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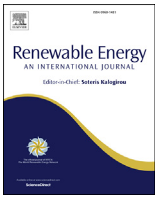

Ethyl biodiesel production from non-edible oils of *Balanites aegyptiaca*, *Azadirachta indica*, and *Jatropha curcas* seeds – Laboratory scale development

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ABSTRACT

By starting first at the laboratory scale, optimal operating conditions for the reaction unit aimed at producing ethyl biodiesels from non-edible vegetable oils (NEVO) were determined with the ultimate objective of proposing an on-farm processing technology that should be sustainable for emerging countries. Three NEVO widely available in Burkina Faso were selected: *Balanites aegyptiaca* (BA), *Azadirachta indica* (AI), and *Jatropha curcas* (JC) oils. Their conversion to fatty acid ethyl esters (FAEE) was conducted via a two-stage procedure under atmospheric pressure: an alkali-catalyzed ethanolysis at ambient temperature for the BA and AI oils (leading to 93 and 87 wt.% FAEE respectively) and an acid-catalyzed ethanolysis at the normal boiling of the alcohol for the JC oil (leading to 89 wt.% FAEE). Based on the intermediate addition of glycerol at ambient temperature, the two-stage procedure combines chemical kinetics, chemical equilibrium, and phase equilibrium phenomena.

1. Introduction

The increase in world energy demand and competition of edible oils for human use and biofuel production led non-edible vegetable oils (NEVO) becoming one of the leading raw materials to produce biodiesel [1,2]. This applies particularly to emerging countries like Burkina Faso, which rely on extensive agriculture complemented by food imports and, at the same time, have a heavy reliance on imported fossil fuels. Diversification of energy resources while bearing in mind food security would ensure energy independence and security, new national income and employment sources [3,4]. In addition, NEVO plants can be grown in large scale on non-cropped marginal and wastelands, with various advantages including low water and fertilizers requirements, resistance to pests and diseases, wide adaptability to different climatic conditions, and high oil yield [5]. Also, within the concept of an integrated whole-crop bio-refinery [6,7], the non-edible feedstocks which are already less expensive to grow than edible ones [5] should lead to significant reduction in biodiesel production cost [8]. Hence, to guarantee biodiversity and continuous supply of sustainable feedstock for biofuels (and other bio-products), research of new potential candidates among NEVO is still pursuing. However, neat vegetable oils (or any lipid resources) are unsuitable as fuel for modern diesel engines, leading to engine failures

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Abbreviations: AI, Azadirachta indica; ALSI, Automatic liquid sampler injector system; BA, *Balanites aegyptiaca*; DG, Diglyceride(s); EO, Ethyl oleate; EtOH, Ethanol; FAEE, Fatty acid ethyl ester(s); FAME, Fatty acid methyl ester(s); FFA, Free fatty acid(s); FID, Flame ionization detector; g[KOH], Global catalyst concentration related to the whole of the reaction; GC, Gas-chromatography; gMR, Global molar ratio related to the whole reaction; IS, Internal standard; JC, *Jatropha curcas*; $[KOH]_i$, Catalyst concentration related to the ith stage; MG, Monoglyceride(s); MHD, Methyl heptadecanoate; MRs_i, Alcohol to oil molar ratio related to the ith stage; MS, Mass spectrometry; NEVO, Non-edible vegetable oil(s); S.I., Supporting information; s [KOH], Catalyst concentration related to each stage of the reaction; SBO, Soybean oil; s_i, ith stage; sMR, Alcohol to oil molar ratio related to each stage of the reaction; TG, Triglyceride(s); x_i, mass proportion of the [alcohol – catalyst] mixture corresponding to the ith fraction added for the ith stage.

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over time [1,9–11] and mutagenic emissions during combustion [12,13]. Therefore, prior to use as fuel, neat vegetable oil requires to be converted into biodiesel via alcoholysis (i.e. transesterification). During processing, triglycerides (major components of lipidic resources) react with methanol (or by extension, ethanol) to form fatty acid methyl esters (FAME) leading to the commercial biodiesel (or by extension, fatty acid ethyl esters (FAEE)) and glycerol (by-product). Although methanol has been preferred to bioethanol in industrial applications because of its lower cost and reduced tendency to form emulsions, replacing it with bioethanol is an attractive alternative. Indeed, in addition to be non toxic, bioethanol may be produced from local and renewable agricultural resources (including residues [7,14,15]) leading thus to a 100% renewable biodiesel [13,16], with access to greater energy independence [17]. However, some impurities like free fatty acids (FFA) naturally present in NEVO, and especially water present both in bioethanol and NEVO, limit the use of these sustainable feedstocks in large-scale biodiesel production. Hence, efforts need to be focused on the production process in order to solve impurity issues without additional purification steps, reducing thus the processing cost and energy demand, while enhancing the sustainability of the produced biodiesel [10].

The purpose of this work is to determine, by starting first at the laboratory scale, optimal operating conditions for the reaction step of a unit aimed at producing ethyl biodiesels from three NEVO. The latter were selected from trees locally available in Burkina Faso: *Jatropha curcas* (JC), *Azadirachta indica* (AI, commonly named Neem), and *Balanites aegyptiaca* (BA, commonly named Desert date). Indeed, these trees are well adapted to tropical arid lands (particularly BA [18] and AI [2]) with additional merits as medicinal values [2,18,19] and production of pesticides for AI [2]. The resulting ethyl biodiesels will thus be referred to as BAEE, AIEE, and JCEE respectively. However, this objective was also subject to several constraints (additionally to those relating to the use of readily available and sustainable resources): maintaining a simple and low-cost homogeneous-catalyzed process inducing low effluents in order to be the most sustainable as possible for human and environment. Hence, for the process development at the pilot scale, dry-washing of biodiesel with natural and readily available adsorbent will be used instead of wet-washing. An option in agreement with the bio-refinery concept would be to use, as natural adsorbent, the ashes obtained via combustion of Jatropha seed husk [19,20] or even rice husk [21,22]. Furthermore, cogenerated heat and power could be used for processing biodiesel. A compromise of the whole of these objectives and constraints would help to result in an on-farm processing technology that should be a sustainable alternative.

Last but not least, the fundamental aspects underpinning the whole work are available in the supporting information (S.I., Appendix A). They focus on the main physicochemical features of ethanolysis (NEVO to biodiesel via transesterification methods; coupling of chemical kinetics, phase equilibria and chemical equilibrium; key parameters of the ethanolysis process and best compromise [23–83]), while positioning the present work among recent literature on the same topic and highlighting its novelty.

2. Experimental section

2.1. Materials

BA, AI, and JC oils were obtained by extraction (cold pressing and filtration) of the seed kernels [84]. The characterization of each vegetable oil was conducted in a previous work [85] (Table 1). With respect to their content in FFA (Table 2), alkali-catalyzed ethanolysis with potassium hydroxide (KOH) was conducted for BA and AI oils, while acid-catalyzed ethanolysis with sulfuric acid (H_2SO_4) was selected for JC oil (Section A.1, S.I.). Indeed, KOH is easily available in Burkina Faso and the effluents resulting from biodiesel purification may act as fertilizer for soil due to potassium content [53]. Thus, additionally to the NEVO, the chemicals required in this work were: ethanol, KOH, H_2SO_4, citric acid, sodium bicarbonate ($NaHCO_3$), ethyl oleate (EO), methyl heptadecanoate (MHD), 1-decanol, and n-heptane; all were purchased from Sigma-Aldrich or Fluka and were of analytical grade. Crude wine bioethanol, before and after dehydration, was also provided by UNGDA (France).

Table 1
Composition in terms of fatty acids (molar fractions %) for the three NEVO investigated: *Balanites aegyptiaca* (BA), *Azadirachta indica* (AI), and *Jatropha curcas* (JC) [85]. Major components are indicated in bold.

Fatty acids – Formulae *(name)*	Burkina Faso NEVO		
	BA	AI	JC
C10:0 *(Capric acid)*	0.05	0.05	0.05
C12:0 *(Lauric acid)*	0.02	0.02	0.01
C13:0 *(Tridecanoic acid)*	0.02	0.02	0.03
C14:0 *(Myristic acid)*	0.06	0.05	0.06
C16:0 *(Palmitic acid)*	**13.79**	**17.65**	**15.56**
C16:1c9 *(Palmitoleic acid)*	0.14	0.11	0.92
C17:0 *(Heptadecanoic acid)*	0.11	0.13	0.08
C18:0 *(Stearic acid)*	**11.07**	**17.46**	**7.34**
C18:1t9 *(Elaidic acid)*	0	0.21	0
C18:1c9 *(Oleic acid)*	**28.25**	**46.84**	**42.53**
C18:1c11 *(cis-Vaccenic acid)*	0.72	0.52	1.23
C18:2c9c12 *(Linoleic acid)*	**45.32**	**14.90**	**31.84**
C18:3c9c12c15 *(Linolenic acid)*	0.06	0.44	0.16
C20:0 *(Arachidic acid)*	0.33	1.55	0.19
C22:5c7c10c13c16c19 *(Docosapentaenoic acid)*	0.06	0.05	0
Total	100.00	100.00	100.00
Saturated species	25.45	36.93	23.32
Monounsaturated species	29.11	47.68	44.68
Polyunsaturated species	45.44	15.39	32.00

Table 2
Key properties of the three NEVO (*Balanites aegyptiaca* (BA), *Azadirachta indica* (AI), and *Jatropha curcas* (JC)) investigated as feedstocks for the transesterification process.

Key properties	Burkina Faso NEVO		
	BA	AI	JC
Average molecular weight[a]	857	829	849
Water content (wt.%)[b]	0.06	0.07	0.08
Acid value (mg KOH/g)[c]	0.46	4.54	25.36
Acidity (%)[c]	0.23	2.29	12.74

[a] Calculated from the oil molar composition in terms of fatty acids.
[b] Determined by Karl-Fischer titration.
[c] Determined by following the standard EN-14104 [86].

2.2. Laboratory-scale experimental setup and experimental design features

All ethanolysis reactions were carried out in a 250 mL three-necked flask equipped with a thermometer (±0.5 °C), a reflux condenser, a heating silicone oil bath, a magnetic stirrer, a stirrer/heat controlled plate (±1 °C), and a sampling outlet (a 2 mL syringe with a long needle).

The operating conditions related to the selected experiments (together with the corresponding FAEE contents) are summarized in Tables 3–5. Due to the complexity of the lipidic feedstocks and of the physical and chemical phenomena involved in the ethanolysis reaction, conversion models of triglycerides (TG) based on factorial