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Research Article

Geoffroea decorticans for Biofuels: A Promising Feedstock

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In this work, chañar (*Geoffroea decorticans*) fruit is evaluated as a potential feedstock for biodiesel and biomass pellets production with reference to some relevant properties. The fatty acid profile of this oil (83% unsaturated acids) is found to be comparable to similar seed oils which have been attempted for biodiesel production. As a result, the methyl esters (biodiesel) obtained from this oil exhibits high quality properties. Chañar biodiesel quality meets all other biodiesel international standards (ASTM D6751 and EN 14214). Moreover, the husk that surrounds the kernel showed a high potential for usage as densified solid fuels. The results demonstrate that chañar husks pellets have a higher calorific value when compared with other biomass pellets, typically, approximately 21 MJ kg^{-1} with 1.8% of ashes (which is equivalent to that obtained from the combustion of pellets produced from forest wastes). This study indicates that chañar can be used as a multipurpose energy crop in semiarid regions for biodiesel and densified solid fuels (pellets) production.

1. Introduction

Biomass and biofuels production are growing industries as interest in sustainable fuel sources is increasing. Based on the positive energy balance, biofuels (e.g., biodiesel and biomass pellets) are shown to be sustainable due to the fact that their combustion does not contribute to any net increase in atmospheric carbon dioxide, since no carbon is added to the current carbon cycle [1, 2]. Biodiesel is biodegradable, nontoxic, and renewable, possesses inherent lubricity, and substantially reduces particulate emissions and air toxins [3, 4]. On the other hand, biomass pellets are relatively cleaner and safer compared to coal [5]. They do not release air polluting gases such as sulfur oxide. Also, storage and transportation of biomass pellets are not as complicated. In spite of that, destruction of natural habitats and competition for agricultural land resulting from energy crop plantation are relevant issues which require further attention.

The mechanized and large-scale production of energy crops is not feasible for many developing countries due to food security concerns [6]. This is particularly inappropriate when high quality soils are predominantly used for energy crop production and not available for food production. One of the ways to reduce the dependence on agricultural lands utilized to produce biofuels is to use raw materials from plants suitable to grow on low quality soils [7].

There are large quantities of arid and semiarid lands around the world. Furthermore, every year this amount increases due to desertification and the abandonment of agricultural lands by farmers [8]. Some nonedible plants, suitable to grow in these lands, have an additional advantage over conventional crops like drought-resistance and ability to survive on abandoned and fallowed agricultural lands [9, 10]. This would provide extra income for the local farmers without affecting the fertile land used for other crops.

Geoffroea decorticans (chañar), belonging to Leguminosae plant family, is a valuable and well-known tree in the semiarid regions of the Great Chaco vegetation [11, 12]. This species grows in Paraguay, southern Peru and Bolivia, northern half of Chile, southern Uruguay, and northern to central south-east of Argentina [13]. The fruits have provided a good food source for humans and their animals in rural communities since a long time and the leaves, flowers, and bark have several uses in popular medicine [13]. The fruit contains a single high-oil seed inside a woody husk (Figure 1). Oil of these seeds has the potential to become biodiesel while the woody

Figure 1: Appearance and size of chañar seeds (kernel).

husk may be used to produce densified solid fuels (pellets), both with high value as biofuels. However, there are no commercial cultivations of this leguminous tree yet. Therefore, there is lack of information on the quality of biofuels obtained from these raw materials and their agronomic requirements.

The objective of this study was to evaluate the quality of biofuels (biodiesel and biomass pellets) obtained from the fruits of chañar.

2. Materials and Methods

2.1. Vegetable Source. Mature fruits of chañar were collected from Elqui Province, Coquimbo Region, Chile. The average annual rainfall in the study area is approximately 104 mm (with June being the wettest month with 25.9 mm). Estimated evaporation is 1220 mm a year, with a maximum of 172 mm in January and a minimum of 47 mm in June. The dry season lasts nine months. The average monthly temperature stays above 10°C throughout the year [14].

2.2. Extraction of the Oil. All chemicals and reagents used for analysis and reactions were of analytical reagent grade and were purchased from Merck Ltd.

The mesocarp (pulp) and the endocarp (hard cover) of the chañar fruits were removed by hand to obtain the seeds (kernels). The seeds samples were then dried in an oven at 45°C for 48 h. To extract oil from seeds, a screw press (IBG Monforts Oeokotec Komet model CA59G) was used. The oil extraction was performed at 60°C to liquefy the oil contained in the seeds tissues, facilitating the process and decreasing the action of lipase enzymes that increase the level of free fatty acids and, therefore, the oil acidity. The remaining oil in the seed cake was extracted using n-hexane and a Soxhlet apparatus for 8 h. The solvent was evaporated in a rotary evaporator under reduced pressure and N_2 flow. The relative oil content was gravimetrically calculated on a dry seed weight basis using the equation:

$$\%\ \text{oil content} = \frac{\text{weight of oil obtained (g)}}{\text{weight of sample (g)}} \times 100. \quad (1)$$

The obtained oil percentage was used to estimate the amount of oil present in the seed based on biomass. The oil was stored at 4°C until further analysis could be conducted. The extracted oil was used for (i) determination of seeds oil content, (ii) preparation of biodiesel, and (iii) determination of biodiesel quality properties.

Table 1: Summary of test methods used for quality determination of chañar biodiesel.

Physical and chemical properties	Test methods
Flash point (°C)	ASTM D-93
Free glycerin (% mass)	ASTM D-6584
Total glycerin (% mass)	ASTM D-6584
Acid number (mg KOH/g oil)	ASTM D-664
Kinematic viscosity, 40°C ($mm^2\ s^{-1}$)	ASTM D-445
Density, 15°C ($g\ mL^{-1}$)	ASTM D-1298
Sulfur content (% mass)	ASTM D-4294
Methanol content (% volume)	EN 14110
Oxidation stability (min.)	EN 14112
Pour point (°C)	ASTM D-97
Gross calorific value ($MJ\ kg^{-1}$)	ASTM D-240

2.3. Transesterification Reaction. The transesterification reaction was carried out as described by Freedman et al. [15] using methanol as the alcohol reactant due to its physical and chemical advantages as the shortest chain alcohol that can quickly react with triglycerides. Sodium hydroxide (NaOH) was used as a catalyst. A 6 : 1 methanol to oil molar ratio and 1.0% of NaOH by oil weight were mixed together and added to the oil. The reaction mixture was stirred in an electric stirrer for 1 h at room temperature and left for phase separation. After separation into two phases, the lower glycerol phase was removed and the upper methanol phase was washed several times with distilled water for removal of the excess reactants and catalysts. The moisturized fuel product was dried by air bubbling. The dried fuel product was then tested.

The yield (% basis) of the transesterification process was calculated as the total weight of methyl esters divided by the total weight of oil in the sample.

2.4. Biodiesel Analysis and Testing. The fatty acid profile of the chañar oil and biodiesel was analyzed by gas chromatography coupled with mass spectrometry according to [16].

The methyl ester of chañar oil as a biodiesel product was analyzed for physical and chemical properties according to the international diesel standards [17]. The flash point, free and total glycerin content, acid number, kinematic viscosity, and sulfur content were determined by the American Society for Testing and Materials (ASTM) methods (ASTM D6751). The density of chañar biodiesel was tested by a hydrometer at 15°C. Test methods are listed in Table 1.

2.5. Preparation of the Chañar Husks and Pelletization. The woody husk of chañar was broken down into particles using a wood particle mill. For homogenization of particle size, a sieve having 4 mm sieve diameter was used during grinding. The pellets were manufactured using a laboratory type pelleting machine. Tests for determining physical-mechanical and thermal properties of pellets were measured for determining

Table 2: Detailed profile of the fatty acids of chañar oil and biodiesel obtained from transesterification reaction with methanol.

Fatty acids	Structure	Chañar oil (wt%)	Chañar biodiesel (wt%)
Palmitic	16 : 0	9.5	8.9
Stearic	18 : 0	3.8	4.3
Oleic	18 : 1	40.5	46.5
Linoleic	18 : 2	42.3	37.6
Arachidic	20 : 0	0.9	0.7
Gadoleic	20 : 1	1.3	0.9
Behenic	22 : 0	1.2	1.4
Lignoceric	24 : 0	0.8	0.7
	Total saturates	17	16
	Total unsaturates	83	84
	18 : 1/18 : 2	0.96	1.24

the quality of raw material and pellets. The EN 14774-1 test procedure was applied to determine the moisture content of the raw material. Ash content of the chañar husk was determined based on EN 14775 EU standards and nitrogen and sulfur content was determined according to EN 15104. The high heating value (HHV) of the chañar husk was determined using the PARR 1266 Bomb Calorimeter according to EN 14918 EU standards. The soluble chlorine content was calculated by using a Mettler Toledo compact titrator G20 with silver nitrate as a reaction agent.

The pellets of the chañar husk were cylindrical in shape. In order to determine dimensions, the length and diameter of each sample were measured using a digital vernier caliper.

Bulk density of the chañar husk pellets was calculated according to the EU norms EN 15103. Mechanical durability of the pellets was determined by mass loss of samples according to EN 152010-1 EU standards.

3. Results and Discussion

Chañar seeds have a very high oil content (44.8%) which makes them a good potential candidate for producing feedstock oils for biodiesel. The high product recovery percentage (88.6%) indicated that product loss due to saponification was very low.

The FAME composition of oil and biodiesel is shown in Table 2. The chañar biodiesel had a fatty acid composition similar to their raw materials, confirming the efficiency of the conversion of triglycerides to methyl esters. Eight fatty acids were identified in seed oil. Oleic and linoleic acids were predominantly detected in the seeds of chañar. Chañar oil and biodiesel were found to be highly unsaturated (83% and 84%, resp.), which is a desirable quality, since several studies suggest that unsaturated acids show better lubricity than saturated species [18, 19].

Chañar oil and biodiesel are specially rich in 9-octadecenoic (oleic, 18 : 1) and 9,12-octadecadienoic (linoleic, 18 : 2) acids, representing about 83% of the total FAME content. In addition, palmitic (16 : 0) and stearic (18 : 0) acids are found in moderate amounts. The oleic to linoleic (O/L) ratio of oil and biodiesel is 0.96 and 1.24, respectively. Saturated acids are mainly composed of octadecanoic (stearic, 18 : 0) and hexadecanoic (palmitic, 16 : 0) acids. Additionally, tetracosanoic (lignoceric, 24 : 0), docosanoic (behenic, 22 : 0), eicosenoic (gadoleic, 20 : 1), and eicosanoic (arachidic, 20 : 0) acids were detected at low concentrations. No unusual fatty acids were found.

Table 3: Properties of Chañar biodiesel compared to ASTM D6751 or EN 14214 standards.

Property	Units	Result	ASTM or European standard
Flash point	°C	138	130 min
Total glycerine	% mass	0.17	0.24 max
Free glycerine	% mass	0.006	0.02 max
Acid number	mgKOH/g oil	0.38	0.50 max
Kinematic viscosity, 40°C	$mm^2\ s^{-1}$	3.14	1.9–6.0
Density	$g\ mL^{-1}$	0.85	0.86–0.90
Sulfur content	% mass	0.01	0.05 max
Methanol content	% volume	0.18	0.2 max
Oxidation stability, 110°C	min	2.8	3.0 min
Pour point	°C	0.91	*
Gross calorific value	$MJ\ kg^{-1}$	44.4	35 min

*Not specified.

3.1. Physical and Chemical Properties of Chañar Biodiesel. The physicochemical properties of chañar biodiesel are shown in Table 3, and these values were compared with the specifications of the American Society for Testing and Materials (ASTM D6751) and European Committee for Standardization (EN 14214).

Flash point is a fuel property related to safety issues involved in fuel handling and storage. It is also indicative of the amount of residual unreacted alcohol remaining in the finished fuel. The flash point of chañar biodiesel was 138°C which met the ASTM specification. This parameter was enhanced by improving the process of removal of unreacted alcohol remaining in the biodiesel through successive washes with distilled water [20].

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 feedstock incompletely converted during the transesterification process.

The total glycerin content was 0.17 wt.% and the free glycerin content was less than 0.006 wt.%, well within ASTM specifications.

With respect to acid number, if this parameter is too high, excessive engine corrosion can occur. The total acid number was relatively low in chañar biodiesel and was consistent with the limits established by ASTM D6751 standard.

The kinematic viscosity is important for proper transport of fuel from tank to engine. In general, kinematic viscosity of biodiesel is higher than that of conventional diesel. Thus,

Table 4: Characteristics of chañar husk before pelleting.

Parameter	Avg	SD	EN plus B standard
Ash content (w-%)	1.8	0.09	≤2.0
N (w-%)	0.36	0.05	≤1.0
S (w-%)	0.11	0.00	≤0.05
HHV (MJ kg^{-1})	21.2	0.65	≥16.0
Cl (w-%)	0.02	0.00	≤0.03

Table 5: Characterization of chañar husk pellets.

Parameter	Avg	SD	EN plus B standard
Durability (w-%)	99.4	0.30	≥97.5
Diameter (mm)	8	0.45	8 ± 1
Length (mm)	24.6	2.41	$3.15 < L \leq 40$
Bulk density (kg m^{-3})	708.7	12.1	600 ≤ BD ≤ 750
Moisture (w-%)	9.01	0.26	≤10

biodiesel is more affected by use in cold climate areas. The kinematic viscosity of chañar biodiesel at 40°C was 3.14 mm^2 s^{-1}, which is well within the ASTM specification.

The density of chañar biodiesel was 0.85 g mL^{-1}, which is in the range of typical biodiesel from vegetable oils and is lower than those reported for castor bean biodiesel (0.92 g mL^{-1}), a plant species commonly used as feedstock for biodiesel [21]. It should be noted that species desirable for the biofuel industry have low-density values [22]. According to Gunstone [23], the density is higher when the oil is more highly unsaturated.

The sulfur content of fuels is associated with emissions of sulfur dioxide. Chañar is not a plant that contains high sulfur in its structure, so the sulfur content of chañar biodiesel was only 0.01% (or well under the 0.05% sulfur specification). Because the chemical structure of fatty acid methyl esters of biodiesel ages faster than conventional diesel, it is essential to determine the oxidation stability of biodiesel. This quality parameter is closely related to the viscosity and acid number of biodiesel [24]. The oxidation stability reported is below the ASTM specification. In general, biodiesel has a relatively high pour point compared to conventional diesel. Thus, special precautions have to be taken in cold weather areas to avoid gelling and formation of crystals in the fuel system. The extent to which pour point is higher than typical conventional diesels depends on the raw oil source. Chañar biodiesel showed a pour point of 0.91°C. Therefore, if it is used in its pure form, it should be incorporated with an additive to prevent solidification of saturates and formation of crystals. Chañar biodiesel showed a gross calorific value of 44.4 MJ kg^{-1} which is very similar to the value found in the conventional diesel and meets widely the EN 14214 standard.

3.2. Characteristics of Chañar Husk. The results from the analyses are summarized in Table 4 which shows the average values of the parameters.

Regarding the ash content, chañar husk (1.8%) showed common ash values for woody materials [25] and was below the allowable maximum value. Nitrogen content (0.36%) and chlorine content (0.02%) showed similar values to those obtained from woody materials and fulfilled the limits of the EN plus B standard. However, the sulfur content (0.11%) is higher than the maximum allowed by this standard. Therefore, this raw material could not be used in nonindustrial boilers. The HHV associated with the chañar husk samples is observed to be higher (21.2 MJ kg^{-1}) than that of other biomass residues like straw, pine sawdust, or vineyard pruning, for which HHV ranges from 17.8 to 19.7 MJ kg^{-1} [26].

3.3. Characterization of the Pellets. The characterization of the pellets is shown in Table 5. The pellets displayed a high value of durability (99.4%). This is attributed to remnants of fruit pulp that remains in the husk, which acts as an effective binding agent.

Since all the pellets were made with pellet die of 8 mm in diameter, they fulfilled the requirements established for this parameter. The same occurred with the pellet length, which ranged between 28.2 to 30.6 mm. Despite the differences, all the pellets tested showed a length within the range between 3.15 and 40 mm established by EN plus B. The ratio length/diameter was calculated because of the guideline in EN 14961-1 which establishes 5 as a maximum value for diameters of 6 mm and 4 for those of 8 mm of diameter. All the samples fulfilled this guideline, with an average value of 3.1.

Bulk density is an important parameter because of being related to the space required for storage and transport, as well as to the derived cost for transport. EN plus B established a minimum for nonindustrial pellets of 600 kg m^{-3}. This requirement was fulfilled by all the samples.

The moisture content of the pellets is limited by EN plus B with a maximum value of 10%. Pellets made from chañar husk fulfill this requirement, showing moisture contents lower than this limit.

4. Conclusions

Chañar seeds have high oil content and a woody husk, both with high potential as raw material to become valuable biofuels. This would allow that chañar can be used as a multipurpose energy crop for biodiesel and biomass pellets production.

The parameters analyzed for chañar biodiesel are consistent with the ASTM D6751 and EN 14214 standards and, in some cases, are better when compared with traditional oil seeds (e.g., castor bean).

In addition, the results demonstrated that chañar husks pellets have a higher calorific value and a lower ash content when compared with other biomass pellets. As a consequence of the high content of fruit pulp that remains in the husk, there is no need to add binders or other additives for the production of chañar pellets, showing a high durability value.

The findings of this work address the objectives of sustainable biofuels production using an underexploited and neglected but highly adapted marginal leguminous tree. Chañar cultivation would enable the energy supply to rural and isolated areas, especially in semiarid regions of Chile, where conventional crops are difficult to produce. However, further studies are needed for a better understanding of their productivity and commercial exploitation of this multipurpose energy crop in semiarid areas.

Competing Interests

The authors declare that they have no competing interests.

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