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Shea nut shell based catalysts for the production of ethanolic biodiesel

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ABSTRACT

This work focused on the synthesis of charcoal as carbonaceous catalyst support for the ethanol transesterification of vegetable oil to produce biodiesel. Shea (*Vitellaria paradoxa*) nut shells (SNS) were used as raw material to prepare an activated carbon based catalyst by chemical activation with potassium hydroxide (KOH). A central composite design of the response surface methodology (RSM) was used to investigate the interactive effect of the SNS-K catalyst synthesis parameters (pyrolysis temperature, residence time and KOH impregnation ratio) and its catalytic activity in sunflower ethanol transesterification. Experimental yields reached >90% ester content in the biodiesel, with a catalyst prepared under mild pyrolysis conditions. Results showed that the temperature of pyrolysis and the KOH ratio used to impregnate SNS are the most important factors influencing the SNS-K catalytic activity. Catalyst prepared between 400 °C and 650 °C, with 120 min residence time and a biomass: KOH ratio of between 14% and 17.5% produced the highest ethyl ester content (96%) with an optimal catalyst prepared at 650 °C, with 120 min residence time and 14% KOH loading. SNS-K catalyst characterization by X-ray diffraction (XRD) showed potassium carbonate to be the main active potassium species responsible for catalytic activity. Recyclability tests showed that the catalyst can be reused after a thermal post treatment without catalytic activity loss. Thus, this new simple catalytic process allows biodiesel production under mild conditions, using local reactant (i.e. bioethanol, vegetable oils and char from local agricultural residues). This can be a realistic alternative process for a shift towards sustainable energy in sub-Saharan Africa.

Introduction

In response to their high energy needs, African countries are increasingly interested in biofuels as a way of freeing their economies from the contingencies of the crude oil market (Tatsidjodoung et al., 2012). The development of local technologies to facilitate access to new sources of liquid fuels, particularly biodiesel, is one possible solution. The production of biodiesel as a substitute for fossil diesel is thus the subject of increasing interest (Anuar and Abdullah, 2016; Demirbas, 2008; Mardhiah et al., 2017; Rathore et al., 2016). The most widely used conventional industrial technique for the production of biodiesel is methanol route transesterification (FAME) using homogeneous chemical catalysts like potassium hydroxide or sodium hydroxide (Munoz et al., 2012).

Likewise, when homogeneous catalysts are used to produce biodiesel, depending on the reactants, it can result in undesirable reactions (e.g. saponification) as the catalysts are dissolved in the reaction medium.

Heterogeneous catalysts are a possible alternative to homogeneous catalysts. They have been reported to produce good catalytic activity in methyl ester production, are easy to separate from the reaction medium and can be reused several times, thereby keeping production costs down (Avhad and Marchetti, 2016; Jyoti et al., 2014; Lee et al., 2014; Mardhiah et al., 2017).

Among possible heterogeneous catalytic supports, activated carbon made from biomass has recently attracted considerable interest. The advantage of this type of catalytic support is its availability, particularly if they are produced using agricultural residues, their potentially low cost of preparation and their stability at low pressures and temperatures. The resulting activated carbon is used as a support for active species (acid or basic) known for their catalytic activity in transesterification reactions (Baroutian et al., 2010; Endalew et al., 2011; Jyoti et al., 2014). Different preparation routes were used for catalyst design with commercial activated carbon or an activated carbon obtained by chemical or physical activation. The activated carbon was then “doped” with a precursor that has to be activated through pyrolysis to produce active catalytic species for the reaction. Different types of alkali metal-based precursors (potassium hydroxide (KOH) potassium carbonate (K_2CO_3), potassium fluoride (KF), or calcium oxide (CaO)) have been used with biomass including palm nut shells, coconut shells, and shells of *Jatropha curcas* (Baroutian

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et al., 2010; Buasri et al., 2012a, 2011; Hameed et al., 2009; Li et al., 2013).

In all these studies, which only concern FAME production, long reaction times (more than 2 h) were necessary to obtain good conversion yields (>90%). Furthermore, all these catalysts have the disadvantage of requiring three step preparation processes: i) preparation of the activated carbon by physical or chemical activation of the biomass raw material to develop textural and structural properties, ii) impregnation of the resulting support with the catalytic metal precursor, and iii) pyrolysis of resulting material to fix and obtain the active species of the metal within the support porosity, where transesterification reaction occurs, to obtain the carbon based heterogeneous catalyst (Chouhan and Sarma, 2011; Jyoti et al., 2014).

Recent research works by the same authors as this paper (Blin and Ouedraogo, 2014; Ouédraogo et al., 2017) described a patented innovative method to prepare biomass based carbonaceous material to be used as catalyst in ethanolic transesterification to produce fatty acid ethyl ester (FAEE). The authors found that it is possible to obtain the catalyst in a two-step method by first impregnating Shea nut shells (SNS) with an alkaline solution (KOH or K_2CO_3) followed by pyrolysis-activation at 600 °C and 800 °C. The result was the conversion of >98% of *Jatropha curcas* oil using the produced catalyst. However, in that study, the authors did not investigate the effect of catalyst synthesis parameters, nor optimize catalyst preparation and reusability, nor discuss the effect of transesterification reaction parameters on catalytic activity.

The aim of this study thus was to assess the influence of biomass charcoal supported catalyst synthesis parameters on catalytic activity. SNS are a major source of agricultural waste in West Africa and were used as raw material. These shells have high potassium content (up to 25% in the ash) and have been shown to produce good quality activated carbons, i.e. mechanically stable with high porosity (Noumi et al., 2013; Ouédraogo et al., 2017). The catalysts were prepared using the two-step patented method (impregnation followed by pyrolysis-activation) by biomass impregnation with potassium hydroxide (KOH). The influence of the preparation parameters of the catalyst (pyrolysis temperature and time, ratio of the activating agent) on its catalytic activity is investigated through statistical analysis of the experimental results to identify the key parameters that influence catalytic activity. This paper focusses on the influence of these preparation parameters on the properties of the catalyst (weight loss, porosity and specific surface area, potassium content) and catalyst activity (ester content in the resulting biodiesel). The optimization of the catalyst preparation conditions by promoting mild design conditions (i.e. low temperature, low pyrolysis time and amount of activating agent as low as possible) is described. Finally, the reusability of catalysts is investigated to explore the possibilities of maintaining and/or regenerating the catalyst properties in order to catalyze several ethanolic transesterification reactions thereafter.

Table 1
Proximate and ultimate analysis of SNS.

Proximate analysis (%)			Ultimate analysis (%)			
Ash	Volatiles	Fixed carbon	C	H	N	O
1.95	70.83	27.22	51.42	6.34	0.22	42.02[a]

[a] By difference.

Experimental section

Material

SNS collected from local Shea butter producers in Burkina Faso were used as biomass. Potassium hydroxide (KOH, Sigma Aldrich, ≥85%) was used both as biomass activating agent and as a precursor of the active species. Sunflower oil (acid value: 0.07 mg KOH/g) and anhydrous ethanol (Sigma Aldrich, 99.8%) were used as reagents in the transesterification reaction. N-heptadecane (Aldrich, analytical grade) was used as internal standard for biodiesel analysis by gas chromatography with flame ionization detector (GC-FID) and n-hexane (Sigma Aldrich, analytical grade) was used as solvent. Glycerol (Sigma Aldrich, ≥99%) was used for thermogravimetric analysis.

Preparation of SNS-K catalyst

Biomass preparation

SNS was first washed with cold water to remove impurities (sand, stones and dust), ground and sieved to a particle size of between 400 and 800 μm. Proximate analysis was performed according to standards XP CEN/TS 15104, XP CEN/TS 15148 and XP CEN/TS 14775; and ultimate analysis was conducted using the XP CEN/TS 15104 method (Table 1). To understand the thermochemical behavior of the SNS during pyrolysis, thermogravimetric analysis (using the derivative thermogravimetric analysis curve (DTg)) was performed using a SETSYS Evolution TGA 16/18 Setaram instrument (Fig. 1).Samples were heated to 950 °C at a heating rate of 10 °C/min under N_2 flow.

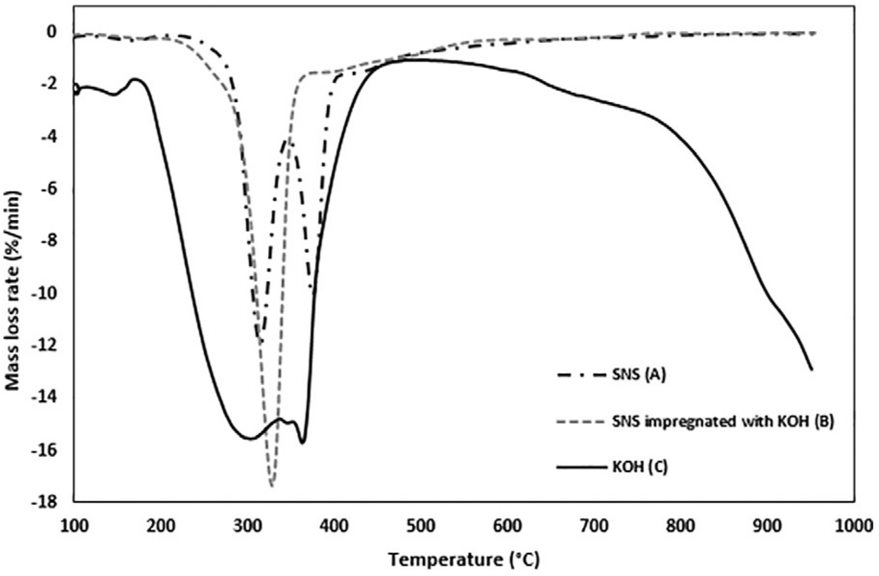

Fig. 1. DTg curves of non-impregnated SNS (A), SNS impregnated with KOH (B), and KOH (C).