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Fuel properties of *Brassica juncea* oil methyl esters blended with ultra-low sulfur diesel fuel☆

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ABSTRACT

Brassica juncea is a drought-tolerant member of the Brassicaceae plant family with high oil content and a short growing season that is tolerant of low quality soils. It was investigated as a feedstock for production of biodiesel along with evaluation of subsequent fuel properties, both neat and in blends with petroleum diesel fuel. These results were compared against relevant fuel standards such as ASTM D6751, EN 14214, ASTM D975, EN 590, and ASTM D7467. Crude *B. juncea* oil was extracted from unconditioned seeds utilizing a continuous tubular radial expeller. The oil was then chemically refined via degumming, neutralization and bleaching to render it amenable to direct homogeneous sodium methoxide-catalyzed transesterification. The principal fatty acid detected in *B. juncea* oil was erucic acid (44.1%). The resulting biodiesel yielded fuel properties compliant with the biodiesel standards with the exception of oxidative stability and kinematic viscosity in the case of EN 14214. Addition of *tert*-butylhydroquinone and blending with soybean oil-derived biodiesel ameliorated these deficiencies. The fuel properties of B5 and B20 blends of *B. juncea* oil methyl esters (BJME) in ultra-low sulfur (<15 ppm S) diesel (ULSD) fuel were within the ranges specified in the petrodiesel standards ASTM D975, EN 590 and ASTM D7467 with the exception of derived cetane number in the case of EN 590. This deficiency was attributed to the inherently low cetane number of the certification-grade ULSD, as it did not contain performance-enhancing additives. In summary, this study reports new fuel property data for BJME along with properties of B5 and B20 blends in ULSD. Such results will be useful for the development of *B. juncea* as an alternative source of biodiesel fuel.

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1. Introduction

Biodiesel is prepared from domestically available renewable lipids via transesterification to produce fatty acid methyl esters (FAMEs) as a substitute or blend component for conventional petroleum diesel (petrodiesel) fuel. Miscible with petrodiesel in any proportion, biodiesel enjoys enhanced lubricity and biodegradability relative to petrodiesel as well as superior cetane number, higher flash point, lower toxicity, negligible sulfur and aromatics content, and lower overall exhaust emissions. Disadvantages include high feedstock cost and limited availability, inferior oxidative stability and cold flow properties, lower energy content, and incompatibility with existing fuel distribution (pipeline) infrastructure [1,2]. Biodiesel must meet the requirements of fuel standards such as ASTM D6751 or EN 14214 (Table 1) before it can be blended with petrodiesel. Currently, blends up to B5 (5 vol % biodiesel in petrodiesel) and B7 are permitted in ASTM D975 and EN 590 (Table 2), the U.S. and European diesel fuel standards, respectively. Additionally, in the U.S. B6-B20 blends are regulated by ASTM D7467.

Biodiesel is principally prepared from canola oil in Europe, palm oil in tropical countries and soybean oil and animal fats in the U.S.

Abbreviations: AV, acid value; BJME, *B. juncea* oil methyl esters; BJO, *B. juncea* oil; CFPP, cold filter plugging point; CP, cloud point; DCN, derived cetane number; FA, fatty acid; FFA, free fatty acid; FAME, fatty acid methyl ester; FP, flash point; HHV, higher heating value; IP, induction period; IV, iodine value; KV, kinematic viscosity; PP, pour point; SG, specific gravity; SME, soybean oil methyl esters; ST, surface tension; TBHQ, *tert*-butylhydroquinone; ULSD, ultra-low sulfur diesel.

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Table 1
Properties of *B. juncea* oil methyl esters (BJME) with a comparison to results obtained in our previous study and to the biodiesel standards ASTM D6751 and EN 14214.

	ASTM D6751	EN 14214	BJME from Ref. [7]	BJME this study
AV, mg KOH/g	0.50 max	0.50 max	0.06 (0.05)[a]	0.03 (0.01)
Glycerol content:				
Free, mass %	0.020 max	0.020 max	0.002	0
Total, mass %	0.240 max	0.250 max	0.224	0.031
Flash point, °C	93 min	101 min	N/D[b]	193 (2)
Cold flow:				
CP, °C	Report	N/S[c]	4 (1)	11 (1)
CFPP, °C	N/S	Variable[d]	−3 (1)	−3 (1)
PP, °C	N/S	N/S	−21 (1)	−21 (0)
Oxidative stability:				
IP, 110 °C, h	3 min	6 min	4.8 (0.1)	5.5 (0.1)
Cetane number	47.0 min	51.0 min	61.1 (1.8)	62.6 (2.1)
IV, g I_2/100 g	N/S	120 max	112	109
KV, 40 °C, mm^2/s	1.9–6.0	3.5–5.0	5.33 (0.01)	5.39 (0.01)
Moisture, ppm	N/S	500 max	N/D	247 (3)
Sulfur, ppm	15 max	10 max	11	9
Phosphorous, ppm	4.0 max	4.0 max	0[e]	0[e]
Sodium and potassium, combined	5.0 max	5.0 max	N/D	4.6
Magnesium and calcium, combined	5.0 max	5.0 max	N/D	1.9
Density, 15 °C, kg/m^3	N/S	860–900	N/D	880 (0)
Specific gravity, 15 °C	N/S	N/S	N/D	0.881 (0)
Wear scar, 60 °C	N/S	N/S	151 (7)	150 (6)
Higher heating value, MJ/kg	N/S	N/S	N/D	39.95 (0.09)
ST, mN/m				
25 °C	N/S	N/S	N/D	30.6 (0.1)
40 °C	N/S	N/S	N/D	28.9 (0.1)
Gardner color	N/S	N/S	10	3

[a] Values in parentheses are standard deviations from the reported means (n = 3; n = 1 otherwise).
[b] N/D = Not determined.
[c] N/S = Not specified.
[d] Varies by location and time of year.
[e] None detected (detection limit: 0.1 ppm).

[1,2]. However, the combined supply of these lipids is sufficient to substitute only a small amount of petrodiesel. For example, an estimated 6% of domestic petrodiesel demand would be displaced if all U.S. soybean oil production were dedicated to biodiesel [3]. Furthermore, refined commodity oils may account for more than 80% of biodiesel production expenses [4]. Employment of alternative low-cost lipids may offset the high cost of feedstock acquisition while simultaneously enhancing feedstock supply [1]. Consequently, reports of biodiesel prepared from alternative feedstocks such as jatropha (*Jatropha curcas*) and microalgae have been reported, among numerous others [1,2,5,6].

In a previous contribution, we described production of biodiesel from crude wild mustard (*B. juncea* L.) oil [7]. Otherwise known as field mustard, Indian mustard, Chinese mustard or leaf mustard, *B. juncea* belongs to the Brassicaceae family of which canola (*Brassica napus*) is also a commercially significant member. Other promising oilseed feedstocks such as field pennycress (*Thlaspi arvense*) and camelina (*Camelina sativa*) also belong to the Brassicaceae family [2,8,9]. Native to central Asia, *B. juncea* is an annual herbaceous plant that is distributed worldwide. Generally considered to be invasive in many parts of the world, *B. juncea* is compatible with land not otherwise suited for traditional agriculture, can tolerate annual precipitation of 50–420 cm, annual temperatures of 6–27 °C, and soil pH of 4.3–8.3. *B. juncea* thrives in regions with hot days and cool nights, is drought resistant, and grows best in sandy loamy soil. Its growing period is 40–60 days, its seeds contain around 38% oil, and seed yields range from 0.5 to 2.5 MT/ha depending on factors such as cultivar, soil type, irrigation, season, and fertilizer inputs [7,10–13]. Cultivated for centuries in many parts of Eurasia for various medicinal and culinary applications, recent studies demonstrated that defatted *B. juncea* seed meal efficiently controlled nematodes, wireworms and pathogenic fungi when used as a soil amendment during production of various commercial crops [14–19].

The objectives of the current study were to demonstrate pilot-scale production of *B. juncea* oil (BJO), correct fuel property data described in our previous contribution [7] for *B. juncea* oil methyl esters (BJME), report new data for BJME, describe the effect of

Table 2
Properties of B5 and B20 blends of *B. juncea* oil methyl esters (BJME) with ultra-low sulfur diesel fuel along with a comparison to petrodiesel standards ASTM D975, EN 590 and ASTM 7467.[a]

	ASTM D975	EN 590	ASTM D7467	ULSD	B5	B20
Percent biodiesel, vol %	5.0 max	7.0 max	6.0–20.0	0.0	5.0	20.0
AV, mg KOH/g	N/S	N/S	0.30 max	N/D	0.01 (0.01)	0.01 (0.01)
Flash point, °C	52 min	55 min	52 min	69 (1)	69 (1)	72 (1)
Cold flow:						
CP, °C	N/S[b]	N/S	N/S[b]	−17 (1)	−15 (1)	−8 (1)
CFPP, °C	N/S[b]	N/S	N/S[b]	−19 (0)	−19 (1)	−18 (1)
PP, °C	N/S	N/S	N/S	−24 (1)	−23 (1)	−23 (1)
Oxidative stability:						
IP, 110 °C, h	N/S	20 min	6 min	>24 h	>24 h	10.9 (0.1)
Cetane number	40.0 min	51.0 min	40.0 min	42.5 (0.8)	50.5 (1.0)	51.9 (0.8)
KV, 40 °C, mm^2/s	1.9–4.1	2.0–4.5	1.9–4.1	2.23 (0.01)	2.42 (0.01)	2.74 (0.01)
Moisture, ppm	N/S	200 max	N/S	17 (1)	25 (1)	57 (2)
Sulfur, ppm	15 max	10 max	15 max	8	8	8
Phosphorous, ppm	N/S	N/S	N/S	0	0	0
Sodium and potassium, combined	N/S	N/S	N/S	0	0.2	0.9
Magnesium and calcium, combined	N/S	N/S	N/S	0	0.1	0.3
Density, 15 °C, kg/m^3	N/S	820–845	N/S	837 (1)	842 (1)	848 (1)
Specific gravity, 15 °C	N/S	N/S	N/S	0.848	0.848	0.849
Wear scar, 60 °C	520 max	460 max	520 max	571 (6)	222 (7)	174 (6)
Higher heating value, MJ/kg	N/S	N/S	N/S	46.23 (0.10)	45.74 (0.75)	42.76 (1.58)
ST, mN/m						
25 °C	N/S	N/S	N/S	26.2	27.5 (0.1)	28.4 (0.1)
40 °C	N/S	N/S	N/S	24.7	25.2 (0.1)	26.6 (0.1)

[a] See footnotes from Table 1.
[b] No specific limits are specified, but guidance is provided.