3-2009

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Abstract: The demand for diesel fuel far exceeds the current and future biodiesel production capabilities of the vegetable oil and animal fat industries. New oilseed crops that do not compete with traditional food crop are needed to meet existing energy demands. Hybrid hazelnut oil is just such an attractive raw material for production of biodiesel. Hazelnut oil was extracted from hybrid hazelnuts and the crude oil was refined. Hazelnut oil-based biodiesel was prepared via the transesterification of the refined hazelnut oil with excess methanol using an alkaline catalyst. The effects of reaction temperature, time and catalyst concentration on the yield of diesel were examined, and selected physical and chemical properties of the biodiesel were evaluated. The biodiesel yield increased with increasing temperature from 25 to 65 °C and with increasing catalyst concentration from 0.1 to 0.7 wt%. The increase in yield with reaction time was nonlinear and characterized by an initial faster rate, followed by a slow rate. Hazelnut oil-based biodiesel had an average viscosity of 8.82 cP at 25 °C, which was slightly higher than that of the commercial soy-based diesel (7.92 cP at 25 °C). An approximate 12 °C higher onset oxidative temperature and a 10 °C lower cloud point of hazelnut oil biodiesel than those of its commercial soy counterpart indicated a better oxidative stability and flowability at low temperature. The average heat of combustion of hazelnut oil biodiesel was 40.23 kJ/g, and accounted for approximately 88% of energy content of diesel fuel. The fatty acid composition of hazelnut oil-based biodiesel was the same as the nature oil.

Keywords: hazelnut oil, biodiesel, yield, viscosity, thermal stability, cloud point, heat combustion

1. Introduction

The annual worldwide demand for diesel fuel approaches 1.0 billion tons, with 188 million tons used per year in the US. This far exceeds the current and future biodiesel production capabilities of the vegetable oil and animal fat industries. Worldwide, vegetable oil feedstocks are estimated to be 100 million tons, which would supply only 10% of the demand for diesel fuel even if none were diverted to other uses. In the USA, soybean oil is the feedstock of choice for biodiesel production. Current soybean oil supply is between 450 and 900 thousand tons, of which only half can be diverted to biodiesel (or only <0.3% of total diesel fuel use in USA) (Hanna et al., 2005). Clearly, we need to develop new oilseed crops that can be produced with fewer inputs and on marginal lands to meet existing energy demands. Recently, hazelnut oil has emerged in Nebraska as an alternative oilseed crop with especially promising potential.

Hazelnuts (*Corylus* spp.), also known as filberts, are an important commercial crop in many countries. In the USA, commercial hazelnut production occurs largely in Oregon, which produces 3% of the world's hazelnuts (Thompson et al., 1996). Currently, all commercial hazelnut cultivars come from the European hazel (*Corylus avellana*). Even through they produce

nuts of higher quality, larger size, and thinner shells, the European hazel cannot tolerate the harsh winters of the Upper Midwest, nor are they resistant to Eastern filbert blight (a native disease of hazelnuts in the eastern US that is uniformly fatal to the European hazelnut). On the other hand, American native species are cold-tolerant and disease resistant, but the nuts produced are small and of little commercial value. Commercial-quality hybrid hazelnut shrub cultivars which combine the superior qualities of the European hazel with disease resistance and cold hardiness of the American species show great potential as an oilseed crop in the Upper Midwest (Hammond, 2006).

Further, preliminary evaluations of the top 25 producing hybrids hazelnuts planted at Arbor Day Farm in Nebraska City, NE showed that the average oil content was 60% of dry weight of the kernel (ranging from 56 to 75%). Combining the nut yield, percent kernel and oil content of the kernel indicated that hybrid hazelnuts could produce approximately twice the oil (>1000 kg/ha) as soybeans (~500 kg/ha). Initial results documenting the oil characteristics from these hybrids have been very positive. Oleic acid was the predominant fatty acid. High oleic acid content and low iodine values greatly increase the thermal stability of hazelnut oil, which has an approximately 40 °C higher onset oxidative temperature than soybean oil. These analyses suggest that hybrid hazelnut oil could be an attractive low-cost feedstock for biodiesel fuels which is superior to soybean oil (Xu et al., 2007).

Many efforts have been made to optimize the parameters for biodiesel production and the effects of the factors on characterization of biodiesel (Vicente et al., 1998; Goodrum and Geller, 2005).

In this research, we prepared hazelnut oil-based biodiesel via transesterification using an alkaline catalyst. The objectives of this work were to investigate the effects of a set of variables (reaction temperature, time and catalyst concentration) on biodiesel yield and to evaluate selected properties of produced hazelnut oil-based biodiesel.

2. Materials and methods

2.1. Materials

Hybrid hazelnuts, selected from high yielding shrubs, were hand harvested from Arbor Day Farm, Nebraska City, NE. Husks (or the involucre) were removed mechanically and nuts were sorted mechanically by size and cracked using mechanical crackers. Oil was extracted from kernels using mechanical expression in a stainless steel test cell. Suspended solids were removed by centrifuging. Crude oil was subjected to refining as described by Karabulut et al. (2005). The free fatty acid content was determined by titration according to AOAC official method 940.28 (2000). The amount of potassium hydroxide (KOH) was calculated based on the titration result, and then an aqueous solution of KOH (6N) was added to neutralize the free fatty acids in the crude oil. The oil was heated to 85 °C and then cooled to room temperature. The precipitated brown solids were settled and then centrifuged. The oil was further washed by agitation with 10% water and centrifuged again. Finally, magnesol and diatomaceous earth (1%, w/v)

were mixed into the oil. The mixture was heated to 110–120 °C for 30 min and then filtered for further use. The free fatty acid content of the clear oil was determined and the value was less than 0.05 mg KOH/g oil. Methanol and sodium hydroxide were reagent grade and were used as provided. Commercial soy-based biodiesel was provided by Sapp Brothers Petroleum (Lincoln, NE) to use as control.

2.2. Preparation of biodiesel

Methyl esters of hazelnut oil were prepared by a refluxing method. Hazelnut oil (50 mL) was weighed accurately into a 100 mL three neck flask, which was assembled with a condenser, a stirrer and a thermometer. The oil was heated to a prescribed temperature between 25 and 65 °C. Solid sodium hydroxide was crushed into a powder, weighed and dissolved into methanol. The amounts of catalyst varied based on oil weight. The mixture was added to the heated hazelnut oil at the ratio of 30% (v/v) with vigorous stirring. The reaction was timed and continued heating for the prescribed times. After that, the heating and stirring were stopped. The warm reaction mixture was poured into a separatory funnel and was settled into two layers by gravity. After settling was complete, the bottom layer, mainly containing glycerol and residual methanol, was drawn off and heated to remove the residual methanol. The top layer (biodiesel product) was transferred to a clean flask and was washed with water by agitation to remove residual methanol, glycerol and catalyst, and then dried over anhydrous Na_2SO_4. The biodiesel yield was calculated based on the weight of the methyl esters produced and the amount of hazelnut oil that was added into the flask initially.

2.3. Characterization of oil and biodiesel

Selected physical and chemical properties of the hazelnut oil, the biodiesel, and commercial soy biodiesel, including viscosity, oxidation stability, cloud point, heats of combustions, and fatty acid composition, were determined. Dynamic viscosity was determined with a Brookfield viscometer (Brookfield Engineering Lab. Inc., Middleboro, MA, USA) at 25 °C with LV-1 spindle speed of 100 rpm.

Oxidative stability was measured by differential scanning calorimetry (DSC, Mettler, Columbus, OH, USA) using ASTM E 2009-02 method (2002) and was expressed as oxidative onset temperature (OOT). The test specimens (about 3 mg) in aluminum pans, and an empty reference aluminum pan were heated at a heating rate of 10 °C/min in an air environment. Heat flow out of the specimen was monitored as a function of temperature until the oxidative reaction was manifested by heat evolution on the thermal curve. OOT is defined as the temperature when a rapid increase in the rate of specimen oxidation is observed. This temperature was obtained by extrapolating the tangent drawn on the steepest slope of the reaction exothermic curve.

Cloud point was determined using DSC (Mettler, Columbus, OH, USA) according to. The samples (35–40 mg) were cooled from 10 °C to −50 °C at a cooling rate of 1 °C/min, held at −50 °C for 1 min, and then heated to 10 °C at a heating rate of 1 °C/min. The cloud point was the onset temperature of the initial small exothermic peak on the cooling curve.
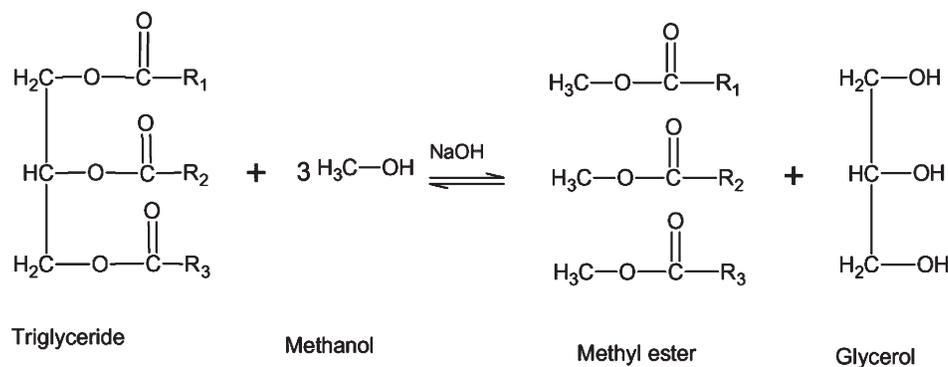
Figure 1. A scheme of transesterification process of triglyceride with methanol under a base catalyst.

The heats of combustions were measured using a model 1108 Adiabatic oxygen chamber (bomb) and the 1241 calorimeter (Parr Instrument Company, Moline, IL). The oil and biodiesel first were filled into tared gelatin capsules and weighed. A 10 cm length of fuse wire was cut and attached to the electrodes of the chamber. The weighed capsule was placed in the loop holder and the wire was bent down to touch the surface of the charge. The chamber was closed tightly and was charged with oxygen. The calorimeter bucker was tared and filled with 2000 (±0.65) g of water, and then set in the calorimeter. The chamber was placed in calorimeter and the cover was closed. Before starting a measured run, the stirrer was run for 5 min to reach equilibrium. The bomb was fired by pressing the ignition button and holding it down until the indicator light went out. The bucket temperature started to rise within 20 s after firing. This rise was rapid during the first few minutes; then it became slower as the temperature approached a stable maximum. The temperature was read and the stable maximum temperature was recorded. The chamber was removed from the bucket and opened. The interior surface of the chamber was washed with distilled water and tirated with a standard sodium carbonate. Unburned pieces of fuse wire were removed and measured for length that was subtracted from the initial 10 cm length to get the net amount of wired burned. The heat of combustion of the sample was determined based on the change in temperature of the calorimeter system, the heat capacity of the calorimeter system, and the grams of sample used.

An HP 5890 Series II Gas Chromatograph (Hewlett Packard Company, Wilmington, DE), equipped with a flame ionization detector and a Hewlett Packard 3396 A Integrator (Avondale, PA), was used to determine fatty acid composition of hazelnut oil and biodiesel. A fused silica capillary column DB-Wax (30 m × 0.25 mm i.d.) with a 0.25 μm coating (Alltech, Deerfield, IL) was used as the stationary phase. Hazelnut oil first was derivatized to volatile methyl esters. The biodiesel was diluted directly with hexane prior to injecting into the chromatograph using a microliter syringe.

2.4. Statistical analysis

Three replications were used to obtain mean values for each measurement. All of the results were analyzed with SAS version 8.0 statistical software (SAS Institute Inc., Cary, NC). Duncan's multiple range test was employed to estimate the significance of the treatments. Probability (p) < 0.05 indicates significance, while $p > 0.05$ indicates non-significance.

3. Results and discussion

3.1. Synthesis of biodiesel

Production of biodiesel is a transesterification process. In this process, the triglyceride of hazelnut oil reacts with methanol in the presence of a base catalyst, and forms glycerol and low molecular fatty acid methyl esters, which is the biodiesel. Three moles of methanol are required to react with one mole triglyceride to produce three moles of fatty acid methyl esters and one mole of glycerol from a stoichiometry viewpoint, as shown in Figure 1. Further, it is worthy to note that this reaction is reversible. Therefore, excess amounts of methanol are needed to shift the reaction equilibrium to the product side and to produce more methyl esters. Based on preliminary experiments, a 30% volume ratio of methanol to hazelnut oil was considered to be excess and was used in all experiments.

Figure 2 shows the effects of reaction temperature and time on methyl ester yield. The highest reaction temperature
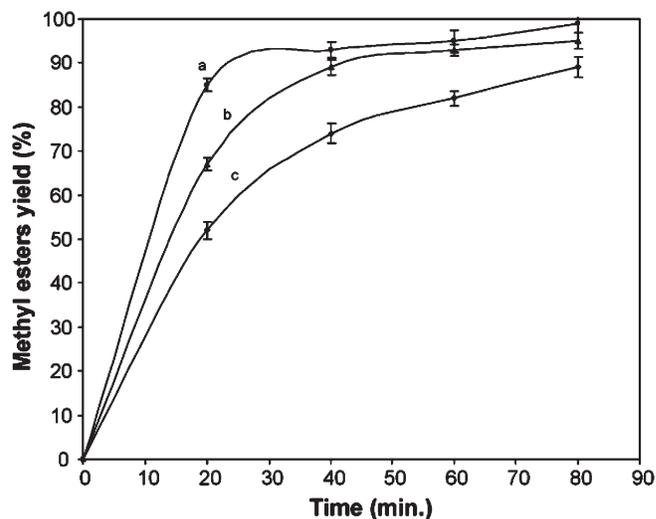

Figure 2. The methyl esters yield as functions of reaction temperature and time. Curves for 65 °C (a), 45 °C (b) and 25 °C (c).
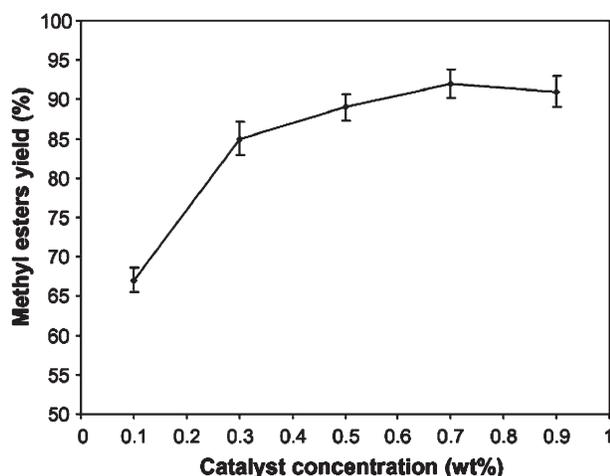
Figure 3. The effect of catalyst concentration on the hazelnut methyl esters yield. Reaction temperature was 45 °C; reaction time was 40 min, and methanol/oil volume ratio was 30%.

of 65 °C was chosen based on the boiling point of methanol. The methyl esters yield was increased with the reaction temperature increasing from 25 to 65 °C. This was a consequence of the favorable effect of the high temperature on the diffusion of methanol molecules and reaction with triglyceride molecules. At the reaction time of 20 min, methyl esters yield increased from 52% to 67% and 85% as the reaction temperature increased from 25 to 45 and then to 65 °C. When the reaction time was 40 min, methyl esters yield increased from 74% to 89% and 93% with the reaction temperature increasing from 25 to 45 and then to 65 °C. It was observed that although the rates of increase in methyl esters yield at higher temperature of 45 and 65 °C were slower than that at 25 °C with the reaction time further increasing, overall yield at higher temperature was higher than that at 25 °C. For example, at 80 min, the methyl esters yield reached 99% at 65 °C, while there was an 89% yield at 25 °C.

Regarding the effect of reaction time, methyl esters yield increased as the reaction time increased from 0 to 80 min at each temperature profile. However, this increase was nonlinear and characterized by an initial faster rate, followed by a slower rate. At the reaction temperature of 65 °C, in the fist 20 min, the methyl esters yield quickly reached 89%. After that, it increased slowly to 99% as the reaction time increased further from 20 to 80 min. This can be explained that at the beginning of reaction, a fast transesterification reaction occurred under a

base catalyst. However, as the reaction proceeded and more methyl esters produced, the reaction tended to reverse direction to obtain a new chemical equilibrium. Fortunately, due to the presence of excess methanol, the overall reaction was guaranteed to maintain a forward direction, but the reaction rate became significantly slower.

The effect of the catalyst (NaOH) concentration on methyl ester yield is presented in Figure 3. The methyl esters yield increased from 67% at the catalyst concentration of 0.1% to a maximum value of 92% as the catalyst concentration was increased to 0.7 wt% (based on the hazelnut oil weight). Further increasing the concentration to 0.9% brought about a slight decrease in yield. Within the proper range (0.1–0.7 wt%), the catalyst concentration had a favorable effect on yield of biodiesel. However, the presence of excess NaOH resulted in the formation of soap through saponification of the triglyceride. The resulting soap increased the emulsification of methyl esters and glycerol and made the separation difficult, thus reducing the biodiesel yield (Ikwuagwu et al., 2000).

3.2. Fuel properties

Selected fuel properties of refined hazelnut oil and its methyl esters are compared with commercial soy biodiesel in Table 1. Refined hazelnut oil had an average viscosity of 60.8 cP at 25 °C. Transesterification of hazelnut oil substantially reduced its viscosity from 60.8 cP to 8.82 cP for its methyl ester at 25 °C ($p < 0.05$). Viscosity is one of the most important criteria in evaluating diesel quality. High viscosity often leads to operational problems including engine deposits (Knothe and Steidley, 2005). The viscosity of hazelnut oil-based biodiesel was slightly higher than that of the commercial soy oil-based biodiesel (7.92 cP at 25 °C) ($p > 0.05$). This difference was attributed to the different fatty acid composition as described by Xu et al. (2007).

Oxidative stability refers to the extent of fuel deterioration when exposed to air during storage. It plays a key role in the industrial applications of biodiesel. In our experiment, oxidative onset temperature (OOT) was used to evaluate the oxidative stability of the oil and biodiesels. A higher OOT value is indicative of a more stable material. The DSC curves of hazelnut oil and its methyl esters, and commercial soy biodiesel are shown in Figure 4, and their average OOTs are presented in Table 1. Refined hazelnut oil had an average OOT of 188.1 °C. OOT was significantly ($p < 0.05$) reduced to an average value of 171.5 °C when hazelnut oil was converted into methyl esters. The decrease in the oxidative stability with transesterifi-

Table 1. Fuel properties of hazelnut oil-based biodiesel in comparison with the hazelnut oil and soy oil-based biodiesel

Properties	Refined hazelnut oil	Hazelnut oil biodiesel	Soy oil biodiesel
Viscosity (cP) at 25 °C	60.8 ± 0.31[a]	8.82 ± 0.09[b]	7.92 ± 0.28[b]
Oxidative onset temperature (°C)	188.1 ± 1.87[a]	171.5 ± 1.68[b]	160.5 ± 2.15[c]
Cloud point (°C)	NA	−14.7 ± 0.5[a]	−4.08 ± 0.12[b]
Heat of combustion (kJ/g)	39.95 ± 0.16[a]	40.23 ± 0.06[b]	40.53 ± 1.17[b]
Acid value	0.05 ± 0.0005	NA	NA

NA means not available. Means within a row with same letters (a–c) indicate no significant ($p > 0.05$) difference by Duncan's multiple range test.
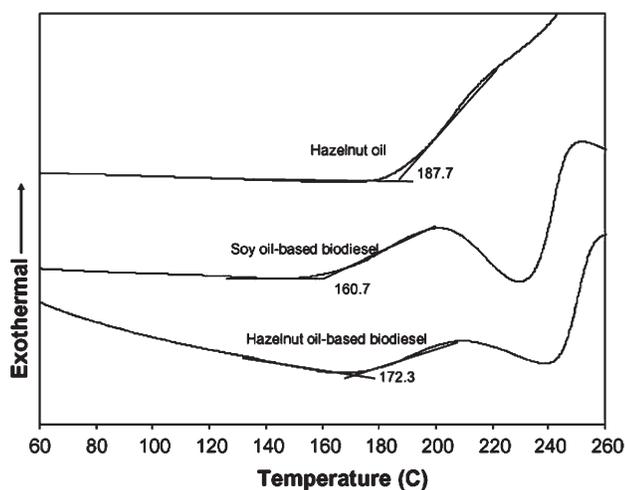
Figure 4. The DSC curves for oxidative onset temperature of hazelnut oil, biodiesel and commercial soy oil-based biodiesel.

cation can be explained by the fact that the methyl esters had a lower viscosity than pristine oil. The low viscosity resulted in a higher oxygen diffusion rate, thus less oxidative stability (Ikwuagwu et al., 2000). In addition, an approximate 12 °C higher OOT of hazelnut biodiesel than commercial soy counterpart was due to the corresponding fatty acid compositions. The degree of unsaturation influences the reactivity of the double bonds. Double bonds in polyunsaturated systems are more reactive than monounsaturated double bonds (AOCS, 2003). Compared to the high oleic acid content in hazelnut methyl esters, the high amounts of linoleic and linolenic acids in soy biodiesel make it more susceptible to oxidation (Bajpai and Tyagi, 2006).

The cloud point is the temperature at which a cloud is formed in biodiesel caused by the first stage of crystallization. It is of importance since high cloud point limits the flow properties of biodiesel, which influences its use in a cold environment. The cloud points of hazelnut oil and its methyl esters, and commercial soy biodiesel were determined by DSC. Their thermograms are presented in Figure 5 and average cloud points are given in Table 1. Refined hazelnut oil had only one large, sharp exothermic peak at −32.2 °C, indicating the oil underwent a main crystallization step. However, after transesterification, the cooling curve of hazelnut oil methyl esters showed an average initial exothermic peak at −14.7 °C. This peak corresponded to the first stage of crystallization and cloud point corresponded to the onset of crystallization. Further, major crystallization peak shifted from −32.2 °C to −39.7 °C after converting triglycerides to methyl esters. The hazelnut oil-based biodiesel had a melting peak at −30.5 °C. For commercial soy biodiesel, average initial crystallization occurred at −4.08 °C, and no major crystallization was observed. Soy-based biodiesel had a melting peak at 1.7 °C. The significantly lower cloud point of hazelnut oil-based biodiesel, compared to soy-based biodiesel, was a result of the lower content of saturated (palmitic and stearic) acids in hazelnut oil.

The heat of combustion refers to available energy in a fuel (Zheng and Hanna, 1996). The average heat of combustion of refined hazelnut oil was 39.95 kJ/g (Table 1). Transesterification
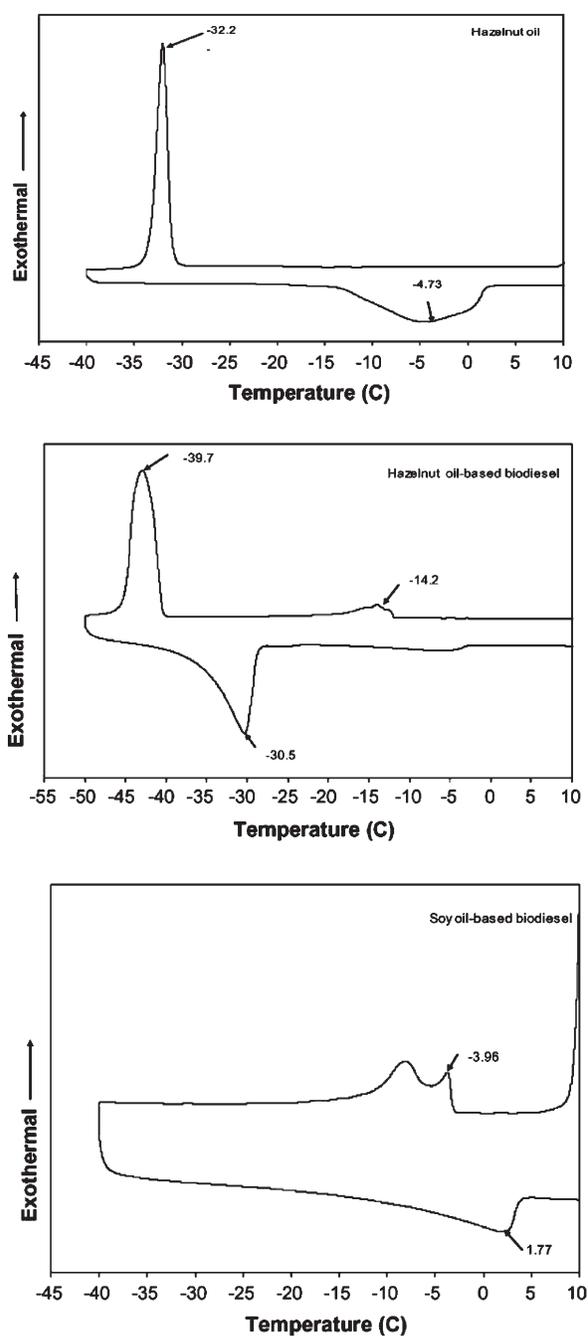

Figure 5. The DSC cooling and heating curves for cloud point of hazelnut oil, biodiesel and commercial soy oil-based biodiesel.

significantly increased average heat of combustion to 40.23 kJ/g for hazelnut oil methyl esters. There was no difference between of the heat of combustion of hazelnut oil methyl esters and their soy counterpart. Diesel fuel had a heat of combustion of 45 kJ/g (Dmytryshyn et al., 2004). Therefore, hazelnut oil and it methyl esters contained approximately 88% the energy content of diesel fuel.

Gas chromatograms of hazelnut oil and its methyl esters are presented in Figure 6. It was found that the fatty acid pro
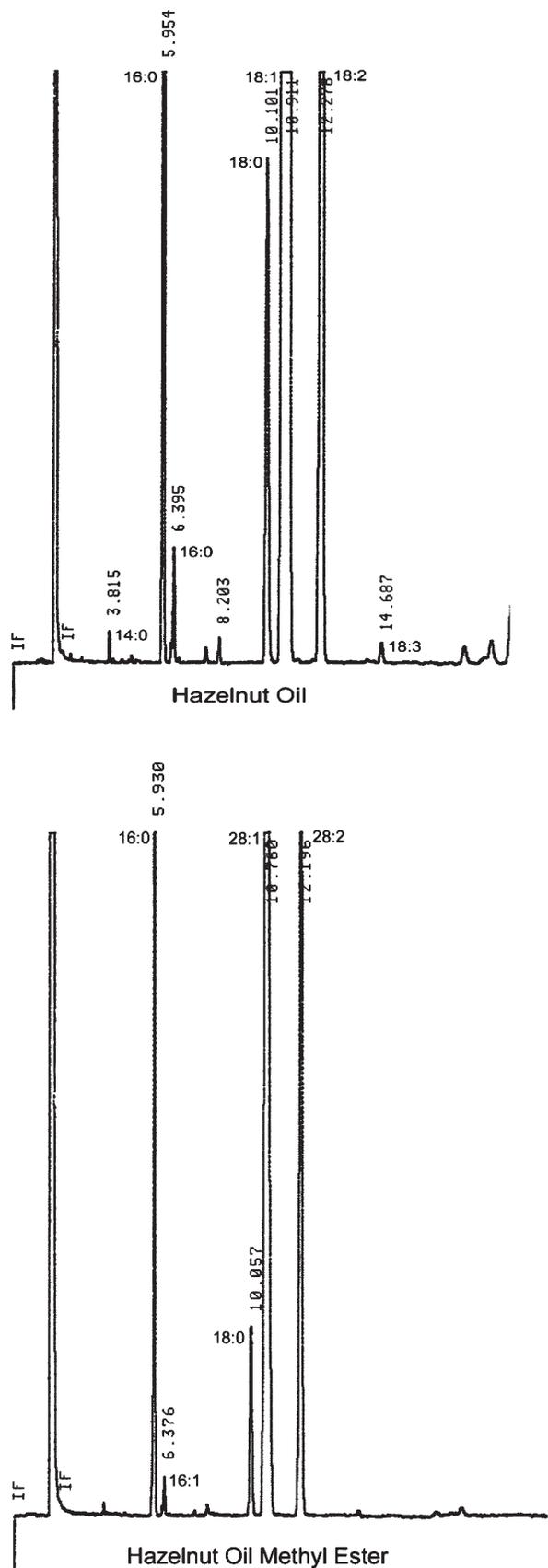
file did not change with transesterification. Oleic acid still was the predominant fatty acid, and oleic and linoleic acids comprised more than 90% of the fatty acid composition.

4. Conclusions

Hazelnut oil-based biodiesel was synthesized. In the presence of excess methanol, high reaction temperature, especially close to the boiling point of methanol (65 °C), had a positive effect on the yield of methyl esters. When the reaction was conducted for 80 min at 65 °C, 99% yield was obtained. The transesterification reaction occurred rapidly in the initial 20 min. The reaction rate became slower with increasing time. The methyl esters yield increased with the catalyst concentration increasing from 0.1 to 0.7 wt%. Excess catalyst resulted in a decrease in biodiesel yield due to the formation of soap. The viscosity (8.82 cP at 25 °C) of hazelnut oil-based biodiesel was slightly higher than that of the commercial soy oil-based biodiesel (7.92 cP at 25 °C). However, an approximate 12 °C higher onset oxidative temperature and a 10 °C lower cloud point of hazelnut oil diesel than those of its commercial soy counterpart implied good oxidative stability and flowability at low temperature. Hazelnut oil-based biodiesel had an average heat of combustion of 40.23 kJ/g, and accounted for approximately 88% of energy content of diesel fuel. The fatty acid composition of hazelnut oil diesel was the same as nature oil. Based on the analyses performed, the hazelnut oil is an excellent feedstock for biodiesel production.

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Figure 6. Gas chromatograms of hazelnut oil and its methyl ester.

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