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Optimization of non-catalytic transesterification of tobacco (*Nicotiana tabacum*) seed oil using supercritical methanol to biodiesel production

Nuria García-Martínez [a,*], Pedro Andreo-Martínez [a], Joaquín Quesada-Medina [a,*], Antonia Pérez de los Ríos [a], Antonio Chica [b], Rubén Beneito-Ruiz [c], Juan Carratalá-Abril [c]

[a] Department of Chemical Engineering, Faculty of Chemistry, University of Murcia, Campus of Espinardo, 30071 Murcia, Spain
[b] Instituto de Tecnología Química, Universitat Politècnica de València - Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, 46022 Valencia, Spain
[c] Asociación de Investigación de la industria del Juguete, Conexas y Afines, Avenida de la Industria, 23, 03440 Ibi, Alicante, Spain

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A B S T R A C T

The biodiesel production from non-edible oils has high potential as renewable and ecological fuel. Few researches have been conducted to date on the production of biodiesel from tobacco (*Nicotiana tabacum*) seed oil. The aim of this study was to optimize the biodiesel production from this crude oil by non-catalytic supercritical methanolysis using response surface methodology (RSM). Triglyceride conversion, total and individual FAME yield, monoglyceride and diglyceride yield, and thermal decomposition degree of biodiesel were determined in the temperature and reaction time ranges of 250–350 °C (12–43 MPa) and 15–90 min, respectively, at a fixed methanol-to-oil molar ratio of 43:1. According to the RSM, the optimal conditions were 303.4 °C and 90 min, reaching a predicted maximum FAME yield of 91.1 ± 3.2 mol%. This maximum was very close to that obtained experimentally (92.8 ± 2.1 mol%) at 300 °C and 90 min. Decomposition of biodiesel became evident at 325 °C and 60 min of reaction due to the thermal instability of unsaturated methyl esters (methyl linoleate and oleate). The biodiesel obtained in the best experimental reaction conditions (300 °C and 90 min), where no thermal decomposition of FAMEs was observed, contained most of the byproduct glycerol generated, which was degraded and incorporated to the product. This biodiesel basically failed to meet the content of FAMEs as required by the standard EN 14214, the content of monoglycerides and total glycerol, and the acid value, being a little above the required upper limits. However, this biodiesel can be blended with other biodiesels of complementary features to produce a biofuel meeting the requirements of the standard EN 14214.

1. Introduction

Cultivated tobacco (*Nicotiana tabacum* L.) is an annual herbaceous plant belonging to the *Solanaceae* family, grown worldwide for its leaves, which are mainly used to produce smoking tobacco and tobacco products such as cigarettes, cigars or snuff. These products are widely commercialized globally due to the addictive nature of nicotine, one of the constituents of tobacco leaves, which is a harmful substance for human health [1].

The total world production of raw tobacco in 2013 was 7.4 million tons, of which about 67.8% were grown in Asia, mainly in China, 20.3% in America, 8.5% in Africa and the remaining 3.4% in Europe [2]. According to the Directorate General for Agriculture and Rural Development of the European Commission [3], the main European producers of *Nicotiana tabacum* crop are Italy, Bulgaria, Greece, Spain and Poland, which, together, account for around 85% of the EU tobacco growing area in 2014 (90,886 ha).

A sharp decrease in the quantity of tobacco produced in Europe has been observed during the past few years (see Fig. 1). This decrease is the result of a fall in consumption of tobacco products caused by the negative connotation of tobacco on people's health, as well as a great productive expansion of emerging countries in this sector such as China, Brazil and India.

A way to increase the benefits of the tobacco industry, and thus provide an additional value to this crop in Europe, may be the use of the byproducts of this industry, as the tobacco seed oil (TSO), for the production of biodiesel. Another interesting approach may be the cultivation of improved tobacco plants with a high content of oil-rich seeds to be used also for biodiesel production, which could lead to an increase of the amount of hectares cultivated with this crop in Europe. In fact, an interesting research project of public-private cooperation (n° IPT-2012-0060-120000) funded by the

* Corresponding authors.
E-mail addresses: n.garciamartinez@um.es (N. García-Martínez), quesamed@um.es (J. Quesada-Medina).

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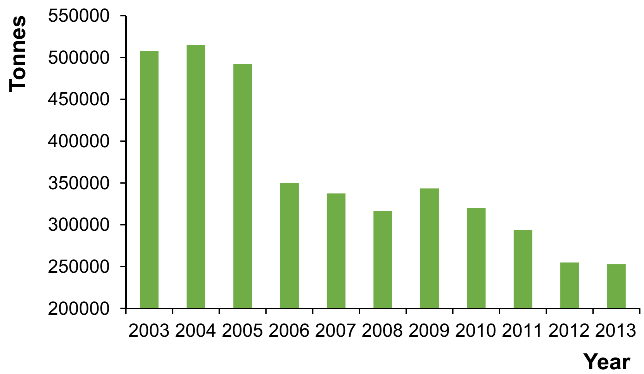

Fig. 1. Production of raw tobacco in Europe (2003–2013) according to the FAO.

Ministry of Economy and Competitiveness (MINECO) of Spain was developed to reactivate the cultivation of *Nicotiana tabacum* in Spain for the production of biodiesel. This project included a varietal selection study of tobacco plants oriented to the production of oil-rich tobacco seeds.

Despite the small size of tobacco seeds (up to 10,000 seeds/g), the amount of seeds per plant is extremely large, varying between 0.6 and 1.2 t seeds/ha for varieties used in leaf production, and 5 t/ha for varieties improved to produce TSO [4]. In addition, tobacco seeds contain 36–41 wt% of free-nicotine oil, suitable for biodiesel production, giving oil yields per hectare (0.2–2 t/ha) similar to other non-edible oils used to produce biodiesel such as jatropha or karanja [5,6]. Taking all of the above mentioned into account, along with the possibility of a future imbalance between the use of edible vegetable oils (mainly palm, rapeseed and soybean oils) for food supply or commercial biodiesel production, non-edible TSO may become a potential and sustainable source for ecological fuel production [7–11].

In recent years, the concern over environmental degradation and over-exploitation of natural resources has driven the search for alternatives to fossil fuels. Biodiesel is the most promising partial substitute for petroleum-derived fuels due to its low level of contaminant emissions, renewable and biodegradable character and similar combustion and ignition properties compared with conventional fuels [12–15].

The transesterification of triglycerides (TG) from vegetable oils or animal fats is the common method to obtain biodiesel. This process involves the reaction of TG with short-chain alcohols (methanol or ethanol) to form mainly fatty acid methyl esters (FAMEs), but also glycerol and intermediate products such as mono- and di-glycerides, which have a great influence on biodiesel quality [13,16–18]. The conventional methods for biodiesel production needs to use an excess of alcohol and catalysts such as acids, alkalis or enzymes. Homogeneous alkaline catalysts such as NaOH or KOH are the most widely used for industrial biodiesel production. These alkalis reduce reaction time, while TG conversion is improved [19,20]. However, when feedstocks contain a high amount of free fatty acids (FFAs) and/or water (more than 0.5 and 0.06 wt%, respectively), the use of conventional alkaline catalysts reduces the FAME yield and leads to the formation of soaps which complicates the separation between glycerol and FAMEs. Therefore, additional separation, neutralization and purification steps, which have a high cost, must be carried out [20–24].

An interesting method to produce biodiesel from low quality feedstocks and improve the FAME yield is to use non-catalytic transesterification using supercritical methanol in a one-step process. In this supercritical process, the TG conversion to biodiesel is not affected by the FFA and water contents, which could even have a positive effect on the reaction rate, and the absence of catalysts simplifies the downstream operations of separation and purification [25–27]. In addition, supercritical conditions (above 239 °C and 8.1 MPa for methanol) allow complete TG conversions to be reached in short reaction times due to the formation of a single phase solution between methanol and oil, which promotes simultaneous reactions of TG transesterification and FFA esterification [21,28,29]. On the other hand, biodiesel production under supercritical conditions requires a great control of variables such as temperature, pressure, methanol-to-oil ratio and reaction time, which have direct influence on the process [30,31]. The common operation conditions for non-catalytic transesterification using supercritical methanol are: temperatures of 280–400 °C, pressures of 10–45 MPa, alcohol-to-oil molar ratios in the range of 40:1–45:1, and reaction times between 4 and 30 min, depending on the type of batch reactor and oil used [26,31–33]. In these intense conditions of temperature and pressure, it is interesting to consider the thermal stability of biodiesel, as it has been demonstrated that FAMEs are vulnerable to oxidation and degradation [34–36].

To date, very little research has been carried out to study biodiesel production from TSO: Usta [4] and Usta et al. [7] were able to convert 86 and 88 wt%, respectively, of TSO to biodiesel in 3–4 h using the classic transesterification process of using methanol in the presence of NaOH as catalyst; Veljković et al. [8] improved the FAME yield to 91% in 55 min by carrying out an acid-catalyzed esterification (ACE) followed by a base-catalyzed methanolysis (BCM) in order to avoid the reduction of TG conversion to biodiesel caused by high levels of FFAs present in TSO (above 10–17%). Despite the fact that supercritical methanolysis may be an effective way for biodiesel production from TSO with a high content of FFAs, to the author's best knowledge, no research has been conducted with this alternative process yet.

The aim of this study was to achieve the maximum efficiency during the supercritical methanolysis of tobacco seed oil to produce biodiesel without using catalysts in a one-step process (this work represents the first study of the supercritical methanol transesterification of tobacco seed oil to biodiesel). For this purpose, a wide range of experimental conditions was explored using statistical design and optimization modeling. The influence of the temperature (250–350 °C) and reaction time (15–90 min) on the process was evaluated by RSM and analysis of variance (ANOVA). Most of the authors working on the supercritical methanol transesterification of vegetable oils to biodiesel in batch reactors reported optimal methanol-to-oil molar ratios ranging from 40:1 to 45:1 regardless of the type of oil used [23,26,37–44]. In addition, Olivares-Carrillo and Quesada-Medina [45] also observed that molar ratios of 43:1 and above not only favored the formation of FAMEs, but also had a certain protective effect against the thermal decomposition of the polyunsaturated ones. Therefore, a methanol-to-oil molar ratio of 43:1 was used in all the experiments carried out in the present study. Under the analyzed conditions, a large number of responses, such as TG conversion and the yields of total FAMEs (biodiesel), intermediate products [monoglycerides (MG) and diglycerides (DG)] and individual FAMEs, was determined. In addition, the effect of tested variables on the degree of thermal decomposition of FAMEs was also studied. Finally, an analysis of some quality standards, as required by the standard EN 14214, of the biodiesel obtained in the best supercritical reaction conditions was carried out.

2. Materials and methods

2.1. Raw material and chemicals

The crude oil extracted from the seeds of *Nicotiana tabacum* for biodiesel production was provided by Innotecno Development, S.L.