



Short Communication

The feasibility of converting *Cannabis sativa* L. oil into biodieselSi-Yu Li^a, James D. Stuart^b, Yi Li^c, Richard S. Parnas^{a,d,*}^a Department of Chemical, Materials & Biomolecular Engineering, University of Connecticut, Storrs 06269, United States^b Department of Chemistry, University of Connecticut, Storrs 06269, United States^c Department of Plant Sciences, University of Connecticut, Storrs 06269, United States^d Institute of Material Sciences, University of Connecticut, Storrs 06269, United States

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ABSTRACT

Cannabis sativa Linn, known as industrial hemp, was utilized for biodiesel production in this study. Oil from hemp seed was converted to biodiesel through base-catalyzed transesterification. The conversion is greater than 99.5% while the product yield is 97%. Several ASTM tests for biodiesel quality were implemented on the biodiesel product, including acid number, sulfur content, flash point, kinematic viscosity, and free and total glycerin content. In addition, the biodiesel has a low cloud point ($-5\text{ }^{\circ}\text{C}$) and kinematic viscosity ($3.48\text{ mm}^2/\text{s}$). This may be attributed to the high content of poly-unsaturated fatty acid of hemp seed oil and its unique 3:1 ratio of linoleic to α -linolenic acid.

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1. Introduction

Biodiesel is the group of monoalkyl esters of long chain fatty acids (called fatty acid alkyl esters) derived from renewable lipid feedstocks (Ma and Hanna, 1999; Zhang et al., 2003). It is a clean and renewable energy alternative to petroleum-based diesel fuel. Additionally, it can be used in conventional diesel engines as well as heating and power systems without modifications. There is commercial production of biodiesel from soybean oil in the US, rapeseed oil in Europe and palm tree oil in the tropical areas in Asia. A transesterification reaction is used to produce biodiesel from the renewable lipid feedstock (Ma and Hanna, 1999; Zhang et al., 2003; Demirbas, 2003; Meher et al., 2006) by mixing with alcohol in the presence of a catalyst, during which the backbone of triglyceride is replaced with three alkyl groups of the alcohol. Catalysts for transesterification can be alkali, acid, enzyme, and heterogeneous catalysts. Since the base-catalyzed transesterification is rapid and easy to scale-up, it has been widely used in industry. Other important parameters for the transesterification reaction includes molar ratio of alcohol to oil, reaction temperature, catalyst concentration, agitation speed, and free fatty acid content. Non-catalytic transesterification through supercritical fluid technology is another promising way to produce biodiesel (Demirbas, 2003; Deshpande et al., 2010).

One promising source for biodiesel production is the fiber crop *Cannabis sativa* Linn, known as industrial hemp. Industrial hemp is an annual herb and its cultivation has a low cost and a low environmental impact. Hemp seeds have high oil content, ranging from 26% to 38% (Kriese et al., 2004). Hemp seed oil is often used as a nutrition supplement due to its high percentage of poly-unsaturated fatty acid (Oomah et al., 2002; Matthäus and Brühl, 2008; Latif and Anwar, 2009). In addition, hemp has another advantage as a fuel source. It has a high biomass content which can be fermented to create low carbon fuels, such as bioethanol or biobutanol. Moxley et al. has successfully recovered 96% of the glucose from the hemp's cellulosic hurds, which allows for the recycling of this hemp fiber industry waste product (Moxley et al., 2008). In fact, industrial hemp is one of the few plants that produce high yields of both oil and biomass, which means it can be used to produce both biodiesel and bioethanol. In order to test hemp seed oil's feasibility as a biodiesel source, hemp seed oil was converted to biodiesel and several fuel properties were determined.

2. Methods

2.1. Materials

Fully refined hemp seed virgin oil was provided by Charkit Chemical Corp., USA. Hemp seed oil was extracted through cold pressing at mild temperature to maintain the quality of the oil. Table 1 shows the fatty acid composition of hemp seed oil provided by Charkit Chemical Corp., USA. All the chemicals used in this study were ACS grade or above.

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Table 1
Fatty acid composition of hemp seed oil (Charkit Chemical Corp., USA).

Symbol	Fatty acid	Hemp seed oil (wt.%) ^a
<i>Saturated fatty acids</i>		
C16:0	Palmitic	6.0–8.5
C18:0	Stearic	2.5–3.0
C20:0	Arachidic	0.5–0.8
<i>Unsaturated fatty acids</i>		
C18:1	Oleic	12.0–15.0
C18:2	Linoleic	52.0–56.0
C18:3	α -Linolenic	15.5–18.0
C18:3	γ -Linolenic	2.3–3.0

^a The exact fatty acid composition is not specified because the industrial hemp used in this study is a mixture of several subspecies, not specified by the supplier.

2.2. Preparation of hemp biodiesel

Fully refined hemp seed oil was converted to biodiesel through a typical two-step base-catalyzed transesterification reaction (Ahn et al., 1995). Methoxide solution was first prepared by dissolving 4.5 g potassium hydroxide (KOH) into 120 mL methanol. This methoxide solution was then mixed with 450 g hemp seed oil in a three-neck flask so that the oil:methanol molar ratio was 1:6 with the presence of 1 wt.% (relative to oil) KOH catalyst. The mixture was heated and stirred at 50 °C for 20 min and then allowed to settle until the completion of phase separation. The bottom layer containing byproduct glycerol and unreacted methanol was drawn out of the three-neck flask. Another 50 mL methoxide solution containing 2.3 g KOH was then added and the stirrer started to permit a second transesterification reaction to take place for 10 min at 50 °C. After the completion of the two-step base-catalyzed transesterification reaction, excess reactants, catalysts and the byproduct in the fuel product were removed by gently rinsing with distilled water. The moisturized fuel product was dried by air bubbling. The dried fuel product was then tested.

2.3. Quality determination methods

The free and total glycerin content, acid number, sulfur content, flash point, and kinematic viscosity were determined by the American Society for Testing and Materials (ASTM) methods (ASTM D6751-09). The density of hemp oil and biodiesel were tested by a pycnometer at 15 °C. The cloud point of the hemp oil and biodiesel were tested by differential scanning calorimetry (DSC). The cloud point was also tested by a polarized light microscope (PLM) (Coutinho and Daridon, 2005). Test methods are listed in Table 2.

3. Results and discussion

3.1. Transesterification of hemp seed oil

Previous studies have shown that a single-pass transesterification reaction achieves conversions between 85% and 95% due to

Table 2
Summary of test methods used for quality determination of hemp biodiesel.

Physical and chemical properties	Test methods
Free glycerin (% mass)	ASTM D6584-08
Total glycerin (% mass)	ASTM D6584-08
Flash point (°C)	ASTM D93-10
Kinematic viscosity, 40 °C (mm ² /s)	ASTM D445-09
Acid number (mg KOH/g oil)	ASTM D664-09
Cloud point	DSC & PLM
Sulfur content	ASTM D4294-08a
Density, 15 °C (kg/m ³)	Pycnometer

the reversibility of the reaction (Noureddini and Zhu, 1997). Therefore, to obtain high conversion, the byproduct glycerol is removed after the reaction is run once, and the reaction run a second time. The separation of glycerol occurs because glycerol is nearly immiscible with the oil phase. Therefore, the reaction mixture was allowed to settle for about 10 min after the first reaction period, and the reaction mixture phase separated into two layers. The dense, bottom layer was glycerol and the light top layer was biodiesel and unreacted hemp oil. Unreacted methanol and potassium hydroxide catalyst partitioned between the oil and glycerol phases. Since a portion of the methoxide was removed with the glycerol phase, another 50 mL of methoxide solution containing 2.3 g KOH was added before the second transesterification to assure a high conversion yield. The molar ratio of methanol:oil used for the second run was estimated as 40:1 and the catalyst concentration was estimated to be 5 wt.%. The estimations were based on two assumptions: a 90% conversion was achieved after the first reaction and half of unreacted methanol was removed with the glycerol phase. It should be noted that the purpose of this study was to obtain a high conversion of hemp seed oil to biodiesel; therefore, the conditions used for the transesterification reaction may not be optimal.

The product recovery yield (mass ratio of actual recovered biodiesel to the theoretical amount of hemp biodiesel) was calculated to be 97% after washing and drying the biodiesel product. The high product recovery yield indicated that product loss due to saponification was minor. Pictures of hemp oil and hemp biodiesel are shown in Fig. 1.

3.2. Physical and chemical properties of refined hemp oil and hemp biodiesel

All tested biodiesel properties are listed in Table 3. ASTM specifications are also listed as well as several properties of the hemp seed oil feedstock. The free and total glycerin content was tested by gas chromatography (ASTM D6584-08). The free glycerin indicates how well the biodiesel product was cleaned of residual glycerin. The total glycerin is the sum of the free glycerin and bound glycerin, and the bound glycerin indicates the level of incompletely converted feedstock. The total glycerin content was 0.1 wt.% and the free glycerin content was less than 0.005 wt.%, well within ASTM specifications and suitable for further physical and chemical quality analysis.

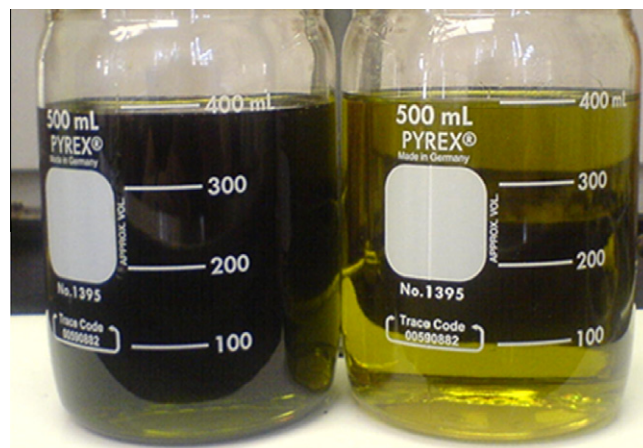


Fig. 1. Dark green liquid at the left hand side is hemp seed oil while the light green liquid at the right hand side is hemp biodiesel. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

Summary of ASTM specifications compared with physical and chemical properties of hemp biodiesel.

	Free glycerin (% mass)	Total glycerin (% mass)	Flash point (°C)	Kinematic viscosity, 40 °C (mm ² /s)	Acid number (mg KOH/g oil)	Cloud point (°C)	Density, 15 °C (kg/m ³) ^a	Sulfur content (ppm) ^b
Refined hemp oil	–	–	232	26.46	0.67	–	918	1.6
Hemp biodiesel (B100)	<0.005	0.10	162	3.48	0.25	–5	884	0.4
ASTM specifications for B100	0.02	0.24	130.0 min	1.9–6.0	0.50 max	Report	860–900	15 max

–' Not applicable.

^a According to EN14214.^b For grade S15.

Flash point is a fuel property related to safety issues surrounding fuel handling and storage, and is indicative of unreacted alcohol remaining in the finished fuel. The flash points of hemp oil and biodiesel were 232 and 162 °C, respectively. While not surprising that the flash point of hemp oil is higher than the biodiesel, the flash point of the biodiesel is 32 °C higher than the ASTM specification.

The sulfur content of fuels is associated with emissions of sulfur. Unlike Brassicaceae family, industrial hemp is not a plant that contains high sulfur. The sulfur content of hemp oil is only 1.6 ppm and the sulfur content of the biodiesel is only 0.4 ppm, well under the 15 ppm sulfur specification. The kinematic viscosity is important for proper transport of fuel from tank to engine. The kinematic viscosity of biodiesel is higher than that of petro-diesel in general. Thus, biodiesel is more affected by use in high latitude areas. The kinematic viscosity of the hemp biodiesel at 40 °C was 3.48 mm²/s, which is well within the ASTM specification. If the acid number is too high, excessive engine corrosion occurs. The total acid number reported is well below the ASTM specification. The densities of hemp seed oil and biodiesel are 918 and 884 kg/m³, respectively, which are in the range of typical vegetable oils and biodiesel. More general discussions of the biodiesel properties can be found elsewhere (Knothe et al., 2005).

3.3. DSC and PLM for cloud point test

The cloud point is related to the cold flow behavior of a fuel. The determination of cloud point is typically measured using light scattering to indicate turbidity. However, the cloud point of hemp biodiesel could not be determined by this method, probably due to the green color of chlorophyll. DSC is an alternative way to measure cloud point (Coutinho and Daridon, 2005). The DSC thermogram of the biodiesel in Fig. 2 shows the first onset point occurring at –5.49 °C. The onset temperature represents the initiation of crystallization in the biodiesel, which indicates the cloud point is approximately –5 °C. This result was supported by PLM. The inset picture in Fig. 2 shows that crystals begin to form at –5 °C. Additional PLM images, not shown, do not show the crystallites at –4 °C, and show increasingly large and numerous crystals at temperatures below –5 °C.

High quality biodiesel has a cloud point between 0 and 2 °C, and a kinematic viscosity near 4.00 mm²/s. The lower cloud point (–5 °C) and kinematic viscosity (3.48 mm²/s) of hemp biodiesel indicates superior cold flow properties. Both the low cloud point and low kinematic viscosity might be due to the high content of poly-unsaturated fatty acid of hemp seed oil and its unique 3:1 ratio of linoleic to α -linolenic acid (Oomah et al., 2002). Note that both soybean and canola biodiesel have cloud points near 0 °C and kinematic viscosities close to 4 mm²/s.

It has been shown in Table 3 that all physicochemical properties tested in this study for hemp biodiesel met the regulations of ASTM

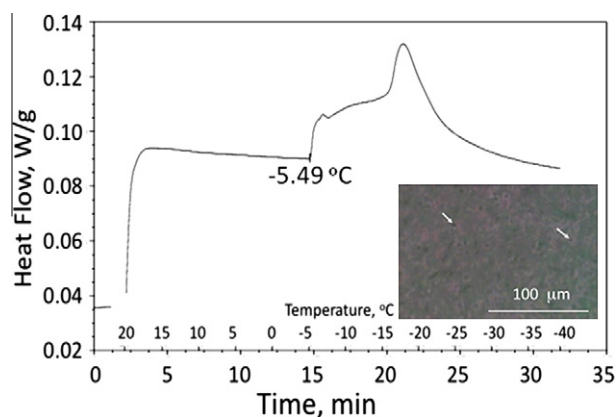


Fig. 2. DSC thermogram of hemp biodiesel indicating the onset of crystallization at –5.49 °C. Inset, PLM image of hemp biodiesel taken at –5 °C illustrating initial formation of small crystals, with scale bar of 100 μm.

D6751-09 or EN14214:2003. This indicates the potential of hemp seed oil as a feedstock for biodiesel production.

Although not all ASTM tests were performed on the hemp biodiesel produced in this study, those conducted indicate a high potential for hemp seed oil derived fuel. However, due to the high level of unsaturated fatty acid chains in hemp oil, we expect that oxidation stability (EN14112) will be relatively poor. Therefore, additives will likely be required to provide oxidation stability of hemp-derived biodiesel.

4. Conclusions

Industrial hemp seeds' high seed yield and high oil content makes it a potentially new crop source for biodiesel production. It has been shown that hemp virgin oil can be converted into hemp biodiesel with a high product yield. Furthermore, hemp biodiesel meets the standards for biodiesel fuel set by ASTM 6751-09. The distinct properties of hemp biodiesel are its low cloud point and low kinematic viscosity. These promising cold flow properties make hemp biodiesel attractive and competitive.

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References

- Ahn, E., Koncar, M., Mittelbach, M., Marr, R., 1995. A low-waste process for the production of biodiesel. *Separat. Sci. Technol.* 30, 2021–2033.
- Coutinho, J.A.P., Daridon, J., 2005. The limitations of the cloud point measurement techniques and the influence of the oil composition on its detection. *Petrol. Sci. Technol.* 23, 1113–1128.
- Demirbas, A., 2003. Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey. *Energy Conversion Manage.* 44, 2093–2109.
- Deshpande, A., Anitescu, G., Rice, P.A., Tavlarides, L.L., 2010. Supercritical biodiesel production and power cogeneration: technical and economic feasibilities. *Bioresour. Technol.* 101, 1834–1843.
- Knothe, G., Van Gerpen, J., Krahl, J., 2005. In: Knothe, G., Van Gerpen, J., Krahl, J. (Eds.), *The Biodiesel Handbook*. AOCS Press, Urbana, Illinois, pp. 76–164.
- Kriese, U., Schumann, E., Weber, W.E., Beyer, M., Brühl, L., Matthäus, et al., 2004. Oil content, tocopherol composition and fatty acid patterns of the seeds of 51 *Cannabis sativa* L. genotypes. *Euphytica* 137, 339–351.
- Latif, S., Anwar, F., 2009. Physicochemical studies of hemp (*Cannabis sativa*) seed oil using enzyme-assisted cold-pressing. *Eur. J. Lipid Sci. Technol.* 111, 1042–1048.
- Ma, F., Hanna, M.A., 1999. Biodiesel production: a review. *Bioresour. Technol.* 70, 1–15.
- Matthäus, B., Brühl, L., 2008. Virgin hemp seed oil: an interesting niche product. *Eur. J. Lipid Sci. Technol.* 110, 655–661.
- Meher, L.C., Vidya Sagar, D., Naik, S.N., 2006. Technical aspects of biodiesel production by transesterification—a review. *Renew. Sustain. Energy Rev.* 10, 248–268.
- Moxley, G., Zhu, Z., Zhang, Y.-P., 2008. Efficient sugar release by the cellulose solvent-based lignocellulose fractionation technology and enzymatic cellulose hydrolysis. *J. Agric. Food Chem.* 56, 7885–7890.
- Noureddini, H., Zhu, D., 1997. Kinetics of transesterification of soybean oil. *J. Am. Oil Chem. Soc.* 74, 1457–1463.
- Oomah, B.D., Busson, M., Godfrey, D.V., Drover, J.C.G., 2002. Characteristics of hemp (*Cannabis sativa* L.) seed oil. *Food Chem.* 76, 33–43.
- Zhang, Y., Dubé, M.A., McLean, D.D., Kates, M., 2003. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresour. Technol.* 89, 1–16.