Fuel 110 (2013) 23–31

Contents lists available at SciVerse ScienceDirect

Fuel

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

Green synthesis of hydrocalumite-type compounds and their evaluation in the transesterification of castor bean oil and methanol

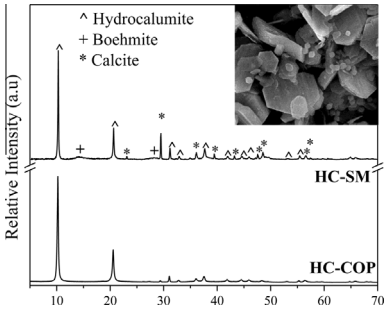
Manuel Sánchez-Cantú [a,*], Lydia M. Pérez-Díaz [a], Nancy Tepale-Ochoa [a], Valeria J. González-Coronel [a], María E. Ramos-Cassellis [a], David Machorro-Aguirre [a], Jaime S. Valente [b]

[a] Benemérita Universidad Autónoma de Puebla, Facultad de Ingeniería Química, Avenida San Claudio y 18 Sur, C.P. 72570 Puebla, Mexico
[b] Instituto Mexicano del Petróleo, Eje Central #152, C.P. 07730 México D.F., Mexico

HIGHLIGHTS

- Hydrocalumite-like compounds prepared by a simple and environmentally-friendly method.
- Catalyst precursor for biodiesel production.
- Thermal treatment enhanced biodiesel obtaining.
- Full conversion of the raw materials was achieved with the annealed sample at 700 °C.
- The catalyst deactivation was caused by the active phase leaching.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 March 2012
Received in revised form 15 June 2012
Accepted 19 June 2012
Available online 2 July 2012

Keywords:
Transesterification
Biodiesel
Anionic clay
Hydrocalumite

ABSTRACT

The search for alternative sources of energy is more important than ever as the extraction of petroleum, the greenhouse gas emissions and the climate changes are getting extremely complicated an unsafe for mankind. In order to find renewable, cheaper and easier methods to obtain energy, a hydrocalumite-type compound was synthesized by a green method here presented and evaluated in the transesterification of castor oil with methanol to obtain biodiesel. The pristine material and its thermally decomposed products were analyzed by X-ray powder diffraction, thermogravimetric analysis and Scanning Electron Microscopy. Biodiesel conversion was determined by ^{1}H NMR. The effect of the precursors' thermal activation on biodiesel production was evaluated at 300, 500 and 700 °C. Similar results were obtained with the solids produced by a conventional method, demonstrating that the materials prepared by the new technique disclosed not only comparable physicochemical properties, but also analogous catalytic activity; revealing the feasibility of producing high active catalyst's precursors by a simple, economic and environmentally-friendly method.

1. Introduction

In 2009 the European Union parliament through the approval of the Commission and Social Committee, issued the Directive 2009/28/EC, which mandates a 20% share of energy from renewable sources and a 10% share of energy from renewable sources in transport in Community energy consumption, which will have to be achieved by 2020 [1]. This tendency is expected to gradually be accepted worldwide. In this sense, biodiesel (BD) has become an alternative for the partial or total substitution of petrodiesel. In the vast literature reported it is generally found that BD production is based on edible oils such as sunflower, canola, soybean, olive, cotton, rapeseed, and palm [2–7]. In fact, in 2008 about 84% of the world's biodiesel production was covered by rapeseed oil. The remaining portion was from sunflower oil (13%), palm oil (1%), soybean oil and others (2%) [2]. The former has originated a severe controversy since nowadays it has to be decided whether these oils must be used for human consumption or for BD

* Corresponding author. Tel.: +52 55 2295500x7265.
E-mail address: manuel.sanchez@correo.buap.mx (M. Sánchez-Cantú).

0016-2361/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2012.06.078

obtaining. Moreover, it has started a polemic debate about deforestation and destruction of the ecosystem assigned for the production of these edible oils together with a reduction in cultivable land that would otherwise have been used to grow food and could be used to produce biodiesel instead. Furthermore, it must be considered that as the population worldwide is growing, the need for energy will also be increasing.

An alternative to this problem is given by non-edible oil crops suitable to be cultivated in lands that are not appropriate for food crops. Among the various non-edible oil seeds considered as BD feedstocks, castor bean (*Ricinus communis*) was identified as a potential BD feedstock since castor is a plant that is easily grown and is resistant to drought. Castor oil, *R. communis* L., (castor bean, castor, castor oil plant, ricin, higuerilla, mamona, mamoeira, and palma christi) is a member of the tropical spurge family (*Euphorbiaceae*) which nowadays may be grown worldwide in the most varied climates [8]. This crop implies not only an alternative for BD production but the promotion of the social and economic development; for instance, in the Mexican South Eastern region known as "La Mixteca Poblana", a semi-arid region characterized by dry and shrub vegetation, where poverty is widespread, the castor oil growing may be a suitable monetary source.

In general, biodiesel is produced by transesterification (alcoholysis) employing homogeneous bases and/or acids [9]. The reported advantages of the homogeneous base-catalyzed reaction are: firstly, very fast reaction rate (in the case of castor oil the reaction can proceed within 30 min achieving 98% yield [10] whereas when an acid such as H_2SO_4 is used a 84% yield is obtained after 8 h) [11]; secondly, catalysts such as NaOH and KOH are relatively cheap and widely available, the reaction can occur under mild reaction conditions and are less energy intensive. In the same way, the advantages of the acid-catalyzed reaction are: (1) its insensitivity to free fatty acids and water content in the oil, it is the preferred-method if low-grade oil is used, (2) esterification and transesterification occur simultaneously and (3) the reaction can occur at mild reaction conditions.

Nevertheless, some of the disadvantages associated with the homogeneous catalysts are, for instance, the high consumption of energy, corrosion on the reactor and pipelines by the use of high alkaline or acid conditions, expensive separation of the homogeneous catalyst from the reaction mixture, the catalyst cannot be reused or regenerated, and generation of large amounts of wastewater during separation of the products [12]. In the base-catalyzed reaction, there is also the unwanted soap formation, produced by reaction of the free fatty acids.

Therefore, the use of solid catalysts represents an attractive solution, since they are noncorrosive, environmentally benign, and present fewer disposal problems. These catalysts are also much easier to separate from liquid products, they can be reused, designed to give a higher activity and selectivity and to have longer catalyst lifetimes. In the literature are examples of heterogeneous catalysts with different composition used in the transesterification process of vegetable oils which include SrO [13], PbO, PbO_2, Pb_3O_4, MgO, ZnO, CaO, Tl_2O_3 [14], MgZr [15], zeolites [16], hydrated lime [17], supported metal oxides [18–20], etc.

Among the solid catalyst employed for BD production, in the last years some members of the anionic clay (AC's) family have been employed as catalysts and catalyst's precursors in the transesterification reaction [21–27].

Anionic Clays (AC's), also known as Layered Double Hydroxides, are a broad group of materials that exhibit the general formula $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2](A^{n-})_{x/n}\cdot mH_2O$ where M^{2+} is a divalent cation such as Mg, Cu, and Zn, M^{3+} is a trivalent cation such as Al^{3+}, and Fe^{3+}, A^{n-} represents an anion which resides in the interlayer region and m correspond to the water amount. Their structure resembles that of brucite, where $M^{2+}(OH)_6$ octahedra share edges to build infinite $M(OH)_2$ sheets. Thus, an AC is created by the partial isomorphic substitution of divalent cations for trivalent ones, in which the layered array is positively charged. This charge is electrically balanced by anionic species located in the interlayer region, along with hydration water molecules.

The hydrocalumite and hydrocalumite-type compounds denote a branch of the anionic clay family which has been scarcely reported in the bibliography in comparison to other members of the anionic clay family such as the hydrotalcite. Their general formula is $[Ca_2M^{3+}(OH)_6](A^{n-})_{1/n}\cdot mH_2O$ where M^{3+} is generally an Al^{3+} cation. The layered structure is built by the periodical stacking of positively charged $[(Ca^{2+}, M^{3+})(OH)_6]$ octahedral layers related to brucite and negatively charged interlayers consisting of anions and water molecules. For hydrocalumite, Ca^{2+} and Al^{3+}, fixed in a molar ratio of two, are seven and sixfold coordinated, respectively, being the seventh ligand of the Ca-polyhedron a water molecule from the interlayer [28].

Campos-Molina et al. reported the use of the hydrocalumite in the transesterification of sunflower oil achieving a conversion close to 100% after 2 h [23]. However, their catalyst precursor was synthesized by the coprecipitation method which restricts their use in high amounts due to the employment of expensive raw materials and purification methods [29].

Recently, we have reported an alternative to produce hydrotalcite and hydrotalcite like-compounds, also members of the AC family, by a simple and environmentally friendly method [30,31]. The advantages of this method include that the final slurry does not require the washing step to eliminate the unreacted ions as is generally performed in the synthesis of these compounds by the coprecipitation method. In addition, the water amount for the preparation of the slurries is reduced to a minimum. Moreover, the use of highly corrosive raw materials and prolonged hydrothermal treatments for crystallization is not required. This method represents a green alternative to obtain anionic clays in high amounts. Furthermore, it would be able to afford a viable alternative for those processes limited by the unavailability of large amounts of high efficient catalysts. It is important to stress that although this method was applied to hydrotalcite and hydrotalcite-like compounds' preparation it can be also applied for the synthesis of other members of the anionic clay family, such as the hydrocalumite, taking into account some synthesis variables such as: pH, ageing time and reaction temperature.

Since the materials produced in this way should disclose analogous physicochemical properties and catalytic activity to those reported by the coprecipitation method, two hydrocalumite compounds were prepared in this work, by coprecipitation and our previously reported method [30,31] and were evaluated in the transesterification of castor oil and methanol for biodiesel obtaining.

2. Experimental section

2.1. Materials

Castor beans were collected from "La Mixteca Poblana" region (18°55′25N, 098°24′50O). Castor oil was extracted under refluxing methanol in a Soxhlet extractor device. Methanol (98% purity) was purchased from Golden Bell and dried with metallic magnesium and iodine. Due to its high hygroscopicity, prior to the transesterification reaction, castor oil was passed through a 3A zeolite bed to remove all the moisture on it.

2.2. Catalyst preparation

Hydrocalumite synthesized from coprecipitation was prepared by a modification of the procedure described by López-Salinas