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Biodiesel from *Citrus reticulata* (mandarin orange) seed oil, a potential non-food feedstock☆

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ABSTRACT

Oil extracted from *Citrus reticulata* (mandarin orange) seeds was investigated as a potential feedstock for the production of biodiesel. The biodiesel fuel was prepared by sodium methoxide-catalyzed transesterification of the oil with methanol. Fuel properties that were determined include cetane number, cloud, pour, and cold filter plugging points, kinematic viscosity, oxidative stability, flash point, sulfur content, ash content, density and acid value. The citrus seed oil methyl esters were found to satisfy both ASTM D6751 and EN 14214 biodiesel standards. The NMR spectra of the methyl esters of *C. reticulata* seed oil are reported.

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1. Introduction

The availability of large scale refining contributed towards petrodiesel becoming the primary fuel for diesel engines during the 20th century and in the beginning of the 21st century, with a large portion of the diesel fuel consumed by the transportation sector. The economics are changing, however, owing to “peak oil” and geopolitical issues. These factors have led to researchers investigating alternate sources of fuel for diesel engines.

Biofuels are produced from organic matter (including plant parts and residues of agricultural crops, municipal wastes and/or by-products of agriculture and forestry). These may be liquid or gaseous fuels. The liquid fuels may be divided into the following categories: (i) vegetable oils and biodiesel; (ii) alcohols; and (iii) bio-crude and synthetic oils. These liquid fuels can provisionally be used in the transport sector as an alternative to compressed and liquid natural gas and liquefied petroleum gas (Balat, 2008). Thus, biodiesel is a viable alternative diesel fuel (Mittelbach and Remschmidt, 2004; Knothe et al., 2010). Biodiesel is non-toxic, biodegradable, possesses inherent lubricity, and a high flash point, besides being free of sulfur and aromatic compounds. Moreover, the use of biodiesel in diesel engines results in a noticeable reduction in unburned hydrocarbons, carbon monoxide (CO) and particulate matter (PM) emissions while oxides of nitrogen (NO_x) are increased. Issues with biodiesel include low oxidative stability and poor cold flow properties besides supply and availability. Biodiesel can be produced by transesterification with an alcohol of various feedstocks such as vegetable oils, animal fats, waste or recycled oil, tallow, and restaurant greases. Non-edible oils such as *i.e. Jatropha curcas* (Rashid et al., 2010), *Cucumis melo* (Rashid et al., 2011a,b), *Hibiscus esculentus* (Rashid et al., 2010), *Thespesia populnea* (Rashid et al., 2011a,b), *Moringa oleifera* (Rashid et al., 2008b), *Carthamus tinctorius* (Rashid and Anwar, 2008), *Hevea brasiliensis* (Ramadhas et al., 2005), *Pongamia pinnata* (Karmee and Chadha, 2005), *Thlaspi arvense* (Moser et al., 2009), *Camelina sativa* (Moser and Vaughn, 2010a) and *Coriandrum sativum* (Moser and Vaughn, 2010b) have found increasing attention as potential feedstocks.

Citrus plants belong to the Rutaceae family and include *Citrus reticulata* (sweet mandarin), *Citrus sinensis* (sweet orange), *Citrus*

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paradisi (grapefruits), and *Citrus limon* (lemons), all of which are among the most popular fruits in the world especially in tropical and sub-tropical countries (Anwar et al., 2008). In Pakistan, *C. reticulata* is locally known as "kinnow". Large varieties of citrus fruit are produced in many countries within Southeast Asia (Anwar et al., 2008). Citrus is the best natural source of Vitamin C (ascorbic acid) and folic acid, besides being an excellent source of fiber (Matthaus and Özcan, 2012). The main purpose of citrus fruits is to produce citrus juice, however, the waste of the citrus industry such as peel, seeds and pulps are also a potential source of by-products (Anwar et al., 2008; El-Adawy et al., 1999). In another study, pulp of *C. reticulata* was used as a potential sorbent for Cr(III) and Cr(VI) (Zubair et al., 2008). Citrus seeds are also used in the food industry, cosmetics and medicine (Schulz et al., 2002; Silalahi, 2002; Saïdani et al., 2004).

Various reports in the literature on the fatty acid profiles of various citrus seed oils such as those of *C. sinensis* and *C. paradisi*, besides that of *C. reticulata*, show that palmitic, oleic and linoleic acids, besides lesser amounts of stearic and linolenic acids, are the most common fatty acids in these seed oils (Anwar et al., 2008; El-Adawy et al., 1999; Filsoof and Mehran, 1976; Neto and Mancini, 1982; Ajewole and Adeyeye, 1994; Saïdani et al., 2004; Mahmud et al., 2006; Jiao et al., 2007; Li et al., 2008; Waheed et al., 2009). Fatty acids such as lauric, myristic, palmitoleic and eicosanoic, however, have also been reported in smaller amounts, usually <1% in these seed oils (Anwar et al., 2008; El-Adawy et al., 1999; Jiao et al., 2007; Waheed et al., 2009). Thus, citrus seed oils resemble major commodity oils such as palm, rapeseed/canola and soybean in terms of the major fatty acids although the amounts vary. The fruit sac lipids of citrus fruits also largely consist of these fatty acids (Nordby and Nagy, 1974).

Citrus seeds are commonly rendered useless and are discarded. The discarded citrus seeds, however, may be economically utilized to extract citrus seed oil which may reduce the cost of biodiesel production in comparison to conventional sources of vegetable oils. Citrus seeds average approximately 30% oil (by weight) although the oil content varies greatly with the particular citrus variety. Globally, the production of citrus is estimated to be 105 million metric tons (MMT) per annum, Brazil being the largest producer (19.2 MMT) followed by the United States. Pakistan, with an annual production of about 1.76 MMT of citrus fruits, stands among the top ten citrus producing countries of the world (Kamal et al., 2011). In Pakistan, 199.9×10^3 ha are under citrus cultivation with 2132.2×10^3 metric tons of annual production and Punjab being the major producer (Anonymous, 2010). Dried citrus pulp was reported to contain an average of 4.8% seeds (Ammerman et al., 1963) so that world-wide 0.072 MMT are produced annually.

Continuing previous work on non-food oils as potential biodiesel feedstocks (Rashid and Anwar, 2008; Anwar et al., 2010; Rashid et al., 2008b, 2010, 2011a,b), the objective of the present work was to evaluate *C. reticulata* seed oil within this context. *C. reticulata* methyl esters (CiRME) as biodiesel were prepared from citrus seeds using alkaline catalysis as well as fuel properties such as kinematic viscosity, oxidative stability, cetane number (CN), acid value, flash point, cloud-, pour-, and cold filter plugging points, copper strip corrosion, ash content, density and sulfur content determined and compared with both ASTM D 6751 (ASTM, 2012) and EN 14214 (CEN, 2012) biodiesel standards.

2. Experimental

2.1. Materials

C. reticulata seeds were collected in Faisalabad, Punjab, Pakistan. The seeds were cleaned manually to remove pulp and other unwanted materials. The seeds were stored in suitable bags at ambient temperature prior to extraction. Pure standards of fatty acid methyl esters (FAMEs) were purchased from Sigma Chemical Company (St. Louis, MO, USA). Other analytical grade chemicals and reagents used were acquired from Merck Chemical Company (Darmstadt, Germany).

2.2. Extraction of citrus oil

The seeds in each batch (500 g) of *C. reticulata* were crushed using a grinder to give a mean particle size of the milled seeds of 0.8 mm. The ground sample (50 g) was then extracted with *n*-hexane for 6 h in a Soxhlet extractor. Excess extraction solvent was removed under reduced pressure using a rotary evaporator at 45 °C and the oil recovered.

2.3. Pre-treatment of citrus oil

The citrus oil had an acid value of 2.80 mg KOH g^{-1}, necessitating an acid pre-treatment step using a previously reported procedure (Rashid et al., 2009a). The acid value of the product was determined over a period of time until less than 1% was achieved for the base catalyzed transesterification process to be carried out.

2.4. Transesterification process

A freshly prepared methanolic solution of sodium methoxide catalyst was added to the calculated amount of methanol and mixed until completely dissolved. The resulting solution was poured to the pre-heated citrus oil (250 g) and this mixture stirred at 720 rpm and 60 °C with a 6:1 molar ratio of methanol/citrus oil for 1 h. The reaction mixture was then transferred to a separatory funnel and allowed to cool to room temperature with separation of the two phases. The upper layer consisted of methyl esters and the lower phase contained glycerol along with other materials such as excess methanol, catalyst, soaps formed during the reaction as well as some entrained methyl esters and partial glycerides. The methyl esters were purified by distilling off residual methanol. Traces of remaining catalyst, methanol and glycerol were removed by successive washes with distilled water. The esters were then dried with Na_2SO_4, followed by filtration.

2.5. Analytical procedure

The fatty acid profile of citrus seed oil and its esters was determined using a previously developed gas chromatography (GC) method (Rashid and Anwar, 2008) using a 2010 Shimadzu GC (Japan) equipped with FID detector and BPX70 (SGE International, Australia) column (30 m × 0.32 mm i.d.; film thickness 0.25 μm). Carrier gas (nitrogen) was used at a flow rate of 1.0 mL min^{-1}. The temperature program was set from 80 to 220 °C at a rate of 10 °C min^{-1}. Initial and final temperatures were held for 1 and 10 min, respectively. Injector and detector temperatures were set at 230 °C and 240 °C, respectively. NMR spectra were obtained on a Varian (Palo Alto, CA, USA) VNMR spectrometer operating at 500 MHz (^{1}H-NMR) with $CDCl_3$ as solvent.

2.6. Fuel properties of citrus seed oil methyl esters (CiRME)

The fuel properties of the CiRME were determined following ASTM and EU methods: cloud point (ASTM D2500), pour point (ASTM D97), kinematic viscosity (ASTM D445), oxidative stability (EN 14112), CN (as derived CN: ASTM D6890), cold filter plugging point (ASTM D6371), ash content (ASTM D874), flash point (ASTM D93), density (ASTM D5002), sulphur content (ASTM D4294), copper strip corrosion (ASTM D130) and acid value (ASTM D664).