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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.

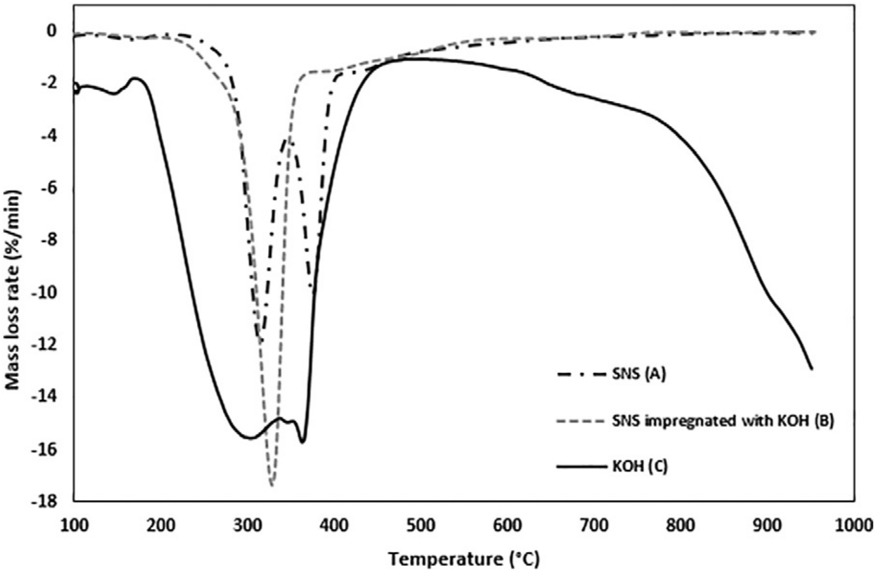

Fig. 1. DTg curves of non-impregnated SNS (A), SNS impregnated with KOH (B), and KOH (C).

Table 2
KOH to SNS impregnation ratios used.

SNS (g)	KOH pellets (g)	Impregnation ratio (%)
50	1.75	3.5
	2.5	5
	8.75	17.5
	15	30
	19.5	39

Chemical activation of SNS

Catalysts, named SNS-K were prepared using the wet impregnating route, according to the patent procedure described by *Blin and Ouédraogo*. SNS was impregnated with a potash solution, with different KOH to SNS mass ratios at a rate of 50 g of SNS for 100 ml of solution (Table 2). Impregnation was carried out at room temperature and under atmospheric pressure with magnetic stirring for 24 h. The resulting product was filtered and dried at 105 °C in a ventilated oven for 24 h. Once dry, the material was pyrolyzed in a Carbolite rotating tubular furnace.

For each test, the resulting impregnated product was placed in the furnace and the temperature was raised from ambient temperature to final temperature at a heating rate of 10 °C/min (Table 3) under a nitrogen flow of 200 ml/min. Depending on the test, the final temperature was maintained for a specified residence time (Table 3), then the furnace was switched off and allowed to cool to ambient temperature under a nitrogen flow. The resulting materials, i.e. the SNS-K catalysts, were stored in a desiccator until needed for the transesterification reaction.

Catalyst characterization

The surface area, pore volume and pore diameter of the catalysts were determined from the corresponding N_2 adsorption–desorption isotherms obtained at 77 K with an automatic ASAP 2020 V3.04 H, (Micromeritics). The specific surface area (SBET) was determined by the Brunauer, Emmett, Teller (BET) method. The Barrett, Joyner and Halenda (BJH) method was used to calculate the average pore diameter.

Weight loss (ΔM) (Eq. (1)) during pyrolysis was obtained by difference between the original mass of impregnated biomass when placed in the furnace and the mass of the resulting carbonaceous product obtained after pyrolysis as calculated below:

$$\Delta M = 100 - ((m_c * 100)/m_b) \tag{1}$$

where m_b and m_c are respectively the mass of the dried impregnated SNS sample introduced into the furnace and the mass of the resulting product after pyrolysis.

The potassium content (%K) of SNS-K catalysts after pyrolysis was determined by ICP/OES (inductively coupled plasma-optical emission) analysis using a Varian Vista spectrometer equipped with a charge coupled device sensor.

X-ray diffraction (XRD) was carried out with a diffractometer Xpert-Pro (Panalytical) equipped with an X'celerator detector, to identify the crystalline phases of the potassium.

Table 3
Pyrolysis experimental conditions (real and coded values).

Pyrolysis conditions	Minimum (coded value)	Maximum (coded value)
Temperature (°C)	500 (−1)	800 (+1)
Time of residence at final temperature (min)	60 (−1)	180 (+1)
Impregnation ratio (%)	5 (−1)	30 (+1)
Heating rate (°C/min)	10	
N_2 flow (ml/min)	200	

SNS-K catalytic behavior in an ethanolic transesterification reaction

In this section, we investigate the influence of catalyst preparation parameters on the catalytic activity in ethanolic transesterification reaction. After which, optimized conditions were used to design an efficient SNS-K catalyst.

Experimental design

The central composite design of the response surface methodology (RSM) was used to study and optimize the preparation parameters. This method consists of a group of mathematical and statistical techniques that can be used to define the relationships between the responses and the independent variable. Conventional experimental or optimization methods (optimization of one factor at a time) apart from being time-consuming, fail to fully explain the effect of the factors taken alone or the effects of their interactions on a process (Bas and Boyaci, 2007). Statgraphics software (STATGRAPHICS centurion XVI, n.d.), was first used for the experimental design, then to perform statistical analysis of the results and finally to optimize SNS-K catalyst preparation parameters. Three preparation parameters were studied: pyrolysis temperature (T), pyrolysis time of residence at the final temperature (t) and the ratio of KOH to SNS impregnation (α_{KOH}). The pyrolysis experimental conditions are summarized in Table 3.

A total of 19 samples were prepared and tested for the experimental design, with five replicates of central point, at a temperature of 650 °C, 120 min pyrolysis residence time and an impregnation ratio of 17.5%, to estimate the variance of experimental error.

The influence of the preparation parameters (i.e. T, t, α_{KOH}) was studied on three experimental responses: ester content of the biodiesel (F_{EE}), weight loss after pyrolysis (ΔM), and potassium content (%K) in each SNS-K catalyst. Each response was analyzed using the RSM method to build a regression model (Eq. (2)) reflecting the quantitative influence of factors:

$$Y = \beta_o + \beta_1 T + \beta_2 t + \beta_3 \alpha_{KOH} + \beta_1\beta_2 Tt + \beta_1\beta_3 T\alpha_{KOH} + \beta_2\beta_3 t\,\alpha_{KOH} + \beta_{11}T^2 + \beta_{22}t^2 + \beta_{33}\alpha_{KOH}^2 + \varepsilon \tag{2}$$

where β_0 is the constant coefficient; $\beta_{1,}$ β_2 and β_3 are the linear coefficients; $\beta_{12,}$ β_{13} and β_{23} are the interaction coefficients; and $\beta_{11,}$ β_{22} and β_{33} are the quadratic coefficients. These coefficients were calculated from the experimental responses by least-squares regression using Statgraphics software.

The results are discussed based on analysis of variance (ANOVA). Terms with a P-value <0.05 were considered significant at 5% of probability. A test of “lack of fit” was performed on the statistical models obtained to see the quality of fitness and to describe the observed experimental response. The model was considered good if P-value of the lack of fit was >0.05.

Sunflower oil ethanolic transesterification reaction

The ethanolic transesterification reaction was carried out in a 100 ml round bottle flask equipped with a magnetic stirrer, a thermometer and a reflux condenser at atmospheric pressure. All SNS-K catalysts were tested with fixed transesterification reaction conditions: ethanol: oil ratio 18:1, one hour reaction time, reaction temperature 65 °C (±2 °C), 10 wt% of catalyst amount (on oil weight basis) under stirring at 650 rpm. The transesterification reaction procedure was as follows: a mixture of 5 ml of ethanol and 0.52 g of catalyst was first stirred for 15 min, then 5 ml of sunflower oil was added to the stirred mixture which constitutes the beginning of the reaction. After one hour reaction time, the catalyst was separated by filtration and excess ethanol in the liquid phase was removed by rotary evaporation. Ethyl esters were analyzed using the EN14105 method with heptadecane as internal standard. The ester content of the biodiesel was determined with a GC-FID, with a nonpolar column (VF-5HT 5%diphenyl-95%dimethylpolysiloxane;

length 15 m, diameter 0.32 mm and film thickness 0.1 μm, 60 °C - 400 °C, Agilent) and using helium as carrier gas.

SNS-K catalyst reusability

In this section, the reusability of optimized SNS-K/OP catalyst is investigated. The aim is to see to what extent it is possible to recycle SNS-K/OP catalyst for reuse in transesterification reactions. To this end, a thermogravimetric analysis was performed on fresh SNS-K/OP catalyst, used catalyst obtained after the first run, and on used catalyst after washing in a solvent, either with hexane or ethanol. The used catalyst without further washing was also thermally treated at identified optimum pyrolysis conditions under N_2 flow. The obtained samples were used in the second run of transesterification under the same reaction conditions: ethanol: oil ratio 18:1, 1 h of reaction time, reaction temperature of 65 °C (± 2 °C), and 10 wt% of catalyst amount (on oil weight basis) under stirring at 650 rpm.

Results and discussion

The aim of this work was to study the influence of preparation parameters on the properties of SNS-K catalysts. Once identified, these preparation parameters were optimized and the reusability of catalysts was explored.

Influence of preparation parameters on SNS-K catalytic efficiency

Selection of the SNS-K catalyst preparation parameters with most influence on the nature and catalyst activity

Several authors have discussed the influence of various key parameters on the nature and properties of activated carbon for different application, especially as a catalyst support (Avhad and Marchetti, 2016; Blin and Ouedraogo, 2014; Fan and Zhang, 2007; Guo and Lua, 2002; Islam et al., 2013; Jyoti et al., 2014; Li et al., 2013). According to this literature, temperature and pyrolysis time, the impregnation ratio and the nature of the activating agent as well as the type of biomass are the main parameters that influence the properties (char yield, porosity, specific surface area and active sites) of activated carbon produced by chemical activation. According to these studies, the range of possible pyrolysis temperature is between 400 °C and 900 °C, the pyrolysis residence times range from as little as 30 min to >10 h and a wide range of concentrations of the activating agent from as little as 10% to >100% (on support weight basis). The values were chosen by the authors firstly according to the known catalytic activity of the precursor in transesterification through homogeneous catalysis. Secondly according to the concentration and ability (related to basicity or acidity) of the precursor to activate the support in order to obtain the desired textural properties (good porosity and high specific surface area). Finally the values were selected according to the physicochemical properties (high fixed carbon content and low ash) of the biomass, and its availability.

In order to select the value range of the parameters (T, t and α_{KOH}) for SNS-K catalysts synthesis in this study, a thermogravimetric analysis of non-impregnated SNS (Fig. 1A) and SNS impregnated with a KOH to SNS ratio of 17% (Fig. 1B) and pure KOH (Fig. 1C) was conducted.

The thermal degradation of pure KOH (m.p: 360 °C) took place in three stages. A first peak was observed between 100 °C and 170 °C, corresponding to the loss of absorbed water in the crystalline phase. A second peak was observed at around 300 °C, corresponding to the decomposition of KOH into potassium oxide. A last peak was observed around 360 °C, corresponding to thermal degradation at the KOH melting point. When the activation temperature exceeded 800 °C, a sharp weight loss was observed and the DTg curve showed weight loss peaks between 800 °C and 950 °C. Consequently, to avoid decomposition of the potassium active phase, the activation temperature should be kept below 800 °C.

The DTg curve of non-impregnated SNS (Fig. 1A) is typical of lignocellulosic biomass pyrolysis behavior with two weight loss peaks, the first at 330 °C, corresponding to hemicellulose degradation, and the second peak at 380 °C that can be attributed to cellulose degradation. Lignin degradation started at around 400 °C and continued up to 600 °C. When temperature reached 800 °C the weight loss stabilized. Beyond 800 °C weight loss was not so significant.

The DTg curve of the impregnated SNS (Fig. 1B) presents a single peak at around 330 °C, corresponding to the simultaneous degradation of hemicellulose and cellulose. As already reported in the literature (Okman et al., 2014; Sebestyén et al., 2011; Sun et al., 1995), this effect can be explained by the fact that the structure of hemicellulose is partially or completely hydrolyzed and solubilized during alkaline impregnation. As a result, there is an increase in the weight loss rate. DTg curve (Fig. 1B) showed that impregnated SNS weight loss was no longer significant at temperatures of between 500 °C and 800 °C. Using this range of temperature enables biomass to be converted into charcoal while avoiding potassium volatilization, which can occur at high temperature > 800 °C.

As discussed in the literature, the impregnation of biomass with potassium hydroxide influences its thermal decomposition (Hu and Vansant, 1995), and the resulting activated carbon textural properties (porosity and specific surface area) are mainly influenced by the ratio of the activating agent, pyrolysis temperature and pyrolysis time (Gueye et al., 2014; Lua and Yang, 2004; Okman et al., 2014; Sudaryanto et al., 2006; Tay et al., 2009). It is also worth noting that optimizing thermal treatment would significantly affect the physicochemical properties of the heterogeneous catalysts (i.e. active and stable catalyst: strong interaction between the active species and the support, strong textural framework) which, in return, would affect the yield and the quality of biodiesel (i.e. more accessible active species for high yield alcoholysis) (Avhad and Marchetti, 2016; Li et al., 2013).

However, the marked increase in the impregnation ratio and thermal treatment can also lead to i) destruction of the carbon structure and increased weight loss due to carbon burn-off, ii) possible decomposition of the precursor, ii) bad dispersion, sintering and weak interactions of the catalytic active species with the support, and iii) possible leaching during catalysis (Avhad and Marchetti, 2016; Guo and Lua, 2002; Jyoti et al., 2014; Lua and Yang, 2004; Okman et al., 2014).

Thus, based on the thermogravimetric analysis and on the literature, our objective was to prepare catalysts by loading biomass with sufficient activating agent to enable a good dispersion of active species in the porous structure using mild pyrolysis preparation conditions. To this end, different SNS-K catalysts were prepared at temperatures ranging between 500 °C ≤ T° ≤ 800 °C with pyrolysis times ranging between 60 min ≤ t ≤ 180 min and impregnation ratio range between $5\% \leq \alpha_{KOH} \leq 30\%$ (g/g).

To perform statistical analysis of the influence of the preparation parameters and finally to optimize SNS-K catalyst preparation, the textural properties (i.e. porosity and specific surface area), potassium content (%K), and also weight loss during pyrolysis of each resulting catalyst (ΔM) were characterized. Then the direct influence of preparation parameters on the catalytic activity in sunflower oil transesterification reaction (F_{EE}) was investigated. The measured values were used as response for the statistical analysis.

According to the experimental design (Table 4), when the preparation parameters were modified, modification affected all the responses used for statistical analysis (i.e. ΔM, %K, and F_{EE}) except the textural properties (i.e. pore mean diameter and volume and specific surface area (SBET)). Indeed the textural properties of all the samples were shown to be very low (SBET between 0 and 5 $m^2\ g^{-1}$, mean pore diameter between 3 and 4 nm; pore volume between 9 and 45 $10^{-4}\ cm^3\ g^{-1}$), and are thus not worth discussing. The absence of porosity was probably due to alkaline impregnation, when the samples

Table 4
Experimental results obtained with RSM. Transesterification experiments were duplicated with a standard deviation of ±5%.

SNS-K catalysts no	Real parameter (coded parameter)			Responses		
	T (°C)	t (min)	α_{KOH} (%)	F_{EE} (%)	ΔM (%)	%K (%)
1	398 (−1.471)	120 (0)	17.5 (0)	91.5	58.98	15.9
2	650 (0)	19 (−1.471)	17.5 (0)	86.4	64.47	18.6
3	650 (0)	120 (0)	17.5 (0)	88.9	60.73	20
4	650 (0)	120 (0)	17.5 ((0)	93.4	57.52	17.2
5	650 (0)	120 (0)	17.5 (0)	94.0	61.92	17.8
6	650 (0)	120 (0)	17.5 (0)	94.1	63.72	19.3
7	650 (0)	120 (0)	17.5 (0)	91.7	64.26	18.3
8	902 (1.471)	120 (0)	17.5 (0)	80.2	71	18.1
9	650 (0)	120 (0)	39 (1.471)	84.3	73.68	25.8
10	650 (0)	120 (0)	3.5 (−1.471)	39.8	67.05	4.5
11	650 (0)	221(1.471)	17.5 (0)	86.4	66.71	20.1
12	500 (−1)	60 (−1)	5 (−1)	12.5	63.92	6.6
13	500 (−1)	180 (1)	5 (−1)	12.8	65.28	6
14	500 (−1)	180 (1)	30 (1)	88.0	65.08	20.8
15	500 (−1)	60 (−1)	30 (1)	76.3	60.73	21.9
16	800 (1)	60 (−1)	30 (1)	85,0	70.92	18.7
17	800 (1)	60 (−1)	5 (−1)	50.4	69.99	7.1
18	800 (1)	180 (1)	5 (−1)	94.2	67.92	6.3
19	800 (1)	180 (1)	30 (1)	16.2	70.98	18.1

Table 5
Analysis of variance of weight loss (ΔM).

Coefficient	Estimation	F-value	P-value	Remark
β_1	3.445	20.14	0.0109**	Significant
β_2	−0.355	0.21	0.6678*	Non-significant
β_3	0.839	1.2	0.3355*	Non-significant
β_{11}	1.429	2.63	0.1799*	Non-significant
$\beta_1\beta_2$	−0.965	1.03	0.3686*	Non-significant
$\beta_1\beta_3$	0.922	0.94	0.3879*	Non-significant
β_{22}	−0.078	0.01	0.9329*	Non-significant
$\beta_2\beta_3$	0.64	0.45	0.5387*	Non-significant
β_{33}	3.912	19.74	0.0113**	Significant
Lack of fit	–	0.87	0.5681	Significant

Effect: **significant, *non-significant at 5% probability. $R^2 = 84.71\%$, $R^2_{ajusted} = 69.42\%$.

are not washed after chemical activation as classically done on activated carbon to eliminate K-compounds (Díaz-Terán, 2001), and prevented accurate measurement of the real resulting porosity and specific surface area.

As a consequence, porosity and specific surface area were not used as responses. The influence of preparation conditions (T, t, α_{KOH}) on each prepared SNS-K catalyst was investigated in terms of:

i. weight loss (ΔM) compared to the initial weight of impregnated SNS placed in the furnace,
ii. potassium content (%K) of the activated carbon in relation to impregnation efficiency. The aim was first to determine the amount of potassium in SNS-K catalysts, compared to the initial amount in the non-impregnated SNS and then investigate possible potassium volatilization during heating treatment,
iii. catalyst activity for biodiesel production through sunflower oil ethanolic transesterification (F_{EE}).

Influence of preparation parameters on SNS-K properties

Table 4 shows the experimental matrix of catalyst synthesis parameters SNS-K and their corresponding responses, in a design using the RSM with Statgraphics experimental design software. Catalysts were tested using the same protocol to measure F_{EE}, ΔM and %K of each SNS-K catalyst.

Effect of SNS-K preparation parameters on weight loss (ΔM). Eq. (3) is the regression model obtained based on experimental results. Table 5 presents the analysis of variance of ΔM.

$$\Delta M = 61.696 + 3.445T - 0.355t + 0.839\alpha_{KOH} + 1.429T^2 - 0.965Tt + 0.922T\alpha_{KOH} - 0.078t^2 + 0.64t\alpha_{KOH} + 3.9129\alpha_{KOH}^{\ 2} \tag{3}$$

The coefficient of determination R^2 indicates that this model explains 84.71% of the total variability of the response ΔM. Adjusted R^2 indicates that 69.42% of the variability of the response is directly linked to the parameters studied, indicating medium accuracy. The lack of fit with a P-value of 0.5681 implies that the model is significant at 5% of probability.

The model shows that pyrolysis temperature is the key parameter influencing ΔM. The KOH impregnation ratio and residence time have less effects. The effect of temperature is almost linear given the low value of the quadratic coefficient. The increase in weight loss is linked with an increase in the KOH impregnation ratio, reaching a minimum that did not depend on the temperature; the interaction between the parameters was not significant. The weight loss was mainly influenced by the pyrolysis temperature and the KOH impregnation ratio, which is in agreement with the literature (Ahmadpour and Do, 1997; Sudaryanto et al., 2006) on KOH activated carbon.

The weight loss observed in our experiments (between 1% and 10% g/g) is lower than the values reported in literature (Ahmadpour and Do, 1997; Sudaryanto et al., 2006). This may be explained by the fact that the impregnating mass ratios we used are quite low (between 3.5% and 39% g/g) and the potassium impregnating the samples was not removed by washing after pyrolysis as conventionally done for activated carbon preparation (Khezami et al., 2007). At a given pyrolysis temperature, when KOH impregnation ratio increased, weight loss increased. And for a given KOH impregnation ratio, as pyrolysis temperature increased, char yield decreased. These effects are known and are reported in the literature but on activated carbon freed from their impregnated potassium by washing (Ahmadpour and Do, 1997; Gueye et al., 2014; Okman et al., 2014; Sudaryanto et al., 2006; Tay et al., 2009).

Effect of SNS-K preparation parameters on potassium content (%K). Eq. (4) represents the regression model obtained based on experimental results. Table 6 shows the analysis of variance of %K.

$$\%K = 18.924 - 0.151T - 0.573t + 6.881\alpha_{KOH} - 1.447T^2 + 0.037Tt - 0.837T\alpha_{KOH} - 1.332t^2 - 0.037t\alpha_{KOH} - 2.302\alpha_{KOH}^{\ 2} \tag{4}$$

The coefficient of determination R^2 indicates that the model explains 96.42% of the total variability of response %K. Adjusted R^2 indicates that 92.84% of the variability of the response is directly linked to the parameters studied, thus indicating good accuracy. The lack of fit with a P-value of 0.1446 implies that the model is significant at 5% of probability.

Table 6
Analysis of variance of potassium content (%K).

Coefficient	Estimation	F-value	P-value	Remark
β_1	−0.151	0.22	0.6631*	Non-significant
β_2	−0.573	3.18	0.1493*	Non-significant
β_3	6.881	457.14	<0.0001**	Significant
β_{11}	−1.447	15.38	0.0172**	Significant
$\beta_1\beta_2$	0.037	0,01	0.9297*	Non-significant
$\beta_1\beta_3$	−0.837	4.39	0.1041*	Non-significant
β_{22}	−1.332	13.2	0.0226*	Non-significant
$\beta_2\beta_3$	−0.037	0.01	0.9297*	Non-significant
β_{33}	−2.302	38.90	0.0034**	Significant
Lack of fit	–	3.15	0.1446	Significant

Effect: **significant, *non-significant at 5% probability. $R^2 = 96.42\%$, $R^2_{ajusted} = 92.84\%$.

Results show that the KOH impregnation ratio is the factor that mainly influences the %K in SNS-K catalysts: the higher the KOH impregnation ratio in the biomass, the higher the %K in SNS-K catalysts. Temperature has little influence on %K, even at high temperatures, and even though it is well known that potassium hydroxide can produce species (K_2O, K_2O_2) that vaporize at temperatures > 600 °C (Díaz-Terán et al., 2003). There was only a small loss of potassium in SNS-K catalysts in all cases, probably due to the fact that all the impregnated potassium remained in the activated carbon after pyrolysis. A small increase in %K of the activated carbon compared to the initial biomass was even observed. This effect can be explained by the decrease in the weight loss of the support during heat treatment. There was little interaction between the various parameters, the effect of KOH ratio remained almost the same regardless of the temperature.

Effect of SNS-K preparation parameters on ester content in the biodiesel (F_{EE}). Eq. (5) presents the regression model obtained based on experimental results. Table 7 presents the analysis of variance of F_{EE}.

$$\begin{aligned}F_{EE} = {} & 95.358 + 3.205T - 1.058t \\ & + 13.055\alpha_{KOH} - 8.471T^2 - 4.638Tt - 22.803T\alpha_{KOH} \\ & - 8.228t^2 - 12.648t\alpha_{KOH} - 19.448{\alpha_{KOH}}^2\end{aligned} \tag{5}$$

The coefficient of determination R^2 indicates that the obtained model explains 80.89% of the total variability of response F_{EE}. Adjusted R^2 indicates that 61.79% of the variability of the response is directly linked to the parameters studied, indicating medium accuracy. The lack of fit with a *P*-value of 0.002 implies that the model is non-significant at 5% of probability.

As can be seen from the ANOVA, the parameters studied cannot totally explain the variability of the response F_{EE}. This effect is probably linked to the influence of other important parameters including the physicochemical properties of the catalyst (i.e. porosity and specific surface area, and accessibility to active sites) (Zabeti et al., 2009); and also to transesterification reaction parameters (reaction temperature and time, alcohol: oil ratio, and the amount of catalyst, etc.) (Baroutian et al., 2010; Li et al., 2013). However the value of the coefficient of determination remains high, showing a significant influence on the catalytic activity in the range of studied parameters.

The KOH impregnation ratio is the parameter that most influences catalytic activity: an increase in the ratio led to an increase in ester content but the influence was nonlinear. An increase in the ratio first led to an increase in ester content, but the influence then decreased and reversed above 17.5%. The optimum value of the KOH ratio to maximize ester content is therefore around 17.5%.

The KOH impregnation ratio had a major influence on ester content when a low pyrolysis temperature was used. On the other hand, there was little interaction between this impregnation ratio and pyrolysis residence time. Pyrolysis residence time had an influence mainly at 800 °C when a drop in yield was observed with an increase in the impregnation ratio.

Table 7
Analysis of variance of ester content (F_{EE}).

Coefficient	Estimation	F-value	P-value	Remark
β_1	3.205	25.98	0.0070**	Significant
β_2	−1.058	2.83	0.1677*	Non-significant
β_3	13.055	430.94	<0.0001**	Significant
β_{11}	−8.471	137.88	0.0003**	Significant
$\beta_1\beta_2$	−4.638	35.3	0.004**	Significant
$\beta_1\beta_3$	−22.803	853.07	<0.0001**	Significant
β_{22}	−8.228	130.09	0.0003**	Significant
$\beta_2\beta_3$	−12.648	262.46	0.0001**	Significant
β_{33}	−19.448	726.74	<0.0001**	Significant
Lack of fit	–	122.24	0.0002	Non-significant

Effect: **significant, *non-significant at 5% probability. $R^2 = 80.89\%$, $R^2_{ajusted} = 61.79\%$.

Therefore, a range of pyrolysis temperatures between 400 °C and 650 °C appears to be adequate to prepare an efficient catalyst for the transesterification reaction using a KOH impregnation ratio of around 17.5%. With these pyrolysis temperatures, active potassium species responsible for catalytic activity appear to be produced and available (Díaz-Terán et al., 2003; Li et al., 2013).

According to our experimental results, a maximum ester content of ≥90% can be obtained with catalyst prepared at $T = 650$ °C and with medium $\alpha_{KOH} \leq 17.5\%$. At low temperatures, i.e. around 400 °C, an ester content of 91% can be obtained but the resulting biodiesel was colored, indicating the presence of volatiles in the catalyst which are solubilized in the organic medium during the transesterification reaction. The presence of volatiles shows that the SNS was not completely pyrolyzed and converted into activated carbon. The presence of volatiles affects the quality of the biodiesel, which no longer meets biodiesel quality standards, specifically light color (ASTM D6751-01).

By increasing the KOH impregnation ratio and the pyrolysis residence time, an ester content of ≥84% can be obtained with a sample prepared at low temperatures. However, heat treatment with a high impregnation ratio, i.e. between 30% and 39% (g/g), reduces char yield. This effect was discussed by (Guo and Lua, 2002), the increase in impregnation ratio promotes gasification reactions and results in a high weight loss due to carbon burn-off. When such material is used to catalyze the transesterification reaction, although the conversion rates are high (i.e. $F_{EE} > 80\%$), the catalysts collapse and produce a very fine powder, which can be a limiting factor for the heterogeneous transesterification reaction process in terms of catalyst recycling and stability (the case of catalysts nos. 9, 14, 15, 16 and 19).

These phenomena are known in the literature. As explained by (Okman et al., 2014), an excessive rise in temperature and high KOH concentrations lead to destruction of the carbon matrix. A sponge-like structure develops and makes the char friable. As discussed by (Li et al., 2013), this friability, which is linked to excess potassium in the SNS during impregnation, may also result in a sintering phenomenon on the support that can limit access to the active sites. Moreover the impregnated potassium in the supported catalyst can leach in the reaction medium and behave like a homogeneous catalyst, since it is no longer securely fixed on the support.

Concerning the influence of pyrolysis residence time at final temperature, the results obtained in this study indicate that even with a low pyrolysis residence time (i.e. 19 min), a good ester content was obtained (i.e. 84%) but the resulting biodiesel was colored due to the presence of volatiles. An increase in the pyrolysis time allows this handicap to be overcome.

When preparing activated carbon with impregnated KOH biomass, depending on the pyrolysis temperature and on the impregnation ratio, the main potassium compounds produced are carbonates (K_2CO_3) and oxide (K_2O) (Díaz-Terán et al., 2003). XRD characterization (Fig. 2) in this study showed diffraction peaks corresponding to a crystalline phase of K_2CO_3, which is the main activation product. K_2CO_3 is produced by the reaction of KOH with the CO_2 resulting from hemicellulose and cellulose thermal degradation (Díaz-Terán et al., 2003). The K_2CO_3 particles are probably the main active species responsible for catalytic activity in the transesterification reaction. The increasing formation of K_2CO_3 depends on the increase in pyrolysis temperature (Díaz-Terán et al., 2003).

The results obtained in this study showed that the KOH impregnation ratio is the key parameter that influences catalytic activity, while pyrolysis temperature and KOH impregnation ratio are parameters that have a great influence on ΔM and %K. An efficient SNS-K catalyst used for sunflower oil transesterification can be obtained under mild conditions, i.e. temperature $T \leq 650$ °C and KOH impregnation ratio $\alpha_{KOH} \leq 17.5\%$ (g/g); and a mild pyrolysis residence time $t = 120$ min.

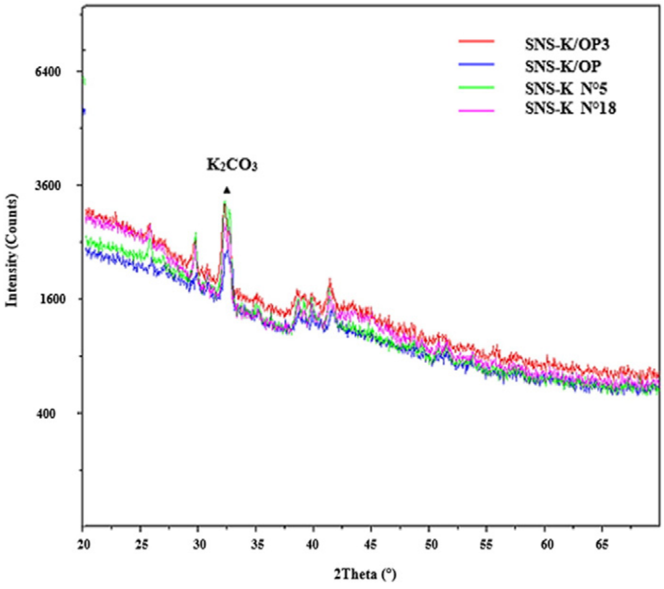

Fig. 2. XRD patterns of SNS-K/OP, SNS-K/OP3, SNS-K N°5 and SNS-K N°18 catalysts.

Optimization of SNS-K catalysts

The aim of this work was to optimize the preparation of SNS-K catalysts for the production of biodiesel through ethanolic transesterification of vegetable oil. Experimental results and statistical analysis were used to determine preparation optimal conditions. Using Statgraphics software optimization tool, it was possible to determine experimental parameters that make it possible to reach an ester content of around 90% in the resulting biodiesel using mild preparation conditions. The mild preparation conditions could have a significant impact on the cost of catalyst preparation, since the parametric study revealed that preparation is possible at low temperatures (less energy intensive process) and low amounts of KOH precursor can be used while keeping excellent catalytic activity (SNS-K catalysts N°5 and 18). The goal is thus to reduce the amount of potassium needed for impregnation ($\alpha_{KOH} < 17.5\%$KOH), to select a pyrolysis temperature as low as possible between 500 °C ≤ T° ≤ 650 °C and a short pyrolysis residence time (t ≤ 120 min).

Optimization results using Statgraphics gave an optimized catalyst prepared at a pyrolysis temperature of 650 °C, a pyrolysis time of 120 min and a KOH impregnation ratio of 14%. A catalyst named SNS-K/OP was then prepared using these “optimum conditions” and tested in transesterification reaction. An ester content of 96% was obtained with SNS-K/OP catalyst. The ester content was also close to that reported in the literature with carbon based catalysts obtained with KOH supported on a carbon material (Baroutian et al., 2010; Buasri et al., 2012b). Some quality parameters, considered as the most relevant (flash point, water content, phosphorus content, acidity, kinematic viscosity, density, and calorific value), were determined for the biodiesel obtained using SNS-K/OP catalyst without further purification. From the obtained results (Table 8) it is seen that properties such as kinematic viscosity, density, flash point and phosphorus content of produced ethanolic biodiesel are very close to the minimum required by standards (Brunschwig et al., 2012). However, the measured values of acidity and water content were above the standard limits. An additional purification step can allow to meet standards specifications.

SNS-K catalyst reusability

The possibility to reuse SNS-K/OP in transesterification reactions was investigated. When the catalyst was used again directly in a second run without any post treatment, the ester content in biodiesel obtained after the second run dropped from 96.8 to 13.4%. Many factors could be responsible for the loss of activity such as poisoning or fouling of the active species by sorbed glycerol, residual glycerides, and fatty acids, or the leaching of active species in the reaction medium (Baroutian et al., 2010; Boro et al., 2013; Islam et al., 2013). As SNS-K/OP catalyst lost its catalytic activity, it has to be regenerated for possible reuse in a second run.

Several catalyst post-treatment methods were tested to select the most suitable for regeneration of the catalyst. The catalyst was washed with hexane (SNS-K/OP1) and ethanol (SNS-K/OP2) or thermally treated like during preparation, i.e. at 650 °C with a 120 min residence time (SNS-K/OP3). Table 9 summarizes the ester content in the resulting biodiesel obtained with each post and non-post treated sample. Fig. 3 shows the thermogravimetric analysis (DTg) conducted on SNS-K/OP, SNS-K/OP1 and SNS-K/OP2 samples; and on sunflower oil and pure glycerol.

The DTg curve of fresh SNS-K/OP catalyst lost weight between 30 °C and 110 °C like used SNS-K/OP catalyst (Fig. 3). This weight loss is probably due to the release of sorbed water in the sample during storage. (Díaz-Terán et al., 2003) discussed this presence of water, which is mainly due to oxidation of activated carbon and hydration reactions that occur at ambient atmosphere.

Many peaks were also observed on used SNS-K/OP, SNS-K/OP1 and SNS-K/OP2 curves, between 160 °C and 300 °C, in particular at 169 °C, 188 °C and 252 °C that were attributed to thermal decomposition of ethyl esters, which are stable up to 169 °C (Jain and Sharma, 2011), and glycerol (degradation of pure glycerol observed between 250 °C and 350 °C) sorbed onto the surface of the catalyst, the same trend was observed by (Dou et al., 2009) on pure glycerol, whose degradation occurred between 150 °C and 283 °C.

Beyond 280 °C weight loss became insignificant and DTg curves, including for the fresh SNS-K/OP, showed similar behavior between 380 °C and 650 °C. Also according to (Correia et al., 2012) thermal degradation of sunflower oil occurs from 320 °C to 590 °C. No peaks corresponding to the thermal degradation of sunflower oil glycerides were observed (the main peak was observed at around 400 °C, Fig. 3). Therefore the weight loss observed can only be attributed to residual impurities in used SNS-K/OP, SNS-K/OP1 and SNS-K/OP2 samples. Thus, we concluded that the loss of catalytic activity was probably due to poisoning of active species (mainly by glycerol). This phenomenon is discussed by (Li et al., 2013).

When the catalyst was washed with hexane (Table 9), catalytic activity was still low (9.24% of ester content). However Fig. 3 (SNS-K/OP1 and SNS-K/OP2) clearly shows a significant decrease in the

Table 8
Physical-chemical properties of biodiesel prepared with SNS-K/OP catalyst.

Proprity	Units	Measured values	FAEE standards
Flash point	°C	130	120
Acidity	mg KOH/g	1.84	0.5
Water content	ppm	1230	500
Phosporus content	ppm	<10	10
Kinematic viscosity at 40 °C	mm^2/s	4.53	3.5–5
Density	kg/m^3	883	860–900
Calorific value	MJ/kg	32.3	37.3–40,6

Table 9
Ester content in biodiesel depending on the recycling method. Experiments were duplicated with a standard deviation of ±1.5%.

Catalysts (run number)	Ester content (%)
SNS-K/OP (1st run)	96.8
SNS-K/OP (2nd run)	13.40
SNS-K/OP1 (2nd run)	9.2
SNS-K/OP3 (2nd run)	96.0

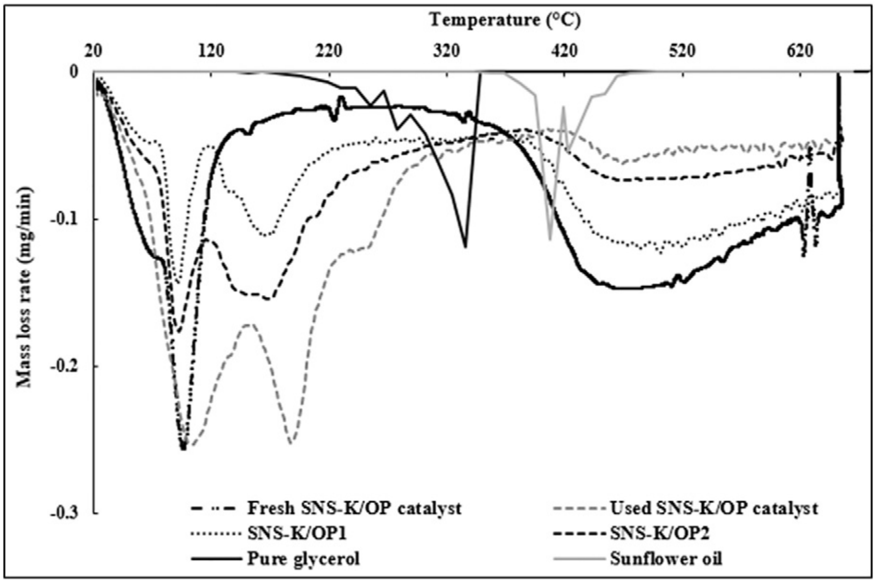

Fig. 3. DTg curves of fresh SNS-K/OP, used SNS-K/OP, SNS-K/OP1 and SNS-K/OP2 catalysts, pure glycerol and sunflower oil.

intensity of the degradation peaks of previously observed sorbed compounds on used SNS-K/OP DTg curve. Washing with a solvent reduces the sorbed amounts of esters, glycerol and residual glycerides on the catalyst, but does not allow catalytic activity to recover. Moreover according to (Yu et al., 2011), washing the catalyst with a solvent can also cause leaching of the active species, thereby decreasing the catalytic activity.

Based on thermogravimetric analysis, a temperature of 500 °C appeared to be sufficient to thermally remove sorbed compounds on the used SNS-K/OP sample. Consequently, after filtration, the catalyst was collected from the first reaction medium and thermally treated at 500 °C with 60 min residence time under nitrogen flow. The resulting material (SNS-K/OP3) was used for a second transesterification run. The ester content of the resulting biodiesel was still high (around 96%), showing good catalyst regeneration. XRD characterization (Fig. 2) of the SNS-K/OP3 catalyst showed that the active species were also mainly composed of K_2CO_3, thus revealing that a significant amount of impregnated potassium was still fixed on the carbon support. Notwithstanding current research on heterogeneous based catalysts (Atadashi et al., 2013; Avhad and Marchetti, 2016; Liu et al., 2011; Lotero et al., 2006), solid bases showing good catalytic activity are most probably catalyzing transesterification reactions through a homogeneous molecular pathway rather than a truly heterogeneous one, due to their probably non-negligible solubility in alcohols. More for supported based catalyst operating at moderate temperature, catalysis probably occurs through a homogeneous-like reaction mechanism that should translate into heavy catalyst deactivation after only a few reaction cycles. Further studies on SNS-K catalyst catalytic stability are now underway to better assess the real nature of the catalytic activity and the mechanism involved in transesterification reaction.

Conclusion

The aim of this work was to optimize the preparation of SNS-K catalysts used to catalyze ethanolic transesterification of sunflower oil. The influence of three preparation parameters, pyrolysis temperature (T), pyrolysis time of residence (t), and KOH impregnation ratio (α_{KOH}) was studied in five responses: porosity and specific surface area, material weight loss upon pyrolysis (ΔM) and potassium content (%K) in prepared SNS-K catalyst and biodiesel ester content (F_{EE}) in transesterification reaction.

Due to the lack of washing of the samples with water after impregnation, porosity and specific surface area were very low and cannot be used to discuss the influence of preparation parameters on catalysts properties in this study.

Pyrolysis temperature (T) and KOH impregnation ratio (α_{KOH}) were identified in this study as the key parameters influencing support properties (ΔM and %K) and SNS-K catalyst catalytic activity (F_{EE}). The "two-step" preparation method makes it possible to design a SNS-K catalyst with excellent catalytic activity in ethanolic transesterification reaction ($F_{EE} > 90\%$ in the resulting biodiesel) and that is reusable. Nonetheless, a more in-depth assessment is required of the mechanism and stability of the carbon based SNS-K catalyst in the transesterification reaction.

Under the experimental conditions investigated, an optimized SNS-K catalyst prepared at a pyrolysis temperature of 650 °C, for a pyrolysis residence time of 120 min and with KOH impregnation ratio of 14% proved capable of maintaining this excellent catalytic activity (i.e. $F_{EE} \geq 96\%$). This catalytic activity is linked to the development of potassium active species mainly composed of K_2CO_3.

The statistical analysis was not capable of predicting SNS-K catalyst transesterification catalytic activity with the chosen experimental parameters. This can be explained by the fact that apart from the influence of the parameters studied here, other effects like transesterification reaction parameters (i.e. temperature, time, catalyst amount, ethanol to oil ratio etc.) or SNS-K catalyst textural and structural properties (i.e. porosity, specific surface area and active sites availability) have to be taken into account for catalytic activity. A further study of the parameters that influence in ethanolic transesterification reaction and also the effect of water content in ethanol, catalyst stability after several transesterification reaction is currently underway to find ways of maintaining SNS-K catalyst activity as high as possible, i.e. an ester content ≥ 96%.

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