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Deoxygenation of waste cooking oil and non-edible oil for the production of liquid hydrocarbon biofuels

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ABSTRACT

Deoxygenation of waste cooking vegetable oil and *Jatropha curcas* oil under nitrogen atmosphere was performed in batch and semi-batch experiments using CaO and treated hydrotalcite (MG70) as catalysts at 400 °C. In batch conditions a single liquid fraction (with yields greater than 80 wt.%) was produced containing a high proportion of hydrocarbons (83%). In semi-batch conditions two liquid fractions (separated by a distillation step) were obtained: a light fraction and an intermediate fraction containing amounts of hydrocarbons between 72–80% and 85–88% respectively. In order to assess the possible use of the liquid products as alternative fuels a complete chemical characterization and measurement of their properties were carried out.

1. Introduction

The European Union has encouraged the utilization of biofuels in the transport sector through directives such as 2003/30/EC, 2009/28/EC and 2014/94/EU. In this context, the use of waste cooking vegetable oil (WCO) and non-edible oils (e.g. *Jatropha curcas* oil, JCO) play an important role as second generation raw materials not only providing economic and environmental benefits, but also improving the efficiency in the use of waste materials (Fernández et al., 2015; Gui et al., 2008). In addition, the waste cooking oil is a typical food waste fully classified in bio-waste category that is attracting the interest of the scientific community for its possible important role in the recycle and energy recovery processes.

In the matter of processes, conventional pyrolysis has been used for many years to obtain a type of bio-oil from biomass, including vegetable oils. However, the main drawback of the bio-oil is its high content of oxygenated compounds, in particular carboxylic acids (Sannita et al., 2012). For example, the pyrolysis of several animal fatty wastes (lamb, poultry and swine) was reported, resulting into bio-oils containing carboxylic acids (C7–C10), alkanes, alkenes and cyclic hydrocarbons (Ben Hassen-Trabelsi et al., 2014). As a consequence of the presence of the oxygenate compounds in the bio-oil, a further improvement should be applied before its use as engine fuel (Ben Hassen-Trabelsi et al., 2014; Bridgwater, 2012). Also, the treatment of WCO and other materials through transesterification and catalytic hydrotreating was reported (Alptekin et al., 2014; Andrade et al., 2013; Bezergianni et al., 2012; Charpe and Rathod, 2011; Felizardo et al., 2006; Madsen et al., 2011; Martinez-Guerra and Gnaneswar, 2014; Mohammadshirazi et al., 2014; Sabudak and Yildiz, 2010). At present, the Directive 2009/30/EC limites at 7 vol.% maximum the blending of biodiesel in conventional diesel, because this fuel showed some drawbacks such as a low heating value, high-density, and tendency to form deposits in the fuel injection systems (Knothe, 2010). On the other hand the catalytic hydrotreating, that allows the production of a high quality biofuel mainly composed of hydrocarbons, has the drawback of a high cost related mainly to the high amount of hydrogen used in the process (Aatola et al., 2009).

In the light of the above analysis, the conversion of vegetable oils into hydrocarbon biofuels without the use of hydrogen appears an important research topic. The conversion of natural oils into hydrocarbons in a hydrogen-free atmosphere using quite inexpensive catalysts such as alkaline earth metal oxides was reported in previous works (Dos Anjos et al., 1983; Romero, 2012; Sannita et al., 2012). The aim is to obtain a selective deoxygenation of natural oils by promoting the reactions of decarboxylation and/or decarbonylation, being the oxygen atoms removed mainly in the form of carbon dioxide and/or carbon monoxide, respectively. As a result, a liquid biofuel mainly composed of hydrocarbons with high atomic ratio H/C and low atomic ratio O/C is expected to be produced. The high atomic ratio H/C and low atomic ratio O/C are a signal of a possible greater amount of energy contained in

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Table 1
Standard analysis performed on the liquid fuel products.

Analysis	Standard method of reference	Instrument	Method
Sulfur content	EN ISO 20846	Antek – MODEL 900 nitrogen/sulfur analyzer	Ultraviolet fluorescence method
Nitrogen content	ASTM D4629	Antek – MODEL 900 nitrogen/sulfur analyzer	Syringe/inlet oxidative combustion and chemiluminescence detection
Carbon residue	ASTM D4530	Micro carbon residue tester Alcor MCRT120	Micro Corradson method
Density	UNI EN ISO 12185	Mettler Toledo DM40 densitymeter	Oscillating U-tube method
Boiling range distribution	ASTM D5307	A.C. Analytical Controls combined gas chromatographic system	GC simulated distillation analysis

the fuel. In fact, in a previous work we have reported encouraging features for a liquid biofuel obtained in batch experiments such as heating value of 44 MJ/kg and a low viscosity of 4 cSt (Romero et al., 2014), although the literature on this topic is still limited (Morgan et al., 2010; Murzin and Mäki-Arvela, 2010; Na et al., 2012; Santillan-Jimenez and Crocker, 2012; Snåre et al., 2006).

In the current research a selective deoxygenation promoting the reactions of decarboxylation and/or decarbonylation of WCO and JCO in the absence of hydrogen was evaluated. For the study two approaches were carried out: batch setup and semi-batch setup (with purge gas flow). Two types of alkaline earth metal oxides as catalysts were tested: Mg–Al mixed oxides (obtained from treated hydrotalcite) and CaO. In order to assess the possible use of the liquid products as alternative fuels to the diesel derived from a fossil source a complete chemical characterization and measurement of their properties were carried out.

2. Materials and methods

2.1. Characterization of raw materials and products

The WCO used in this study was collected after typical domestic use, while the JCO was provided by Ancient Green-Fields Pltd. in India. In order to make a comparison with liquid products, starting raw materials and a conventional fossil fuel (Diesel B7 purchased in fuel station) were subjected to the same analysis.

The elemental composition of WCO, JCO, liquid products and Diesel B7 was determined using an Elemental Analyser (mod. CHN 2400, Perkin Elmer).

Infrared spectra for both raw materials and solid products were recorded using a Fourier Transform Infrared Spectrometer (FTIR Nicolet 380, Thermo), equipped with a DTGS detector and using transmission analysis with the help of potassium bromide (KBr) pastilles (100 scans and resolution 2 cm^{-1}). The different functional groups absorb specific frequencies depending on their structures, they were identified in output spectras (infrared light absorbance on the vertical axis vs. wavelength on the horizontal axis).

A detailed analysis of the chemical composition of liquid products and Diesel B7 was conducted using a GC/MS (Focus-ISQ Thermoscientific) equipped with TG-SQC column (30 m × 0.25 mm × 0.25 μm) and a split injector. TIC signal acquisition mode was used. The starting temperature was calibrated at 70 °C (hold time 5 min), with an initial increase of 5 °C/min up to 130 °C (hold time 1 min), then a second ramp of 5 °C/min up to 270 °C (hold time 1 min), and a final ramp of 25 °C/min up to 320 °C (hold time 5 min).

Also, the properties of the liquid products and Diesel B7 were measured using the similar standard procedures used for petroleum products (reported in Table 1).

On the other hand, the composition of gaseous products was analyzed using a gas chromatograph Chrompack MICRO-GC CP 2002 equipped with a microTCD detector and two parallel columns: the first a PoraPLOT Q column used for analyzing the CO_2 and light hydrocarbons (CH_4 excluded), the second a CP-Molsieve 5A column for analyzing the H_2, O_2, CH_4 and CO.

2.2. Catalyst

PURAL MG70 (aluminum–magnesium hydroxyl carbonate compound with weight ratio of $MgO:Al_2O_3 = 70:30$) commonly known as hydrotalcite was supplied by Sasol and CaO by Sigma Aldrich. In order to obtain Mg–Al oxides, PURAL MG70 was calcinated during 5 h at 500 °C under air atmosphere before use. In order to remove any accumulated moisture in the CaO, this catalyst received the same treatment. After treatment the specific surface area of both catalysts was obtained by the Brunauer–Emmett–Teller (BET) isotherm-equation, the results showed for the treated hydrotalcite and CaO a specific surface area of 159 m^2/g and 1 m^2/g respectively.

2.3. Deoxygenation experiments

The different experiments in the deoxygenation of WCO and JCO were performed in a mechanically stirred 500 mL reactor (mod. 4575A, PARR Instrument Company) operating in two diverse configurations: batch setup (Fig. 1A) and semi-batch setup (Fig. 1B). In a typical experiment, approximately 180 g of raw material and 3 wt.% of catalyst were added to the reactor. Before each experiment, under constant stirring of the mixture, the reactor was purged with nitrogen for 3 min to remove the remaining oxygen. In the batch experiments the reactor was initially pressurized to approximately 3 bar before the heating, depending essentially on the gaseous products produced during the reaction: at the end of the experiments a pressure of around 110 bar was achieved. The temperature was increased to reach in 1 h the desidered value (400 °C), and maintained at this value for 6 h. In

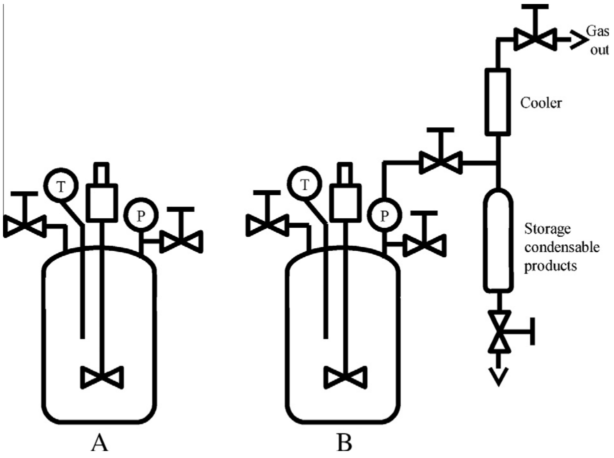

Fig. 1. (A) Batch reactor; (B) semi-batch reactor.