To link to this article : DOI: 10.1021/ef501365u
http://dx.doi.org/10.1021/ef501365u

To cite this this version : Nitiema-Yefanova, Svitlana and Richard, Romain and Thiebaud-Roux, Sophie and Bouyssiere, Brice and Bonzi-Coulibaly, Yvonne L. and Nébié, Roger H. C. and Mozet, Kevin and Coniglio, Lucie *Dry Purification by Natural Adsorbents of Ethyl Biodiesels Derived from Nonedible Oils.* (2015) Energy & Fuels, vol. 29 . pp. 150-159. ISSN 0887-0624

Dry Purification by Natural Adsorbents of Ethyl Biodiesels Derived from Nonedible Oils

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Supporting Information

ABSTRACT: The purpose of this work is to analyze the efficiency of natural adsorbents (rice husk ash (RHA) versus corn husk ash (CHA)) for the dry purification of ethyl biodiesels obtained by transesterification via homogeneous catalysis of nonedible oils (*Balagnites aegyptiaca*, *Azadirachta indica*, and *Jatropha curcas*). The characterization of RHA and CHA was achieved by N_2 adsorption/Brunauer−Emmett−Teller analysis and by scanning electron spectroscopy with microanalysis by energy dispersive X-ray spectroscopy. The quality of the three biodiesels, before and after dry treatment on adsorbent, was evaluated by various analytical methods (^1H nuclear magnetic resonance, gas chromatography with a flame ionization detector, Karl Fischer titration, and inductively coupled plasma−atomic emission spectroscopy). Several operating conditions (presence of activated carbon in the ashes, temperature, contact time, and number of treatment cycles) were tested in order to define the best procedure. RHA combined with the selected procedure showed very satisfactory results for removal of impurities from the produced biodiesels (residual glycerides, free glycerin, water, catalyst, and metals introduced during the oil extraction) and thus may be an alternative to the conventional wet purification process (acidic water washing).

1. INTRODUCTION

Aiming for a sustainable energy supply and climate change mitigation, production of biodiesel fuel from nonedible vegetable oils (NEVOs) and bioethanol (derived from biomass residues) is an attractive alternative based on local and renewable use of agricultural resources.[1−3] Among the NEVOs, extensive attention has been devoted to *Jatropha curcas* (JC) during the past few years,[4] but recent efforts for diversification of the feedstocks to secure biodiversity has directed scientific research toward oilseeds such as *Balanites aegyptiaca* (BA, Desert date), *Azadirachta indica* (AI, Neem), and *Pongamia pinnata* (PP, Pungam), etc.[3,5] However, some impurities (such as free fatty acids (FFAs) naturally present in the NEVOs, especially water present both in bioethanol and the NEVOs) limit the use of these feedstocks in large-scale biodiesel production. Processes based on homogeneous catalysts (mainly alkali ones) are the most widely used for industrial biodiesel production,[6] despite important water consumption and catalyst loss in aqueous effluents during the purification stage. At laboratory scale, adsorptive treatments with Magnesol or rice husk ash (RHA) were reported to replace efficiently the wet-purification stage of biodiesel,[7−13] and would therefore be attractive alternatives. Furthermore, the dry-purification method offers other benefits such as using local agricultural solid waste,[12−14] making the process even more environmentally friendly, while reducing substantially the total production time (as water-washing requires two treatment cycles and one centrifugation stage, which are long processes).[11]

In accordance with the biorefinery concept inciting use of the entire resources, several authors illustrated the feasibility of using *Jatropha* husk activated carbon[15] or activated Neem leaf[16] as adsorbent for the removal of toxic pollutants from water (heavy metals[15] and phenolic compounds[16]). RHA was evaluated with successful results as adsorbent for reducing FFAs of crude vegetable oils.[17] In another scope of applications, ashes from palm oil mill boilers[18,19] or of rice husk[20] have been used as support of alkali heterogeneous catalyst for biodiesel production. Nevertheless, to the knowledge of the authors, no dry-purification test has been carried out for biodiesels produced by homogeneous acid-catalyzed ethanolysis or for removing biodiesel contaminants with corn husk ash (CHA) as adsorbent.

Table 1. Equipment and Operating Conditions Selected

objective	experimental technique	equipment	operating conditions
RHA and CHA Characterization for Relating “Structure” and “Adsorption Efficiency”			
morphology	SEM	JEOL microscope; model JSM-6490 LV (Japan)	accelerated voltage, 5 or 20 kV; spot size, 60; magnification of up to 600×; second electrons analysis when sample metalized with gold−palladium; backscattered electrons analysis without sample gold−palladium coating
elemental chemical composition	SEM-EDS	JEOL microscope; model JSM-6490 LV (Japan) + SAMX-IDFIX system (microanalysis) (France)	same as above
surface area and porosity	N_2 adsorption isotherms + BET method	Sorptomatic 1990, ThermoQuest CE Instruments (Italy)	sample previously degassed for 16 h under vacuum with the temperature program of 1 °C/min from 30 to 120 °C; adsorption isotherms recorded at liquid nitrogen temperature (77.31 K)
Biodiesel Characterization for Evaluation of the Purification Methods			
glycerides (TG, DG, MG), free glycerin, and FAEE contents	GC-FID	PerkinElmer Instrument (USA)	silica capillary column (CP-Sil 8 CB lowbleed/MS; 5% phenyl + 95% dimethylpolysiloxane; 15 m, 0.32 mm, 0.25 μm) from Varian (USA); carrier gas, helium (Air Liquide, France) at 15 psi at the head of the column; injector type and its temperature program, cool-on-column inlet at 55 °C (0.5 min) and 55−340 °C (200 °C/min, 43 min); oven temperature program, 55 °C (0.5 min), 55−80 °C (45 °C/min), and 80−360 °C (10 °C/min, 16 min); detector temperature, 360 °C; automatic injections, 1 μL; silylation of the entire sample with a mixture of *N*-methyl-*N*-trimethylsilyl-heptafluorobutyramide and methylimidazole before GC-FID analysis; standard solutions prepared in cyclohexane (solvent); heptadecane used as internal standard (1 mg/mL)[24,25]
water content	Karl Fischer titration (volumetric)	TIM 550 Titration manager by TITRALAB (France)	hydranal−medium K and hydranal−composite 5K used as solvent and titration reagent, respectively, with hydranal−water standard 10 (10 mg of water/(g of solution))
potassium and other elements (Si, S, Ca, Mg, Fe, P) contents	ICP-AES	ARCOS by SPECTRO; Scott-type double-pass spray chamber combined with cross-flow nebulizer (Germany)	plasma forward power, 1700 W; plasma argon (Ar) flow rate, 14 L/min; sample Ar flow rate, 0.65 L/min; auxiliary Ar flow rate, 1.9 L/min; pump speed, 15 rpm/min; calibration performed via a multielement oil-based standard (S-21 at 100 $\mu g \cdot g^{-1}$) diluted appropriately in xylene to prepare multielement working standard solutions ranging from 0.1 to 10 $\mu g \cdot g^{-1}$; quantification by external calibration with a test sample at 1 $\mu g \cdot g^{-1}$[26,27]
FAEE and residual ethanol contents	^{1}H NMR	Bruker 300 MHz	analysis at 300 K in deuterated chloroform (99.8% D) solutions with naphthalene used as internal standard

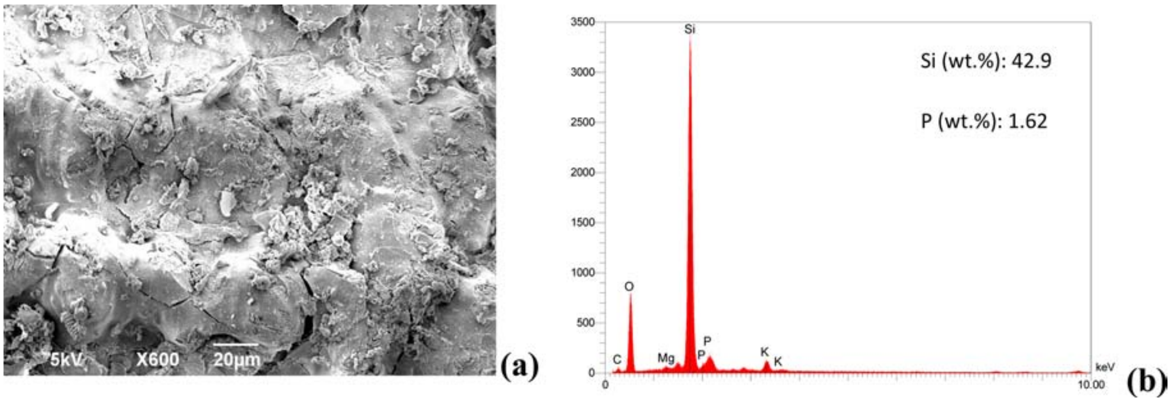

Figure 1. SEM/EDS analyses of outer epidermis of a virgin RHA-GB sample (secondary electrons with gold−palladium coating): image (a) and EDS spectrum (b).

In this work (exclusively based on experimental approach), RHA and CHA performances as natural adsorbents are tested for the dry purification of biodiesels obtained by ethanolysis of three NEVOs via homogeneous catalysis (with KOH for BA and AI oils and H_2SO_4 for JC oils). The dry treatment procedure and the possibility of reusing the waste ashes obtained after biodiesel purification will also be assessed. Efficiency of RHA and CHA in the removal of specific impurities (glycerides, free glycerin, water, catalyst, and metals) without introducing supplementary contaminants (particularly Si, P, and Mg) will be evaluated via the characterization of biodiesel samples obtained before and after treatment. Structure and composition of RHA and CHA (before and after biodiesel purification, with characterization of the latter) will be investigated to provide guidance as to possible interpretation of the behavior observed for these materials. With the global results, it is intended to propose the optimal adsorbent material with the suitable treatment procedure.

2. METHODS

2.1. Materials. Solvents and other reagents were of analytical grade and were purchased with the chromatographic standards from Merck, Acros Organics, or Sigma-Aldrich. In addition to the biodiesels (i.e., fatty acid ethyl esters (FAEEs)) from NEVOs (BAEEs, AIEEs, and JCEEs), rapeseed ethyl esters (RSEEs) were also produced to compare the performance of the dry- and wet-purification methods.

2.1.1. Biodiesel Production. The BAEEs and AIEEs were obtained via alkali catalysis (KOH), and the JCEEs were obtained via acid catalysis (H_2SO_4) according to a two-stage procedure based on intermediate addition of glycerol.[21] The RSEEs were produced in the same way as the BAEEs and the AIEEs. Alkali (acid) catalysis was operated at 35 °C (78 °C), with an ethanol to oil molar ratio equal to 8:1 (30:1), a catalyst concentration of 1 wt % (5 wt %) based on the initial mass of oil, and a reaction time of 50 min (26 h) while the addition of glycerol marking the start of the second step was carried out after 30 min (23 h) of reaction. The ester contents of the four FAEE products (BAEE, AIEE, JCEE, and RSEE) are respectively as follows: 97.4, 89.5, 85.7, and 92.0 wt %. The initial contents of contaminants in the FAEE products (unreacted glycerides, free glycerin, residual catalyst, water, FFAs, soaps, and metals) will be given when evaluating the dry-purification method in Results and Discussion.

2.1.2. RHA and CHA Production. Rice hulls and corn husks were collected from local production units (Burkina Faso), finely ground, then placed in crucibles made of porcelain covered with aluminum foil, and carbonized in a muffle furnace (MF4 Hermann Moritz Regulateur 2068, France). The operating temperature was set to 500 °C, as recommended in the literature to obtain ashes showing optimal adsorption properties.[17,22,23] The recommended ashing time of 10 h[17,23] was reduced in this work to 8 h for practical reasons. After carbonization, the ashes were cooled to room temperature in a desiccator for 8 h minimum. Samples were placed in plastic screw-cap bottles and stored at room temperature.

2.2. RHA and CHA Characterization toward "Structure−Adsorption Efficiency" Relationship. Details of the equipment and operating conditions used to relate the efficiency of the potential adsorbent to its structural features are given in Table 1. Morphology was assessed by scanning electron microscopy (SEM), with elemental chemical composition informed by coupling SEM with microanalysis by energy dispersive X-ray spectroscopy (EDS). Surface area and porosity were evaluated through N_2 adsorption isotherms using Brunauer−Emmett−Teller (BET) method.

2.3. Biodiesel Characterization for Evaluation of the Purification Methods. Details of the equipment and operating conditions used to evaluate the performance of the dry-purification methods (adsorbent type and treatment procedure) are listed in Table 1. FAEE samples obtained before and after dry purification on RHA and CHA were characterized in terms of triacylglycerides (TG), diacylglycerides (DG), monoacylglycerides (MG), free glycerin, and ester contents by gas chromatography coupled with a flame ionization detector (GC-FID), in terms of water content by the volumetric Karl Fischer method, and in terms of potassium and heavy metals (resulting from the catalyst used and the oil extraction stage) by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The comparative performance of the purification treatments with acidified water and with RHA was achieved on the basis of the soap content determined by an acid−base titration method.[28]

2.4. Biodiesel Purification. Dry purification via the natural adsorbents (RHA and CHA) was evaluated with the FAEEs obtained from the three NEVOs (BAEEs, AIEEs, and JCEEs). The comparative performance of the classical wet purification via an acid solution (H_3PO_4) versus the dry purification via a natural adsorbent (RHA) was carried out with the FAEEs obtained from rapeseed oil (RSEEs). Two concentrations in H_3PO_4 (1 and 5 wt % in distilled water[29]) were tested.

2.4.1. Wet Purification with Acidic Water. Acid solution (30 wt % on the basis of the initial weight of FAEEs) was sprayed on the surface of an unpurified RSEE sample without mixing. The resulting mixture was then transferred in a separating funnel. After phase separation and removal of the aqueous phase (lower layer), the remaining FAEE product was washed twice identically. The washed FAEE product was then dried over anhydrous magnesium sulfate and next filtered off. The whole procedure was carried out at ambient temperature.

2.4.2. Dry Purification with RHA/CHA and Treatment Procedure. The dry-purification method proposed in batch mode by Manique et al.[12] was selected as the "reference method" (one-stage treatment with 4 wt % RHA in the unpurified FAEE sample, stirred for 20 min and heated at 65 °C). In an attempt to optimize the treatment procedure, different values of the key variables were tested. Thus, dry purification was conducted in one or two stages (treatment cycles with

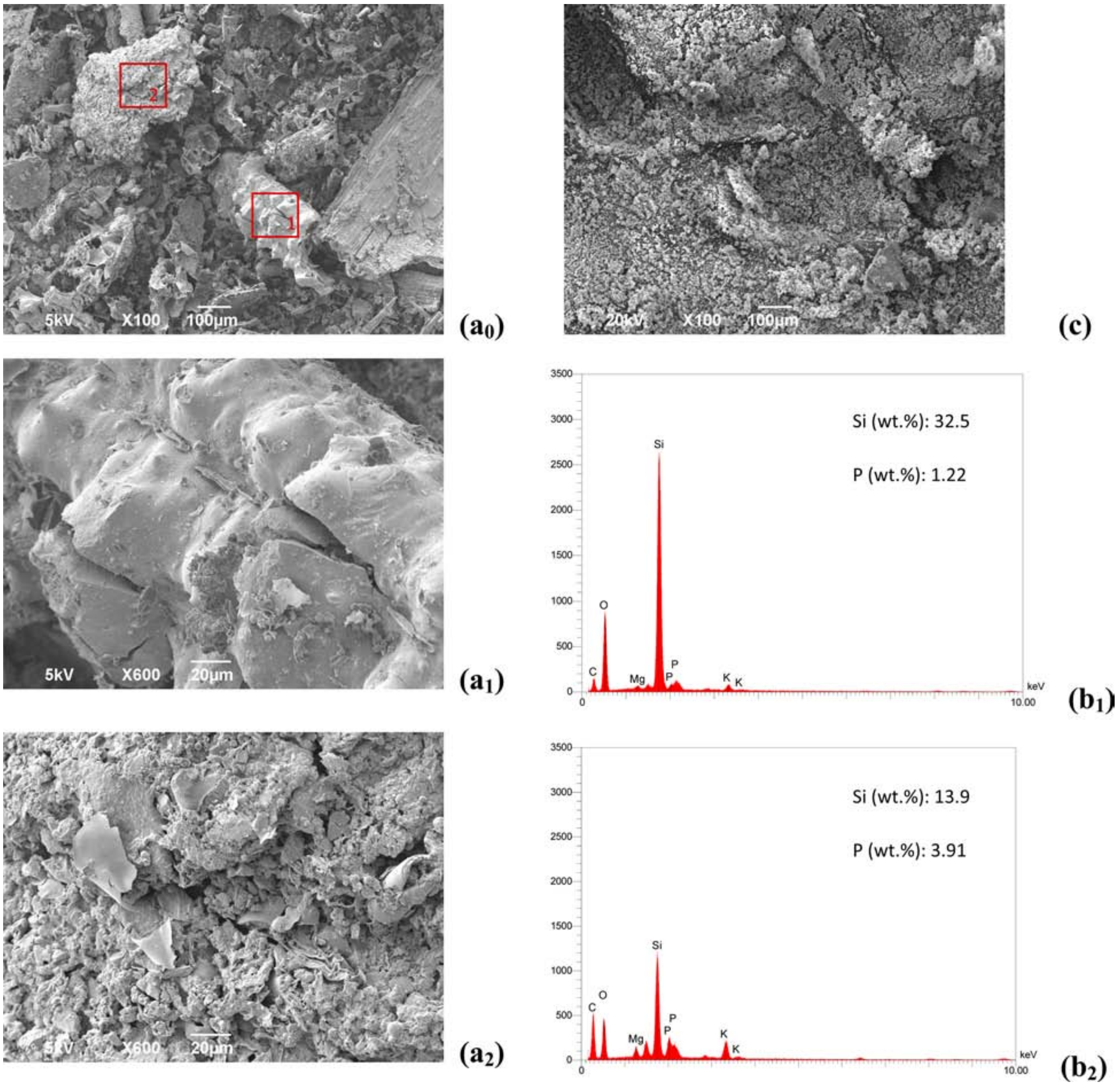

Figure 2. SEM/EDS analyses of CHA (secondary electrons with gold−palladium coating): virgin CHA images (a) and EDS spectra (b), for the whole sample (a_0), for a corncob shaped region (a_1, b_1), and for a porous region (a_2, b_2); image of used CHA after purification of FAEEs produced via alkali catalysis and supplemental incineration (c).

freshly produced ashes as described in section 2.1.2 and intermediate filtration of the FAEE sample) with stirring by combining different processing temperatures (65 and 20 °C), purifying agents (RHA and CHA), and contact times between the purifying agent and the FAEE product to be purified (20 and 5 min). The possibility of reusing the ashes after FAEE purification has also been considered in the case of a dual treatment cycle. Nevertheless, unlike Manique et al.,[12] the same concentration of purifying agent was adopted for all tests (4 wt % was shown to be the optimal value by the same authors).

At the end of the required contact time, the purified FAEE product was filtered under vacuum through a Büchner funnel lined with filter paper and then stored for later analyses in a refrigerated (4 °C) and dry place away from direct sunlight.

In the following text, the treatment carried out at 20 °C during 5 min contact time will be referred as the "flash method".

3. RESULTS AND DISCUSSION

The ^{1}H NMR spectra of each of the three FAEE products before and after dry purification (Figure S.I.1, Supporting Information) were so similar that this method could not be used to evaluate the performance of the process (probably because of the high degree of TG conversion). All experiments and analyses were conducted in duplicate (or further in case of disagreement in the measurements). From each set of duplicates, an average value was then calculated to yield the given data.

3.1. Yields of the Incineration Process and Considered Ash Classes. Regarding rice husk, the mean yield of the incineration process (defined as the average value of the percent ratio of the mass of recovered ashes to the mass of initial rice husk) was 22 wt %. Nevertheless, incomplete carbonization of the rice husk led to a heterogeneous mixture consisting of light-gray, dark-gray, and black ashes (classification made on the basis of ash color), with respective mass fractions of 43, 10, and 47 wt %. Given the small recovered fraction of dark-gray ashes, these were mixed with the black ones to obtain a single batch of purifying agent containing activated carbon (on the basis of the ash color and results obtained in the literature[15]). Thereby, only two classes of RHA respectively named as RHA-LG (for the light-gray ashes) and RHA-GB (for the gray-black ashes) have been considered. Furthermore, incomplete carbonization as observed here for the rice husk clearly shows that the applied operating conditions, particularly the temperature of carbonation (500 °C), are not adequate and should be optimized for the specific materials used.

By contrast, carbonization of corn husk conducted in the same conditions as those selected to produce the RHA has led to an apparently homogeneous mixture of finer ashes (named as CHA) and with a very low mean yield of around 1 wt %.

Incineration yields of used RHA (recovered after dry purification of the BAEEs) were around 41 wt % when the ashes had been used for a single treatment of esters but 26 wt % when the ashes had been used for a dual treatment of esters (instead of $(41\text{ wt }\%)^2 = 17$ wt %), showing a decrease in adsorptive capacity of the used ashes. Furthermore, the resulting ashes became very similar to the RHA-LG (confirming that the initial dark-gray and black color ashes were due to incomplete carbonization). Regarding the used CHA (recovered after dry purification of the BAEEs), their incineration yield was around 57 wt %, revealing that this class of ashes has a significantly lower but not negligible adsorptive capacity.

For all of the preceding incineration yields, standard deviation was inferior to 1 wt %.

3.2. SEM/EDS Analysis of RHA and CHA. In accordance with the literature,[12] the SEM/EDS analyses show that RHA and CHA are not homogeneous in morphology and composition (Figures 1 and 2). Although both types of ashes globally contain a lot of Si, but K and P in equal proportion, the outer epidermis similar to a corncob is richer in Si while the other regions of the samples (inner part and cross-sections) are porous and richer in K, P, and Mg. Nevertheless, RHA (whatever the ash class, -LG or -DG) comprise a higher percentage of Si than CHA (Figure 1b vs Figure 2b_1).

Furthermore, SEM analyses of used RHA and used CHA obtained after one FAEE purification treatment followed by an additional carbonization showed differences in morphology. The same observation appeared for the used RHA as a function of the catalyst selected during ethanolysis (Figure 3). While the used RHA maintained the same morphology in the case of FAEEs obtained by alkali catalysis (Figure 3a,b), used CHA samples lost their corncob structure to become powder (Figure 2c). On the other hand, in the case of FAEEs produced via acid-catalyzed ethanolysis, larger pores appeared in the cross-sections of used RHA, revealing a predominantly macroporous structure that promotes the diffusion of species and their adsorption in this region (Figure 3a,c).

3.3. Textural Features of RHA and CHA from BET Analysis. For a high efficiency in the removal of contaminants, an adsorbent requires a porous structure with a high specific area. From Figure 4 showing the N_2 adsorption curves of RHAs (by distinguishing RHA-LG and RHA-GB) and CHA, it can be observed that the three ash classes have different adsorption profiles.

Although both classes of RHA show predominantly adsorption in high P/P_0 values (above 0.9), which is characteristic of a structure with large mesopores and macropores (of 50 nm diameter or more),[12] RHA-GB can adsorb twice more matter than RHA-LG for the lowest P/P_0 values, indicating specifically in RHA-GB the occurrence of a higher fraction of micropores (with diameters lower than 2 nm).

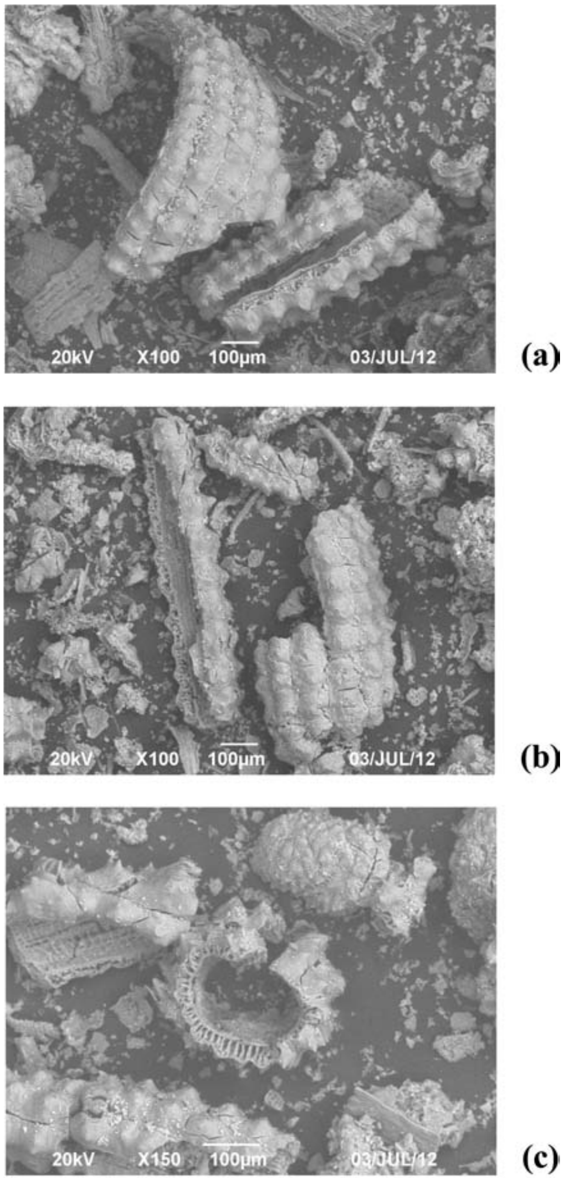

Figure 3. SEM analyses of RHA-GB (backscattered electrons without gold−palladium coating): virgin RHA-GB (a); used RHA-GB after purification and supplemental incineration, for FAEEs obtained via alkali (b) or acid (c) catalysis.

By contrast, the CHA adsorption curve shows an extremely flat profile tending to zero, suggesting poor efficiency as adsorbent of this class of ashes (in agreement with observations of section 3.1).

From the N_2 adsorption isotherms, specific area and pore volume for the three classes of ashes were determined (Table 2). It is important to highlight that although both classes of RHA present quite close pore volumes, specific area of RHA-GB is almost twice as high. This result is in accordance with a higher fraction of micropores and a similar fraction of macropores observed for RHA-GB in comparison with RHA-LG (Figure 2). Actually, the slightly higher pore volume for RHA-GB compared to RHA-LG is probably due to this higher fraction of micropores, even though it corresponds globally to a low percentage of pore volume for the ash. RHA-GB samples should therefore have a better efficiency as adsorbent, probably due to their content of activated coal

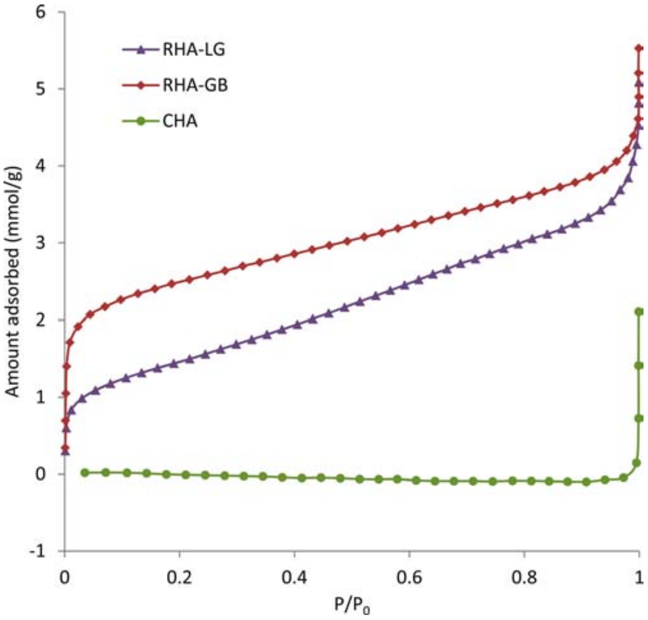

Figure 4. N_2 adsorption isotherms of RHA-LG, RHA-GB, and CHA.

Table 2. Specific Areas and Pore Volumes of RHAs and CHA

adsorbent	pore volume (cm^3/g)	specific area (m^2/g)
RHA-GB	0.191	202 ± 2
RHA-LG	0.176	118 ± 2
CHA	0.073	<1

(section 3.1), which having low-volume pores increases thus the specific area of this class of ashes. By contrast, CHA presents a very low specific area, which is characteristic of a compact structure with a very low pore volume. Thus, this class of ashes should not be a suitable adsorbent for biodiesel purification.

3.4. Comparative Efficiency of the Purification Methods versus Biodiesel Characteristics.

3.4.1. Acidic Water Washing versus Dry Purification. The quality of the resulting FAEE products in terms of soap content and process yields per stage (Y_{I} and Y_{II}) and globally (Y_{global}) are shown in Table 3. The initial soap content of RSEEs was 527 mg/kg. By using a 5 wt % H_3PO_4 solution, no soap residue could be detected in the RSEEs as soon as the first stage of acidic water washing was conducted. Nevertheless, a stable emulsion occurred during this treatment, leading to a difficult RSEE–water phase separation, and, thus, a decrease in the ester yield. The same trend was already observed with phosphorus catalyst, suggesting the use of lower concentrations.[33] Thereby, wet purification of RSEEs was conducted with a more dilute acidic solution (1 wt % H_3PO_4), leading to a significant decrease in the soap content, but with an almost halved global yield in esters due to loss of matter via the two successive washing steps.

By contrast, the dry purification of RSEEs over RHA yielded better results than the water-washing method with H_3PO_4 (solutions at 1 and 5 wt %). In addition to avoiding difficult phase separation, RHA showed better performance in removing soaps, with higher purification yield in FAEEs. Also, a second dry-purification stage over RHA (dual treatment "flash") reduced the amount of soaps below the detection limit of the quantification method.

Finally, it should be mentioned that RHA-LG and -GB had almost equivalent adsorptive capacities (yield of biodiesel dry purification: 92 and 93 wt % for a single ester treatment and 88 and 87 wt % for a dual ester treatment; Table S.I.1 in the Supporting Information).

3.4.2. Dry Purification, Adsorbent Type, and Treatment Procedure. Characterization results of the three FAEE products investigated in this work (BAEE, AIEE, and JCEE) before and after treatment are shown in Tables 4 and 5 for all of the dry-purification methods tested (involving different adsorbents with different treatment procedures). As mentioned previously, this characterization was achieved in terms of key component contents, i.e., esters and contaminants, the latter comprising molecules different in shape and size (TG, DG, MG, free glycerin, total glycerin, and water) as well as chemical elements (Si, K, S, Ca, Mg, Fe, and P). Also, efficiency of the dry-purification treatments was assessed as a function of the removal percentage of each contaminant calculated by the following equation:

$$\eta_{\text{c}} = 100 \times (x_{\text{f}} - x_0)/x_0 \qquad (1)$$

where η_{c} is the efficiency of the dry-purification treatment and x_0 and x_{f} are the contents of each contaminant before and after treatment, respectively. This class of results was also depicted in Tables 4 and 5.

The key observations drawn from these entire results (Tables 4 and 5) are discussed in the following text. It is important to note, however, that GC-FID analyses revealed that no residual triacylglycerides were remaining in the unpurified FAEE products, which moreover contained relatively high ester contents (around 97, 90, and 86 wt % for the BAEEs, AIEEs, and JCEEs, respectively). In addition, the observed iron, magnesium, and phosphorus contents in the initial FAEE products were mostly below detection limits of the analytical method used. These features of the initial material to be purified should also be considered as factors impacting the following observations.

As it could be expected, results showed that the performance of the dry-purification process varies depending on the purifying agent (RHA-LG, RHA-GB, or CHA), the contaminant, the temperature, the contact time, and the number of cycles applied during treatment.

Table 3. Purification Yields and RSEE Product Quality before and after Treatment in Terms of Soap Content

	first stage		second stage		full process
purification method	soap content (mg/kg)[a]	Y_{I} (wt %)[b]	soap content (mg/kg)[a]	Y_{II} (wt %)[b]	Y_{global} (wt %)[b]
wet purification with a 5 wt % H_3PO_4 solution	undetectable	81	not determined[c]	not determined[c]	81
wet purification with a 1 wt % H_3PO_4 solution	68	70	18	61	43
dry purification with RHA (flash treatment)	30	93	undetectable	94	87

[a] Milligrams of soap per kilogram of RSEEs; standard deviation, less than 2 mg/kg. [b] Yield of the *i*th purification process defined (per stage or globally) as Y_i/(wt %) = $(m_i/m_0) \times 100$ where m_i and m_0 are the masses of the RSEE sample before and after purification, respectively; standard deviation, less than 1 wt %. [c] This treatment was conducted in a single stage.

Table 4. Characterization of FAEE Products with Regard to Their Molecular Components before and after Dry Purification with Different Adsorbent Agents and the Treatment Procedures[a,b]

treatment procedure	esters (wt %)	free glycerin (wt %)	MG (wt %)	DG (wt %)	total glycerin (wt %)	water (mg/kg)
Balanites aegyptiaca Fatty Acid Ethyl Esters (BAEEs)						
unpurified BAEEs of departure	97.35	0.13	3.14	0.48	1.00	466
RHA-GB (20 °C, 5 min)	92.13	0.09 (−31)	2.40 (−24)	0.45 (−6)	0.77 (−23)	414 (−11)
RHA-LG (20 °C, 5 min)	88.68	0.10 (−23)	2.26 (−28)	0.39 (−19)	0.73 (−27)	427 (−8)
RHA-GB (20 °C, 20 min)	89.99	0.09 (−31)	2.79 (−11)	0.40 (−17)	0.86 (−14)	311 (−33)
RHA-GB (65 °C, 20 min)	89.46	0.10 (−23)	2.72 (−13)	0.37 (−23)	0.85 (−15)	479 (+3)
RHA-GB [(1) 20 °C, 5 min; (2) 65 °C, 20 min]	**90.62**	**0.04 (−69)**	**2.06 (−34)**	**0.28 (−42)**	**0.61 (−39)**	**291 (−38)**
RHA-GB [(1) 20 °C, 5 min; (2) 20 °C, 5 min]	89.93	0.07 (−46)	2.27 (−28)	0.42 (−13)	0.71 (−29)	337 (−28)
RHA-LG [(1) 20 °C, 5 min; (2) 20 °C, 5 min]	89.02	0.06 (−54)	2.15 (−32)	0.38 (−21)	0.66 (−34)	408 (−12)
RHA-GB [(1) 20 °C, 5 min; (2) reused ashes from step 1, 20 °C, 5 min]	89.33	0.09 (−31)	2.49 (−21)	0.44 (−8)	0.79 (−21)	301 (−35)
RHA-LG [(1) 20 °C, 5 min; (2) reused ashes from step 1, 20 °C, 5 min]	92.24	0.09 (−31)	2.44 (−22)	0.42 (−13)	0.77 (−23)	349 (−25)
CHA (20 °C, 5 min)	89.17	0.09 (−31)	2.88 (−8)	0.45 (−6)	0.89 (−11)	429 (−8)
Azadirachta indica Fatty Acid Ethyl Esters (AIEEs)						
unpurified AIEEs of departure	90.61	0.20	2.75	0.56	0.98	318
RHA-GB (20 °C, 5 min)	90.36	0.08 (−60)	2.22 (−19)	0.40 (−29)	0.70 (−29)	303 (−5)
RHA-GB [(1) 20 °C, 5 min; (2) 65 °C, 20 min]	**87.63**	**0.06 (−70)**	**2.15 (−22)**	**0.35 (−38)**	**0.66 (−33)**	**240 (−25)**
Jatropha curcas Fatty Acid Ethyl Esters (JCEEs)						
unpurified JCEEs of departure	85.67	0.15	2.60	0.91	0.95	875
RHA-GB (20 °C, 5 min)	83.80	0.13 (−13)	3.42 (+32)	0.93 (+2)	1.14 (+20)	918 (+5)
RHA-GB [(1) 20 °C, 5 min; (2) 65 °C, 20 min]	**85.81**	**0.11 (−27)**	**3.42 (+32)**	**0.87 (−4)**	**1.11 (+17)**	**467 (−47)**
specifications of EN 14214[c]	**96.5**	**0.02**	**0.80**	**0.20**	**0.25**	**500**

[a] Efficiency of the dry-purification methods for the focused contaminants is also given in parentheses; the method efficiency was assessed as a function of removal percentage of each contaminant calculated by eq 1. [b] Standard deviation on esters, free glycerin, MG, DG, and total glycerin (wt %): 0.05. [c] All indications are limits, except for the ester content giving the maximum value.

CHA demonstrated a very different adsorptive efficiency according to the contaminants. While this purifying agent was successful in partly removing the organic compounds, very poor results were observed for the chemical elements, particularly K and mostly Si, whose level in the FAEE product increased significantly after treatment. This result can be explained by the SEM image of a sample of used CHA recovered after a purifying treatment and to which a supplemental incineration stage was applied (Figure 2c). The SEM image indeed reveals a radical change in the morphology of the ashes reduced to powder, with a complete destruction of the Si-based structures similar to corncobs. Thereby, CHA cannot be recommended reasonably as adsorbent for dry purification of biodiesel.

RHA-LG showed better efficiency in removing glycerides (DG and MG) than RHA-GB, while this purifying agent was more efficient for adsorbing small molecules such as water. These results are consistent with the SEM/EDS and BET analyses of RHAs, showing a macroporous structure with a higher fraction of micropores in RHA-GB than in RHA-LG.

When considering globally all the variables of the treatment procedure as a function of the contaminants, the efficiency of the dry-purification process is improved when increasing contact time (up to 20 min) and the number of treatment cycles (up to two). One exception is silicon whose level tends to increase with the treatment cycles, due to the ashes releasing gradually this element in the FAEE product (probably because of their high concentration in silicon, Figure 1). Furthermore, increasing the processing time in glass equipment may promote contamination by Si of the material processed. This may also explain the high initial level of Si in the JCEEs which were processed in a borosilicate glass reactor during a much longer reaction time (26 h) than the BAEEs and AIEEs (50 min). Regarding the last key variable of the treatment process, i.e., temperature (the nature of ashes, contact time, and number of treatment cycles have already been assessed previously), various effects were noted as significant according to the considered contaminant. While an increasing temperature (up to 65 °C) promotes retention of large molecules (MG and DG) as well as potassium, the other contaminants (i.e., free glycerin, sulfur, calcium, and particularly water) are removed more efficiently at ambient temperature (20 °C). To illustrate with the case of water as contaminant, the gradient in treatment efficiency over RHA-GB was around −36% by decreasing the operating temperature from 65 to 20 °C and around −25% by increasing the contact time from 5 to 20 min.

Thereby, the most efficient procedure of biodiesel dry purification has been the dual treatment [flash method (20 °C, 5 min) + reference method (65 °C, 20 min)] over RHA-GB. Under these conditions, the dry purification of FAEE products led to a larger reduction in water content: 47% for the JCEEs (obtained via acid catalysis); 38 and 25% respectively for the BAEEs and AIEEs (obtained via alkali catalysis). The levels of free glycerin and DG in the BAEEs and AIEEs were reduced by around 70 and 40%, respectively, but to a lesser extent in the JCEEs, i.e., around 27 and 4%, respectively.

The MG behavior over RHA-GB also appears to depend on the catalysis selected to produce the FAEEs, but more significantly here. Indeed, after the dry treatment over ashes, the MG content decreased in the BAEEs and AIEEs (by 34 and 22 wt %, respectively) but increased in the JCEEs (by 32 wt %). This increase in MG content in JCEEs went hand in hand with a

Table 5. Characterization of the Inorganic Composition of FAEE Products before and after Dry Purification with Different Adsorbent Agents and the Treatment Procedures[a,b]

treatment procedure	chemical element contents (mg/kg)						
	Si	K	S	Ca	Mg	Fe	P
Balanites aegyptiaca Fatty Acid Ethyl Esters (BAEEs)							
unpurified BAEEs of departure	0.63	35.0	6.4	0.72	<0.2	<0.2	<0.2
RHA-GB (20 °C, 5 min)	0.50 (−21)	9.4 (−73)	1.8 (−72)	0.42 (−42)	<0.2	<0.2	<0.2
RHA-GB (20 °C, 20 min)	<0.4 (−37)	3.3 (−91)	<1.0 (−84)	0.22 (−69)	<0.2	<0.2	<0.2
RHA-GB (65 °C, 20 min)	<0.4 (−37)	2.2 (−94)	2.2 (−66)	0.26 (−64)	<0.2	<0.2	<0.2
RHA-GB [(1) 20 °C, 5 min; (2) 65 °C, 20 min]	**<0.4 (−37)**	**<1.0 (−97)**	**1.7 (−73)**	**<0.2 (−72)**	**<0.2**	**<0.2**	**<0.2**
RHA-GB [(1) 65 °C, 20 min; (2) 20 °C, 5 min]	1.83 (+190)	1.5 (−96)	7.7 (+20)	0.34 (−53)	<0.2	<0.2	<0.2
RHA-GB [(1) 20 °C, 5 min; (2) 20 °C, 5 min]	2.36 (+275)	3.9 (−89)	1.4 (−78)	<0.2 (−72)	<0.2	<0.2	<0.2
RHA-GB [(1) 20 °C, 5 min; (2) 20 °C, 20 min]	0.48 (−24)	<1.0 (−97)	1.9 (−70)	0.20 (−72)	<0.2	<0.2	<0.2
reused RHA-GB (20 °C, 5 min)	0.40 (−37)	26.2 (−25)	1.7 (−73)	0.41 (−43)	<0.2	<0.2	<0.2
CHA (20 °C, 5 min]	1.01 (+60)	57.8 (+65)	2.3 (−64)	0.76 (+6)	0.35 (+75)	<0.2	<0.2
Azadirachta indica Fatty Acid Ethyl Esters (AIEEs)							
unpurified AIEEs of departure	4.23	34.6	370	0.49	0.32	0.20	<0.2
RHA-GB (20 °C, 5 min]	4.00 (−5)	12.8 (−63)	360 (−3)	0.42 (−12)	<0.2 (−38)	<0.2	<0.2
RHA-GB [(1) 20 °C, 5 min; (2) 65 °C, 20 min]	**6.81 (+61)**	**2.7 (−92)**	**354 (−4)**	**0.32 (−35)**	**0.32 (+0)**	**0.28 (+40)**	**<0.2**
Jatropha curcas Fatty Acid Ethyl Esters (JCEEs)							
unpurified JCEEs of departure	8.96	2.6	7.9	<0.2	<0.2	<0.2	<0.2
RHA-GB (20 °C, 5 min)	11.92 (+33)	8.4 (+223)	10.3 (+30)	0.21 (+5)	<0.2	<0.2	<0.2
RHA-GB [(1) 20 °C, 5 min; (2) 65 °C, 20 min]	**5.77 (−36)**	**4.8 (+85)**	**4.5 (−43)**	**0.75 (+275)**	**<0.2**	**<0.2**	**<0.2**
specifications of EN 14214[c]	*d*	**5**[e]	**10**	**5**[f]	**5**[f]	*d*	**10**

[a] Efficiency of the dry-purification methods for the focused contaminants is also given in parentheses. The treatment efficency was assessed as a function of removal percentage of each contaminant calculated by eq 1; for a contaminant content below or equal to the observed ICP-AES detection limit, this latter value was used to evaluate the treatment efficiency. [b] Detection limits (mg/kg) of the analytical method used (ICP-AES): 0.2 for Ca, Mg, Fe, and P; 0.4 for Si; 1 for K and S. Maximum standard deviation (mg/kg): 0.01 for Fe; 0.03 for Mg and Ca; 0.06 for Si; 0.3 for K and S (with the exception of AIEEs with sulfur high contents, 1). [c] All indications are limits. [d] No specification exists regarding this species. [e] For (Na + K). [f] For (Ca + Mg).

supplementary production of esters. Indeed, while the dry-purification process led to a reduction in the ester content for the BAEEs and AIEEs despite partial removal of contaminants (probably because of ester retention on the ashes), no reduction in the ester content was observed for the JCEEs. Furthermore, as already noticed in section 3.2, comparison of the SEM images of a sample of virgin RHA-GB with a sample of used RHA-GB (recovered after a purifying treatment of the JCEEs and a supplemental incineration stage) reveals clearly a change in the morphology of the ashes with the appearance of larger size pores in the cross-sections (Figure 3a,c). This phenomenon is not observed with the BAEEs (Figure 3a,b) and is thus due to the content in H_2SO_4 of the JCEEs. Thereby, all of these results seem to suggest that chemical reactions such as DG ethanolysis to MG and esters occur inside the macropores of RHA-GB, where internal mass transfer resistance is decreased. Thus, RHA-GB seems to act as the support of the residual acid catalyst previously used for the JC oil ethanolysis and contributes to restart the acid activity through an heterogeneous catalysis process during the dry-purification treatment of the JCEEs.[34]

Furthermore, K and Ca contents in JCEEs after treatment over RHA-GB are superior than they were before treatment, suggesting that the ashes released these chemical elements in the FAEE product during the treatment. Thereby, one might conclude that dry purification over RHA-GB should not be used for biodiesels obtained via acid catalysis.

Despite its demonstrated effectiveness, dry purification with dual treatment of FAEE products over RHA-GB has not been successful in leading to an acceptable range the contaminant levels in order to fulfill the EN 14214 Standard requirements, with the exception of water, potassium and sulfur (sulfur content of AIEEs being a specific case as will be discussed in subsequent text). Regarding silicon, although concentration in this element in most of FAEE products has been efficiently reduced after the purification process, it would be difficult to conclude whether this level is satisfactory or not since no standard-limiting Si content in biodiesel exists to date.

RHA did not succeed in bringing the sulfur level in the AIEEs below the EN 14214 Standard requirements due to the very high concentration of this element in crude AIEE product (before purification treatment). This very high concentration of sulfur (35 times higher than the limit imposed by EN 14214[35]) probably results from the presence of volatile organosulfur components in the initial lipidic resource.[36,37] Even higher sulfur concentrations were found by other authors[3] in AI oil (1990 mg/kg) and derived methyl biodiesel (473.8 mg/kg).

Similar performance to the dual treatment [flash method (20 °C, 5 min) + reference method (65 °C, 20 min)] was obtained with a single treatment cycle conducted at ambient temperature (20 °C) by increasing the contact time up 20 min. This procedure requiring no heating is more energy efficient. Moreover, its performance could be improved by operating under the ambient temperatures usually encountered in the original subtropical regions of the NEVOs (35−40 °C).

Whatever the class of RHA (-LG or -DG), ashes reused twice have shown poorer performance in removing contaminants than fresh ashes, except for water (probably because of a longer contact time promoting mainly water adsorption). This result prevents *a priori* the potential use of RHA as adsorbent in a continuous process by dry purification.

4. CONCLUSION AND OUTLOOK

Despite a clearly observed adsorptive capacity, CHA proved not to be efficient enough as purifying agent compared to RHA for the application focused on in this work. This different behavior might be ascribed to the difference in structure and composition of the two adsorbents: CHA has a compact structure with a very low specific area and a very low pore volume, while RHA is much richer in Si and has a micro-/macroporous structure with a high specific area. Thereby, the most efficient procedure of biodiesel dry purification was the dual treatment [flash method (20 °C, 5 min) + reference method (65 °C, 20 min)] over rice husk ash containing activated carbon (RHA-GB). The impurity levels of biodiesels, such as organic materials (residual glycerides and free glycerin) or inorganic materials (water and metals), were significantly reduced, without however fulfilling the EN 14214 Standard requirements for most contaminants. Nevertheless, from the obtained results, better performance could be reached with a one-step procedure conducted in 20 min and at 35−40 °C, corresponding to the usual ambient temperatures of the subtropical regions where the considered NEVOs grow. Besides, the used ash loses efficiency as a purifying agent, preventing its application in a continuous process.

However, the previously mentioned conclusions concern only the FAEE products produced by alkali-catalyzed ethanolysis of NEVOs. Indeed, although successful results were obtained in the literature for the removal of FFAs from vegetable oils with RHA,[17] poor performance was observed in this work for dry purification of JCEEs containing residual acid catalyst (H_2SO_4). In such a case, liquid−liquid extraction with crude glycerol resulting from biodiesel production via alkali catalysis[9] might be a better solution. Moreover, during JCEE dry treatment over RHA-GB, some reactions still enhancing esters formation would occur via an acid heterogeneous catalysis inside the macropores of the adsorbent activated by residual H_2SO_4.

Regarding the sulfur content of AIEEs (that dry purification over RHA-GB has not reduced successfully due to the very high initial concentration in this element in the crude AIEE product), it is planned to check the origin both in the initial lipidic resource and in the esters.

Apart from these positive results, dry purification on agricultural solid waste offers various benefits in addition to reducing water needs and aqueous effluent production during biodiesel processing. Indeed, this alternative could also be used to purify biodiesels obtained from other transesterification processes (via heterogeneous catalysis or noncatalytic supercritical route) as it has the potential of removing reaction residues as well as heavy metals resulting from the oil extraction stage or from the use of heterogeneous catalyst. A further option in agreement with the biorefinery concept would be to integrate the matter−heat−electricity cogeneration in the biodiesel production unit. This way, the agricultural solid waste combustion would be used to generate heat and power required in the unit operation,[4,14,38,39] while recovering combustion products (ash) for the purification stage (as natural adsorbent). Ultimately, used RHA-GB containing low amounts of metals could be recycled as a soil corrective[12] due to its content of biodegradable organic matter (biodiesel, free glycerin, and residual glycerides) and potassium (when used as catalyst).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR spectra of each of the three FAEE products investigated in this work before dry purification (Figure S.I.1) and the material balances and yields relative to the BAEE product dry purification (Table S.I.1.). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ ACKNOWLEDGMENTS

This work has been supported by the Fonds National pour l'Education et la Recherche (FONER) from Burkina Faso. Also, we express grateful acknowledgment to Olivier Fabre, Emilien Girot, Jean-François Rémy, Frédéric Roze, and Cornélius Schrauwen for their technical support and Professor Raphaël Schneider for his helpful discussion during the work.

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