Biotechnology Reports xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Biotechnology Reports

journal homepage: www.elsevier.com/locate/btre

Biodiesel production over a catalyst prepared from biomass-derived waste date pits

Ala'a H. Al-Muhtaseb[a,*], Farrukh Jamil[a,b,*], Lamya Al-Haj[c], Myo Tay Zar Myint[d], Eyas Mahmoud[e], Mohammad N.M. Ahmad[f], Ahmad O. Hasan[g], Sikander Rafiq[b]

[a] Department of Petroleum and Chemical Engineering, College of Engineering, Sultan Qaboos University, Muscat, Oman
[b] Department of Chemical Engineering, COMSATS University Islamabad, Lahore, Pakistan
[c] Department of Biology, College of Science, Sultan Qaboos University, Muscat, Oman
[d] Department of Physics, College of Science, Sultan Qaboos University, Muscat, Oman
[e] Department of Chemical and Petroleum Engineering, College of Engineering, United Arab Emirates University, Al-Ain, United Arab Emirates
[f] Department of Chemical Engineering, Faculty of Engineering and Architecture, American University of Beirut, Lebanon
[g] Department of Mechanical Engineering, Faculty of Engineering, Al-Hussein Bin Talal University, Ma'an, Jordan

ARTICLE INFO

Article history:
Received 8 June 2018
Received in revised form 28 September 2018
Accepted 28 September 2018

Keywords:
Biodiesel
Green catalyst
Alkaline earth metal oxide
Waste date biomass
Biomass-derived fuel

ABSTRACT

Date palms are predominately produced in arid regions and the date pits, or seeds, produced from them are sometimes considered to be a waste. Date pits, ground to powder following an oil extraction, were used to synthesize a renewable heterogeneous catalyst. The green carbon catalyst was modified by an alkaline earth metal oxide (CaO). The oil extracted from date pits was transformed into biodiesel. The biodiesel process was optimized and the optimal yield was 98.2 wt% at a reaction temperature of 70 °C, reaction time ~120 min, methanol to oil molar ratio of 12 and catalyst loading of 4.5 wt%. The quality of the produced biodiesel meets the standard limits set by regulating agencies (ASTM, EU) which indicates its suitability to be used as a fuel. Thus, it can be concluded that the green carbon catalyst synthesized from waste date pits has a high potential for biodiesel production.

1. Introduction

Currently, fossil fuels are the major contributor fulfilling the total world energy demand; and they remain the main source of the global energy supply scenario [1–3]. Due to the industrial revolution in the last century, which increased economic activity, energy demand and consumption [4], fossil-based carbonaceous fuel was a major source for energy production and transportation purposes [5]. However, the demand for fossil-based fuel increased drastically owing to a rapid increase in industrialization and human population. This rapid increase in oil consumption increased attention towards the availability and environmental issues due to the burning of fossil-based fuels. Hence, renewable and sustainable resources such as wind, biomass, and solar energy can decrease some concerns related to fossil fuels [6]. Moreover, among all alternative energy resources mentioned, biomass is the most suitable alternative based on the fact that it is an enriched source of carbon besides fossil-based resources, which leads to its uniqueness.

Utilization of biomass as an energy source is one medium to reduce concerns related to fossil-based fuels usage and can also help to reduce the energy crises faced worldwide. Biomass has been used from ancient ages on a small-scale for domestic usage based on its positive environmental effects and high energy density and its applications for biofuels, chemicals, and materials [7]. This requires special focus from different sectors across the world such as industrial, academic, national laboratories, non-profit organization and governing authorities so as to increase the awareness regarding the usefulness of biomass in different aspects.

Date palm is considered the main crop in Oman and occupies 54% of total agricultural land in the country [8,9]. Oman has great potential to supply and utilize waste from dates as biomass for biofuel production. This source of biomass has excellent potential as an alternative energy resource as it avoids the use of the edible parts of the plant and does not compete with the food supplies for biofuel production. The by-product of date fruit processing is the date pits which are largely available and cheap. They can, therefore, be used as a source for producing biofuel. The residues of date palm tree and spoiled dates comprise economic and environmental burden to be managed. Interestingly, date pits contain volatile

* Corresponding authors at: Department of Petroleum and Chemical Engineering, College of Engineering, Sultan Qaboos University, Muscat, Oman.
E-mail addresses: muhtaseb@squ.edu.om (A.H. Al-Muhtaseb), fjamil44@gmail.com, fjamil@cuilahore.edu.pk (F. Jamil).

https://doi.org/10.1016/j.btre.2018.e00284

compounds that make up 15–20 % of the material and can serve as a potential source for biofuel production.

The use of heterogeneous catalysts for the production of biodiesel is an important aspect to be taken into account for the economics of the commercial production of biodiesel [10–12]. Heterogeneous catalyst use for the production of biodiesel may yield a high-quality biodiesel and simplify downstream separation steps associated with glycerol which is obtained as by-product and eliminate the need for an aqueous quench [13–15]. Heterogeneous catalysts are easily separable from the reaction mixture and can be reused which makes the biodiesel process more economical [16,17]. The template material is of high importance for synthesizing heterogeneous catalysts and can affect production cost of associated with the process [18]. A number of supports have been studied such as Al_2O_3, CaO, MgO etc. due their high porosity and stability [19–21]. However, biodiesel production can be more eco-friendly and economical if the green catalyst is utilized. Catalysts synthesized from biomass can be suitable alternatives as compared to conventional catalysts for producing economical and eco-friendly biodiesel. Generally, the biomass-derived carbon material is known to be porous in nature and possess a high surface area after small modification and can successfully be used for the transesterification of plant-based oils [22]. Baroutian et al. reported efficient biodiesel production in the presence of activated carbon catalysts from biomass modified by KOH [10]. Dhawane et al. used Flamboyant pods to synthesize the green carbon catalysts and observed it was a highly active catalyst after alkali modification for the transesterification of Hevea brasiliensis oil [23].

Herein we report the use of date pits powder following oil extraction as a source of a carbon catalyst which was modified by an alkaline metal oxide (CaO) and to produce biodiesel. The synthesized carbon catalyst was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), Brunauer-Emmett-Teller analysis (BET) and X-Ray Photoelectron Spectroscopy (XPS). Date pits oil is used as source oil for transesterification in the presence synthesized catalysts for producing biodiesel. Complete characterization of the produced biodiesel was carried out to prove its feasibility as fuel.

2. Experimental

2.1. Materials

Waste date pits were collected from an industrial firm in the city of Muscat in Oman. All the chemicals and reagents were of analytical grade and were purchased from Merck, Germany. Oil was extracted from date pits using a Soxhlet extractor in a 16.5 wt% yield. Hexane was used as a solvent for extraction and process continued for 7 h followed by solvent separation using a rotary evaporator (Buchi, Switzerland) [24]. The fatty acid profile of the date pit oil was determined using a Perkin Elmer Clarus 600 gas chromatograph mass spectrometer (GC–MS) equipped with a DB-Wax column.

2.2. Catalysts synthesis

The date pit powder remaining after extraction was washed thoroughly with distilled water to remove impurities and chemicals and dried at ambient temperature for 5 h followed by oven drying at 110 °C for 12 h to remove the moisture content. Subsequently, a carbonization process was carried out in a muffle furnace under a nitrogen atmosphere at 500 °C for 4 h. After cooling the carbon material at room temperature, it was impregnated with an aqueous solution of calcium nitrate tetrahydrate at different concentrations of Ca (2 wt%, 4 wt%, and 6 wt%) on the carbon material. The resultant material was calcined in a furnace at 450 °C for 4 h with a ramping rate of 3 °C/min. The resultant catalysts were termed as C1 (carbon with 2 wt% CaO), C2 (carbon with 4 wt% CaO), C3 (carbon with 6 wt% CaO) and C for pristine carbon respectively.

2.3. Catalysts characterization

X-ray powder diffraction (XRD) patterns were measured using a PANalytical, Xpert PRO instrument, USA equipped with rotating anode and CuKα radiations. The measurements were conducted in continuous θ/2θ scan refraction mode. A JEOL JSM-7800 F instrument, Japan, scanning electron microscope (SEM) attached with energy dispersive X-ray spectroscopy (EDS, Oxford instrument, UK) was used to determine the surface morphology and surface elemental composition. The BET surface area, pore size and pore volume of samples were measured using a Micromeritics Instrument Inc. ASAP 2020 (Norcross, GA, USA) using N_2 gas (99.995% pure). X-ray photoelectron spectroscopy (XPS, Omicron Nanotechnology, Germany) was utilized to determine the chemical composition of the sample surface. Al Kα with the energy of 1486.6 eV was used as the monochromatic X-ray. A pass energy of 50 eV was used for the survey scan and 20 eV for the high-resolution scan. All of the obtained binding energies were calibrated with respect to the intrinsic carbon peak which has a binding energy of 284.6 eV.

2.4. Biodiesel production and quality analysis

The biodiesel was produced through a transesterification reaction carried out in two-neck flat-bottom flask. In one neck, cooling water line was attached to use as a condenser; in the second neck, a thermocouple was attached through which heating was controlled using a programmed hot plate on which the reaction flask was placed. The transesterification was carried out on oil extracted from date pits in methanol solvent catalyzed by the synthesized heterogeneous catalyst. The process parameters, which include reaction temperature (55–75 °C), methanol to oil molar ratio (6–18), time (30–150 min) and catalyst amount (1.5–7.5 wt%) were varied to optimize the biodiesel yield. The yield of biodiesel was determined using Eq. (1)

$$Yield(\%) = \frac{weight\ of\ biodiesel}{weight\ of\ oil} \tag{1}$$

The pits oil was heated, and then a calculated amount of methanol and catalyst was added to the heated oil. Prior to the addition of a catalyst in the reaction, the mixture was stirred with methanol for 20 min, and then the reaction mixture was stirred at 600 rpm and ran at the specified conditions. Once the reaction was completed, it was allowed to cool down to room temperature (~25 °C). The water condenser was removed from flask along with the thermocouple controlling temperature and the mixture was centrifuging at 5000 rpm for 30 min to remove the solid catalyst. The reaction mixture, after catalyst separation, was poured into a separating funnel and the mixture was allowed to settle for 8 h. It was observed that two liquid phases formed whereby the bottom layer was glycerol and the upper layer was biodiesel. The bottom layer of glycerol was removed and the upper layer was placed in a funnel and washed with warm deionized water to remove any kind of impurities from biodiesel. Then rotary evaporation was used to remove methanol and water left was biodiesel. To remove any residual moisture from the biodiesel, anhydrous sodium sulfate was added and subsequently filtered.

The quality of biodiesel was analyzed by measuring its properties. Density was measured using an Anton Paar instrument (DMA 4500M, USA) according to ASTM D-4052 and a standard