesterification methods. CP ranged from -0.1 to -2.4 °C and was significantly impacted by year and location. FAME generally met the ASTM B100 specification for OSI (3 h), but increased seed storage decreased stability. No significant differences were detected in FAME composition, and iodine value ranged from 108 to 123 g $I_2/100$ g. A significant relationship between fat saturation and location with CP and stability was not detected among the samples in this study. Variation in fatty acid composition was small; thus, the significant variability in CP and OSI suggests either differences in minor constituents (antioxidants, waxes) or environmental seed stress impacted biodiesel quality. Our study supports the value of examining biodiesel quality in a canola breeding program.

D. M. Haagenson · D. P. Wiesenborn (⊠) Department of Agricultural and Biosystems Engineering, North Dakota State University, Dept 7620, PO Box 6050, Fargo, ND 58108-6050, USA e-mail: D.Wiesenborn@ndsu.edu **Keywords** *Brassica napus* · In situ transesterification · FAME · ASTM D6751 · Cold flow properties · Oxidation stability

Introduction

An alternative to petroleum diesel fuel, biodiesel (fatty acid methyl esters, FAME) is processed via chemical transesterification from vegetable oils, waste cooking oil, or animal fat, and is suitable for use in compression ignition engines [1-5]. Biodiesel may be used as a direct fuel replacement, and as blends with petroleum (i.e., B100 equals 100 percent biodiesel). The American Society for Testing and Materials (ASTM) standard D6751-09, and European EN 14214 stipulate several quality specifications that must be met before biodiesel can be made available for commerce [2, 3]. While many of these specifications are dependent upon process conditions impacting the transesterification reaction, several specifications are also feedstock dependent such as cold flow properties and oxidative stability [6-11]. The composition of FAME is similar to the feedstock fatty acid composition and highly saturated fat feedstocks generally have high oxidation stability but poor cold flow properties when compared to highly unsaturated feedstocks, and vice versa.

Increased saturated fat in biodiesel feedstocks leads to compromised biodiesel cold flow properties as predicted by cloud point (CP) or pour point (PP) temperature, and cold filter plugging point (CFPP) [7, 8]. Biodiesel CP is the temperature upon cooling where wax crystals form and the liquid first appears 'cloudy'. Fuel retailers may specify CP based on location and season. The concentration of higher melting point saturated esters determines CP, regardless of the overall level of fat unsaturation [12]. Minor components such as steryl glucosides may also impact cold flow properties of biodiesel [8].

Biodiesel is susceptible to oxidation, which is dependent upon many factors including the level of fatty acid unsaturation, antioxidants and prior storage conditions [13]. Oils and fats have a natural resistance to oxidation defined as an induction period, after which oxidation increases rapidly. A biodiesel induction period is measured automatically with either the Rancimat method (EN 14112) or oil stability index (OSI) method (AOCS Method Cd 12b-92) [14]. The methods are similar as a purified air stream is passed through a biodiesel sample heated at 110 °C. The effluent air is then bubbled through a vessel containing deionized water in which electrical conductivity of volatile oxidation products is measured. OSI is defined as the point of maximum change of the rate of oxidation, and mathematically is the second derivative maximum [14]. For biodiesel oxidation stability, the EN 14214 biodiesel standard specifies a 6-h minimum oxidative induction period, and a 3-h minimum is specified in ASTM D6751-09 [2, 3]. The European standard EN 14214 also specifies a maximum iodine value (IV) of 120, expressed as grams iodine absorbed/100 g sample. IV reflects the level of fatty acid unsaturation, and an IV of 114 has been reported for canola FAME [10]. Feedstocks possessing high polyunsaturated fat will have increased IV (>120), and are expected to have lower oxidative stability. However, factors impacting oxidation rate are complex and also include the storage environment, presence of metals, antioxidants, temperature, light exposure, and surface area contact between air and biodiesel [13, 15].

In the United States, canola production is primarily confined to the northern Great Plains, which may be attributed to canola's adaptation to cool temperatures. To support the increasing demand for food use and additional biofuel markets, efforts are ongoing to expand canola acreage through improved genetics and agronomic practices. If canola production acreage is expanded southwards, canola may be exposed to increased variability in temperature and precipitation. Numerous field and growth chamber studies have evaluated the effect of genetics and environmental stress (temperature or moisture) on canola yields and oil content [16-19]. Compared to other stages of plant development, yield and oil quality are most severely impacted if high temperature stress occurs during flowering [16, 18]. The canola genotype influenced palmitic acid concentrations, and both genotype and production environment impacted stearic acid concentrations among samples evaluated across 16 Manitoba production environments [17]. In addition, the genetic by environment interaction accounted for little variation in saturated fat content, and relationships between weather data and fatty acid saturation were weak [17]. More recently, canola yield, oil content and fatty acid composition was evaluated among irrigated spring canola varieties grown across several US High Plains regions [19]. Although no differences in oleic acid content were detected among the four varieties examined, oleic acid was significantly impacted by growing region.

Although plant genetics and growing environment impact fatty acid composition, reports documenting their impact on biodiesel quality are limited [20, 21]. In growth chamber studies, FAME derived from two sunflower cultivars across a range of temperatures exhibited a large variation in CP temperatures ranging from 3 to -5.5 °C [20]. Significant differences in viscosity and density (15 °C) were detected among biodiesel samples processed from eight peanut cultivars [21]. Increased concentrations of long-chain saturated FAME were associated with enhanced low temperature crystallization. The time and labor involved in oil extraction, refining, and transesterification does not permit a high throughput analysis of biodiesel quality. However, an in situ transesterification method was proposed for the screening of canola lines for biodiesel quality [22]. The objective of this study was to evaluate the impact of canola variety and North Dakota growing location on FAME quality across several production years.

Materials and Methods

Materials

Canola seed (Brassica napus L.) was obtained from North Dakota Agricultural Experiment Station experimental plots and from private growers. In Experiment 1, biodiesel was processed from hybrid canola varieties collected across 2003-2009. Canola varieties were pooled from a minimum of three field locations for each ND county examined (Table 1). Canola samples were combined from three counties (1:1:1) in each of 2003, 2004, and 2005 and analyzed as one bulk sample per year. Biodiesel was processed separately for each county sampled in 2006, 2008, and 2009. In 2007, two varieties (InVigor 2663 and InVigor 5550) were processed separately from fields harvested in Ward county. Experiment 2 evaluated biodiesel quality from one variety (Interstate Hyola 357RR) at two locations over four years (2003, 2004, 2005, and 2007) (Table 1). Seed was cleaned according to USDA-GIPSA methods [23], and oil content prior to transesterification was determined from intact seeds by NIR spectroscopy (DA 7200, Perten Instruments, Springfield, IL, USA). All reagents were of analytic reagent grade and were purchased from EMD Chemicals (Gibbstown, NJ, USA).

	2003 2004 2005 2006 2007 2008 200								
	2005	2004	2005	2000	2007	2000	2007		
Exp 1 ^a	Bottineau	Bottineau	Bottineau	Cavalier	Ward	Williams	Williams		
	Cavalier	Cavalier	Cavalier	Ward		Cavalier	Cavalier		
	Pembina	Pembina	Pembina			Cass	Cass		
Exp 2 ^b	Griggs	Renville	Wells		Williams				
-	McClean	Pennington ^c	Towner		Cavalier				

Table 1 North Dakota county harvest location

^a For each ND county, hybrid canola varieties were pooled across a minimum of three field locations. Canola samples were combined (1:1:1) from three counties in each of 2003, 2004, and 2005, and analyzed as one bulked sample per year. Samples were collected and analyzed separately from two or three counties in 2006, or 2008 and 2009, respectively. In 2007, canola biodiesel was processed from two varieties (InVigor 2663 and InVigor 5550) located in Ward county

^b Canola biodiesel was processed from a single canola variety, Interstate Hyola 357RR

^c Pennington county, Minnesota

Transesterification

Canola biodiesel was produced directly from seed via in situ alkaline transesterification as reported previously [22]. Canola seed was ground at room temperature with a coffee grinder and flour particle size was such that 86.5 and 31.0 wt% passed through #20 and #50 mesh sieves (ASTM E-11), respectively. Transesterification was carried out in 500-mL Erlenmeyer flasks with canola flour containing an equivalent oil wt of 40 g. The canola flour was dried at 70 °C for 3 h or until 1.0% dry basis moisture content was obtained. The dried flour was transesterified with a 275:1:1.05 molar ratio methanol:triacylglycerol:KOH, for 6 h at 60 °C, and FAME was refined with water washing [22]. Fatty acid profiles of canola oil and FAME were determined by gas chromatography according to methods described previously [24].

Quality Tests

Kinematic viscosity (40 °C), acid value, Karl Fischer moisture content, CP, and OSI from the refined FAME were analyzed according to tests included in ASTM D6751-09 standard for biodiesel [2]. Total glycerol was quantified by the SafTest for total glycerin according to the manufacturer's recommendations (MP Biomedical, Solon, OH, USA).

Experimental Design and Statistical Analysis

The experimental design was completely randomized and FAME was pooled from duplicate reaction flasks to obtain sufficient biodiesel for quality analysis. Each experiment was replicated three times. Data were analyzed using the ANOVA procedure [25]. An *F*-protected LSD ($P \le 0.05$) was calculated for comparisons of means. Relationships among FAME composition, production location, CP, and

OSI were evaluated with SigmaPlot statistical software Version 8 (SPSS Inc., Chicago, 2002). Seasonal rainfall totals and accumulated growing degree days (GDD) from May 1st to August 31 were provided by the North Dakota Agricultural Weather Network (NDAWN) center. Accumulated growing degree days (GDD) were the sum of daily GDD = [(Daily Max Temp °C + Daily Min Temp °C)/2] - 5.0 °C. For regression analyses, relationships were determined significant at $P \le 0.10$.

Results and Discussion

The impact of North Dakota production location and canola seed selection on biodiesel quality was evaluated across several production years. Two separate experiments were conducted. Experiment 1 evaluated canola biodiesel quality from bulked and individual canola varieties, and Experiment 2 examined biodiesel quality from a single canola variety, Interstate Hyola 357RR, harvested at two locations over four production years.

Biodiesel Processing Quality

Biodiesel was produced from seed via in situ alkaline transesterification methods. Prior to analysis of CP and OSI, four additional parameters were measured for process quality control: kinematic viscosity, total glycerin, acid value and moisture. These parameters are typically dependent upon processing and we wanted to confirm high quality biodiesel was produced among all canola samples and locations, to ensure that any detected differences in CP or OSI did not result from processing variability. Biodiesel samples from both experiments met the ASTM D6751 standard specification limits for acid number, kinematic viscosity, water and sediment, and total glycerin (Tables 2, 3). No significant differences were detected

among samples, and values were similar to those reported in an earlier investigation of in situ processed canola biodiesel [22]. Therefore, processing provided uniform, high quality FAME samples among all locations and years included in the study.

Cloud Point and Oil Stability Index

In both experiments, production year significantly impacted CP temperature, and location within a year also influenced CP in Experiment 2 (Tables 4, 5). CP temperatures ranging from -0.1 to -2.4 °C were slightly lower than the 1 °C previously reported for canola methyl esters [9, 10]. Direct transesterification of seed (in situ transesterification) in our study may have resulted in decreased CP as CP temperatures from sunflower methyl esters processed via an in situ transesterification reaction were lower than those derived from conventional processing [20]. In Experiment 1, the average CP temperatures from samples collected in 2003–2007 was significantly higher (-0.8 °C) than that from 2008 (-2.2 °C), with samples collected in 2009 having an intermediate CP (-1.5 °C). The lowest CP temperatures in Experiment 2 were observed from samples collected in 2003 (Griggs), 2005 (Towner) and 2007 (Cavalier). Location was significant in 2003, 2005, and 2007, but CP was not influenced by the 2004 sample locations. Interestingly, canola sampled from 2003 in Experiment 2 had the lowest and highest CP temperatures of -2.1 and -0.1 °C, respectively.

OSI is another important quality test and characterizes the susceptibility of biodiesel to oxidation. ASTM D6751 specifies a minimum OSI of 3 h for 100% (B100) biodiesel. Samples possessing higher OSI are sought after as they

have improved resistance to oxidative deterioration in storage. OSI was impacted by production year and location in both Experiments 1 and 2 (Tables 4, 5). In Experiment 1, all samples met the OSI ASTM standard (3 h minimum) with the exception of 2004 (2.1 h). OSI generally decreased with extended seed storage time, and OSI values ranged from 7.1 to 2.1 h. Nine of the thirteen biodiesel samples maintained an OSI > 5.5 h, with three samples collected in 2003-2005 near 3 h, and one sample, 2006-Cavalier, approaching 5 h. In Experiment 1, OSI also varied among locations in three years (Table 4). When compared to the other locations within each year, OSI was decreased from samples collected at Cavalier 2006, Cavalier 2008, and Williams 2009. All of the biodiesel samples processed in Experiment 2 exceeded the minimum OSI requirement (3 h). Averaged across locations, OSI values in Experiment 2 were lowest in 2003 and gradually increased in 2004 and each subsequent year (2005 and 2007).

In an effort to identify factors related to the variation in CP and OSI within these two experiments, seed fatty acid composition and composition of methyl esters were evaluated and regression analysis was conducted on FAME composition and production environment GDD and seasonal rainfall. The average content of saturated fat was 7 and 10% for Experiments 1 and 2, respectively. Canola oil from Experiment 2 was 28 and 47% higher in palmitic and stearic fatty acids when compared to canola oil samples from Experiment 1. Also, the content of saturates in Experiment 2 is higher than published reports [10], where 0.7 and 0.5% arachidic and behenic fatty acid contents may have contributed to the increased saturates of Experiment 2 (data not shown). The percentage of oleic acid was 67 and

Table 2 Impact of canolaproduction year and location onbiodiesel ASTM processing	Year	Location	Acid number (mg KOH/g)	Kinematic viscosity (mm ² /s)	Water and sediment (vol%)	Total glycerin (wt%)
quality (Experiment 1)	2003	Bulked	0.130	4.7	0.031	0.042
	2004	Bulked	0.153	4.8	0.036	0.050
	2005	Bulked	0.127	4.6	0.032	0.055
	2006	Ward	0.156	4.6	0.036	0.034
	2006	Cavalier	0.175	4.6	0.042	0.038
	2007	Ward-2663	0.200	4.4	0.038	0.034
	2007	Ward-5550	0.155	4.4	0.035	0.038
	2008	Cavalier	0.179	4.7	0.040	0.037
	2008	Cass	0.139	4.7	0.036	0.035
	2008	Williams	0.178	4.8	0.036	0.028
	2009	Cavalier	0.157	4.7	0.037	0.035
Biodiesel was produced from	2009	Cass	0.130	4.7	0.033	0.040
canola seed by in situ alkaline	2009	Williams	0.197	4.7	0.036	0.028
transesterification and data	Mean		0.160	4.6	0.036	0.040
represent the mean of three replicates	ASTM Limits		0.5 max	1.9–6.0	0.050 max	0.240 max

Biodiesel canola see transesteri represent replicates

Table 3 ASTM biodiesel

(Experiment 2)

replicates

Minnesota

quality from a single canola

variety, Hyola 357 RR, across several North Dakota

Biodiesel was produced from

canola seed by in situ alkaline

transesterification and data represent the mean of three

^a Pennington County,

Year Location Acid number Kinematic Water and Total glycerin (mg KOH/g) viscosity (mm²/s) sediment (vol%) (wt%) 2003 4.6 0.044 0.040 Griggs 0.134 production years and locations 2003 McClean 0.179 4.8 0.038 0.037 2004 Renville 4.9 0.149 0.045 0.058 2004 Pennington^a 0.125 4.8 0.036 0.029 2005 Wells 0.133 4.6 0.031 0.039 2005 Towner 0.206 4.8 0.028 0.046 2007 Williams 4.8 0.161 0.026 0.023 2007 Cavalier 0.148 4.7 0.031 0.053 Mean 0.155 4.7 0.035 0.041 ASTM Limits 0.5 max 1.9 - 6.00.050 max 0.240 max

Table 4 Annual and local variability in cloud point (CP) temperature, oil stability index (OSI), and fatty acid composition of bulked canola biodiesel samples (Experiment 1)

Year	Location ^a	СР		OSI	OSI		Biodiesel composition ^b			
		(°C)		(h)		Sat	IV ^c	Oleic		
2003	Bulked	-0.9	a	3.2	e	8.2	113	63.5		
2004	Bulked	-0.7	а	2.1	f	8.4	114	61.7		
2005	Bulked	-0.7	а	3.2	e	8.1	114	61.6		
2006	Ward	-0.9	а	6.8	ab	7.2	115	64.6		
2006	Cavalier	-0.8	а	4.8	d	7.3	123	58.1		
2007	Ward-2	-0.8	a	6.1	bc	7.7	119	59.5		
2007	Ward-5	-0.6	а	6.6	ab	7.1	121	60.3		
2008	Cavalier	-2.1	b	5.6	c	7.3	115	64.1		
2008	Cass	-2.4	b	7.0	a	7.4	115	63.0		
2008	Williams	-2.1	b	6.5	ab	7.8	114	64.0		
2009	Cavalier	-1.4	c	7.1	a	7.6	117	62.7		
2009	Cass	-1.4	c	6.7	ab	7.5	115	64.1		
2009	Williams	-1.5	c	6.1	bc	7.9	115	62.8		

CP and OSI means (n = 3) followed by the same letter are not significantly different ($P \le 0.05$)

A minimum of three varieties were processed across location years, except for Ward county 2007, where InVigor 2663 (Ward-2) and InVigor 5550 (Ward-5) varieties were processed separately

^b The weight % of saturated (sat) and oleic methyl esters

^c Biodiesel iodine value (IV) was calculated from the fatty acid composition

63% for Experiments 1 and 2, and was in agreement with published reports [10, 19]. Iodine values were generally lower in Experiment 2, but the average IV of 116 and 111 for Experiment 1 and 2 were similar to previously published canola methyl ester iodine values of 115 and 110, respectively [10, 15] (Tables 4, 5). Biodiesel processed from Cavalier (2006), Ward-5 (2007), and Ward-2 (2007) had the highest IV of 123, 121, and 119, respectively (Table 4), but there is no clear explanation for the increased IV found in Experiment 1.

1443

Table 5 Annual and local variability in cloud point (CP) temperature, oil stability index (OSI), and fatty acid composition of biodiesel processed from a single canola variety, Interstate Hyola 357RR (Experiment 2)

Year	Location	СР		OSI		Biodiesel composition ^a			
		(°C)		(h)		Sat	IV^b	Oleic	
2003	Griggs	-2.1	c	4.2	d	9.2	108	64.6	
2003	McClean	-0.1	a	4.0	d	10.0	105	65.5	
2004	Renville	-0.9	ab	5.7	b	9.1	114	61.6	
2004	Pennington	-0.7	ab	4.4	cd	9.3	114	60.7	
2005	Wells	-1.3	bc	5.6	b	8.0	118	59.1	
2005	Towner	-2.2	c	5.2	bc	8.9	111	63.6	
2007	Williams	-0.7	ab	7.9	a	10.0	106	65.2	
2007	Cavalier	-1.9	c	4.5	cd	8.3	116	61.3	

CP and OSI means (n = 3) followed by the same letter are not significantly different (P < 0.05)

^a The weight % of saturated (sat) and Oleic methyl esters

^b Biodiesel iodine value (IV) was calculated from the fatty acid composition

Attempts to correlate weather data to biodiesel quality were not successful in Experiment 1 as weather data accounted for a small variation in CP or OSI and results were inconsistent among experiments. Environmental stress is known to impact yield and oil composition and stages of plant development such as flowering may be more sensitive to temperature and moisture stress [16, 18]. Since the time of flowering may fluctuate among production years, accumulated growing degree days (GDD), based on plant phenology were used in regression analysis, in additional to total seasonal (May 1-August 31) rainfall totals (Tables 6, 7). In both experiments, IV, saturated and oleic methyl esters were compared with CP, OSI, accumulated GDD and seasonal rainfall totals. In Experiment 1, CP was impacted by oleic ester content (r = -0.55, P = 0.05), and in contrast to our expectations, OSI was negatively impacted by increased saturate concentrations

	СР		OSI		GDD		Rainfall	
	r	P value	r	P value	r	P value	r	P value
Sat (wt%)	0.24	0.42	-0.71	0.01	-0.32	0.29	0.02	0.96
IV	0.30	0.32	0.24	0.43	0.32	0.28	0.16	0.60
Oleic ME	-0.55	0.05	0.22	0.46	0.26	0.39	0.38	0.20
GDD	0.07	0.81	0.16	0.61				
Rainfall	-0.20	0.51	-0.10	0.74				

Table 6 Linear correlation coefficients (r) and P values of biodiesel fatty acid composition and production environment with biodiesel cloud point (CP) and oil stability index (OSI). (Experiment 1)

Significant relationships ($P \le 0.10$) highlighted in bold. Weight % of saturated (sat) and oleic methyl esters, and calculated iodine Value (IV) of biodiesel samples. Accumulated growing degree day (GDD) and total seasonal rainfall (May 1–August 31)

(r = -0.71, P = 0.01). This was surprising as past research has documented a positive relationship between saturates and increased OSI. Decreased oxidative stability occurs with increased unsaturation as the bis-allylic methylene group is susceptible to oxidation, resulting in hydroperoxide formation that further decomposes fatty acids to secondary oxidation products. In a study evaluating OSI of several biodiesel blends, significant variation in OSI was accounted for by both IV and saturated FAME content [15]. However, the practical importance of IV and saturated FAME on OSI was debated as different fatty acid compositions can provide similar IV possessing varied OSI [15, 26]. Furthermore, the storage history and presence of natural antioxidants also significantly contribute to OSI. It is unclear why the negative relationship between saturates and OSI was detected in Experiment 1, but the lack of significant relationships among IV, oleic ester content, and OSI underscore the complexity of factors impacting storage stability.

When compared to unsaturated fat, saturated fat has higher melting point temperatures, and biodiesel high in saturates may crystallize at warmer temperatures [6]. In Experiment 2, increased CP was associated with increased saturated ester content (r = 0.62, P = 0.10). The positive association between saturates and elevated CP temperatures is in agreement with several studies documenting factors impacting biodiesel cold flow properties [9, 15]. Approximately 98% of the variation in CFPP was accounted for by the concentration of saturates when saturate concentrations exceeded 12%, but no significant relationship was detected at lower saturate concentrations [15]. In addition to the significant relationship between saturates and CP, seasonal rainfall totals had a significant influence on CP, saturates, and IV in Experiment 2 (Table 7). Increased rainfall decreased saturated FAME and increased IV, and may have contributed to the decreased CP. However, discrepancies in significant relationships were detected between Experiments 1 and 2. The increased genetic variability of bulked varieties processed in Experiment 1 may have confounded any environmental impacts; whereas, a single hybrid variety was examined in Experiment 2.

In addition to genetics and production environment, quality of biodiesel feedstocks may be dependent upon agronomic or cultural practices such as maturity of seed at harvest and seed storage environment. The extended storage of some seed samples may have resulted in deterioration of the triacylglycerol and/or natural antioxidants, therefore causing a substantial decline in OSI (Tables 4, 5). Alternatively, oil processed from immature green canola seed may be more susceptible to oxidation [27]. While the assessment of green seed quality was not an objective of

Table 7 Linear correlation coefficients (*r*) of biodiesel fatty acid composition and production environment with biodiesel cloud point (CP) and oxidative stability index (OSI). (Experiment 2)

	СР		OSI		GDD		Rainfall	
	r	P value	r	P value	r	P value	r	P value
Sat (wt%)	0.62	0.10	0.20	0.64	0.22	0.60	-0.86	0.01
IV	-0.33	0.42	-0.15	0.73	-0.58	0.13	0.73	0.04
Oleic ME	0.13	0.76	0.09	0.83	0.60	0.11	-0.61	0.11
GDD	-0.19	0.65	0.40	0.33				
Rainfall	-0.78	0.02	-0.45	0.26				

Significant relationships ($P \le 0.10$) highlighted in bold. Weight % of saturated (sat) and oleic methyl esters, and calculated iodine value (IV) of biodiesel samples. Accumulated growing degree day (GDD) and total seasonal rainfall (May 1–August 31)

this research, the green seed count of samples collected in 2006 Experiment 1, had been evaluated in an earlier study. Cavalier-2006 contained 10% green seed whereas the content of green seed from the Ward-2006 sample was less than 2%. The elevated green seed content from Cavalier was associated with a higher IV and lower OSI when compared to samples collected from Ward, 2006 (Table 4). Although green seed count may have accounted for variation in OSI between these two samples, no correlation between IV and OSI was established in either experiment (Tables 6, 7).

Conclusions

Canola Biodiesel CP and OSI were impacted by year and ND production location. CP temperatures ranged from -0.1 to -2.4 °C. All but one sample met the ASTM D6751 minimum OSI specification of 3 h, and biodiesel stability decreased with increased storage time. Variability in the content of saturated, oleic methyl esters, and IV among biodiesel samples was detected, but poor relationships between biodiesel composition and CP or OSI reveal the complexity of factors impacting biodiesel quality. Increasing sample size and evaluating the response of multiple varieties among several environments may have improved our ability to detect significant relationships impacting biodiesel CP and OSI.

Acknowledgments The authors are thankful for research support from the North Dakota Agricultural Experiment Station and North Dakota Center of Excellence for Oilseed Development. Mukhles Rahman (NDSU Plant Science) and Barry Coleman (Northern Canola Growers Association) kindly provided canola samples. The GC analysis provided by Leonard Cook, (USDA-ARS, Fargo, ND), and laboratory analysis conducted by NDSU undergraduate research assistants, Mukesh Kumar and Harjot Sidhu, is gratefully acknowledged.

References

- Knothe G (2005) Introduction. In: Knothe G, Krahl J, Van Gerpen J (eds) The biodiesel handbook. AOCS Press, Champaign, pp 1–3
- American Society for Testing, Materials (2009) Standard specification for biodiesel fuel blend stock (B100) for distillate fuels, designation D 6751–09. ASTM, West Conshohocken
- European Committee for Standardization (2003) Automotive fuels—fatty acid methyl esters (FAME) for diesel engines requirements and test methods. Brussels: European Committee for Standardization (CEN). Method EN 14214
- Van Gerpen J (2005) Biodiesel processing and production. Fuel Proc Technol 86:1097–1107
- Ma F, Hanna MA (1999) Biodiesel production: a review. Bioresource Technol 70:1–15
- Knothe G (2005) Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Process Technol 86: 1059–1070

- Knothe G (2008) 'Designer' biodiesel: optimizing fatty ester composition to improve fuel properties. Energy Fuels 22:1358– 1364
- Dunn RO (2009) Effects of minor constituents on cold flow properties and performance of biodiesel. Prog Energ Combust Sci 35:481–489
- Ramos MJ, Fernández CM, Casas A, Rodrígez L, Pérez A (2009) Influence of fatty acid composition of raw materials on biodiesel properties. Bioresource Technol 100:261–268
- Lang X, Dalai AK, Bakhshi NN, Reaney MJ, Hertz PB (2001) Preparation and characterization of bio-diesels from various biooils. Bioresource Technol 80:53–62
- Dmytryshyn SL, Dalai AK, Chaudhari ST, Mishra HK, Reaney MJ (2004) Synthesis and characterization of vegetable oil derived esters: evaluation for their diesel additive properties. Bioresouce Technol 92:55–64
- Imahara H, Minami E, Saka S (2006) Thermodynamic study on cloud point of biodiesel with its fatty acid composition. Fuel 85:1666–1670
- Knothe G (2007) Some aspects of biodiesel oxidative stability. Fuel Process Technol 88:669–677
- Firestone D (ed) (1999) Official Methods and Recommended Practices of the AOCS, 5th edn. AOCS Press, Champaign. Method Cd 12b-92
- Moser BR (2008) Influence of blending canola, palm, soybean, and sunflower oil methyl esters on fuel properties of biodiesel. Energy Fuels 22:4301–4306
- Angadi SV, Cutforth HV, Miller PR, McConkey BG, Entz MH, Brandt SA, Volkmar KM (2000) Response of three *Brassica* species to high temperature stress during reproductive growth. Can J Plant Sci 80:693–701
- McCartney CA, Scarth R, McVetty PBE, Daun JK (2004) Genotypic and environmental effects on saturated fatty acid concentration of canola grown in Manitoba. Can J Plant Sci 84:749–756
- Kutcher HR, Warland JS, Brandt SA (2010) Temperature and precipitation effects on canola yields in Saskatchewan, Canada. Agric For Meterol 150:161–165
- Pavlista AD, Santra DK, Isbell TA, Baltensperger DD, Hergert GW, Krall J, Mesbach A, Johnson J, O'Neill M, Aiken R, Berrada A (2011) Adaptability of irrigated spring canola oil production to the US High Plains. Ind Crop Prod 33:165–169
- Harrington KJ, D' Arcy-Evans C (1985) A comparison of conventional and in situ methods of transesterification of seed oil from a series of sunflower cultivars. J Am Oil Chem Soc 62:1009–1013
- Davis JP, Geller D, Faircloth WH, Sanders TH (2009) Comparisons of biodiesel produced from unrefined oils of different peanut cultivars. J Am Oil Chem Soc 86:353–361
- Haagenson DM, Brudvik RL, Lin H, Wiesenborn DP (2010) Implementing an in situ alkaline transesterification method for canola biodiesel quality screening. J Am Oil Chem Soc 87:1351–1358
- GIPSA, USDA (2004) Grain Inspection Handbook- Book II, Chapter 3, USDA, Grain Inspection. Packers and Stockyards Administration, Washington, DC, p 13
- Espinoza-Pérez JD, Haagenson DM, Pryor SW, Ulven CA, Wiesenborn DP (2009) Production and characterization of epoxidized canola oil. Trans ASABE 52:1–9
- 25. Institute SAS (2008) Release version 9.2 for windows. SAS Institute, Cary
- 26. Knothe G (2002) Structure indices in FA chemistry. How relevant is the iodine value? J Am Oil Chem Soc 79:847–854
- Kulkarni MG, Dalai AK, Bakhshi NN (2006) Utilization of green seed canola oil for biodiesel production. J Chem Technol Biotechnol 81:1886–1893