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Subcritical ethylic biodiesel production from wet animal fat and vegetable oils: A net energy ratio analysis

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ABSTRACT

Ethylic transesterification process for biodiesel production without any chemical or biochemical catalysts at different subcritical thermodynamic conditions was performed using wet animal fat, soybean and palm oils as feedstock. The results indicate that 2 h of reaction at 240 °C with pressures varying from 20 to 45 bar was sufficient to transform almost all lipid fraction of the samples to biodiesel, depending on the reactor dead volume and proportions between reactants. Conversions of 100%, 84% and 98.5% were obtained for animal fat, soybean oil and palm oil, respectively, in the presence of water, with a net energy ration values of 2.6, 2.1 and 2.5 respectively. These results indicate that the process is energetically favorable, and thus represents a cleaner technology with environmental advantages when compared to traditional esterification or transesterification processes.

1. Introduction

The transesterification reaction of vegetable oils to produce fatty acid methyl or ethyl esters (FAMEs or FAEEs) can be catalyzed by acids, bases or enzymes, among other processes [1]. The predominant FAMEs employed in the biodiesel industry in the world are derived from soybean, rapeseed, and palm oils [2]. Currently, most commercial processes employ methanol to perform the transesterification of triglycerides, catalyzed by a strong base (KOH) in a homogeneous process to produce FAMEs. This is due to the fast transesterification reaction in the presence of alcohol soluble bases and to the low cost of alkaline material, but this process involves many treatment steps previous to and post-reaction, with generation of large amounts of effluents and waste. Besides, the use of a soluble base as a catalyst is not suitable for processing low quality raw materials, such as animal fat and palm oil that usually contain traces of water and high amounts of free fatty acids which readily react via the saponification reaction, generating soaps and hindering the separation of the products, consumes the catalyst and reduces its efficiency [3]. Likozar and Levec [4] performed a very detailed kinetic study of the transesterification reaction of various vegetable oils, using various alcohols, via homogeneous catalysis with KOH. The authors showed that the alcohol influences the mass transfer rate-determining region through its physical properties and the reaction rate-determining region depending on its chemical properties and reactivity. Using methanol, the initial emulsion formed, gradually becoming a pseudo-homogeneous phase with the progress of the transesterification reaction may explain its better performance among all alcohols tested. However, methanol is very toxic in comparison with ethanol [5]. The transesterification reaction using ethanol is safer and an environmental friendly alternative. In Bazil, where ethanol is produced at large scale and is more cost effective, fatty acid ethyl esters (FAEEs) should be produced instead of fatty acid methyl esters (FAMEs). The proposed reaction mechanism for the traditional alkaline transesterification occurs by a nucleophilic attack of the methoxide groups (resulting from the reaction of the alkali with the alcohol) at the triglyceride carbonyl groups. An undesirable saponification reaction occurs between the alkali and triglyceride, generating a fatty acid salt (soap) and glycerol. The use of acid catalysts solves this problem, but the kinetics of the reaction is much slower [1,6–9], and presents problems of corrosion of the equipment used in the process. The reaction mechanism for acid catalysis is initiated by an electrophilic attack of the acidic

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Nomenclature

AF	animal fat
FFA	free fatty acids
FAEEs	fatty acid ethyl esters
FAMEs	fatty acid methyl esters
GC	gas chromatography
IS	internal standard
NER	net energy ratio
TG	triglycerides
TGpcar	TG peak corrected after reaction
TGpar	TG peak area after reaction
TGpbr	TG peak area before reaction
ISpbr	IS peak area before reaction
ISpar	IS peak area after reaction
TGtc	TG total conversion
TGpcar	TG peak corrected area after reaction
FAEEsmax	maximum possible formation of FAEEs peak area
FFApbr	FFA peak area before reaction
E_{FAEEs}	energy obtained from FAEEs
E_{cpm}	energy consumption from the power meter
E_{rfr}	energy requirements for the reaction.

proton, generating protonic intermediate species, followed by a nucleophilic attack of the alcohol to the triglycerides [8]. Currently both the alkaline and acid transesterification processes feature a number of technological and environmental challenges among which are: (a) the conditioning of the reactants with acids and strong bases prior to the alkaline transesterification reaction; (b) the generation of large volumes of contaminated water resulting from the neutralization of the produced biodiesel; (c) the generation of waste in the purification of glycerol's step; (d) the lack of modularity of the processes; (e) batch operation; (f) the generation of soap when using the alkaline catalyst (KOH); (g) the high toxicity of methanol; and (h) the slowest kinetics of the reaction catalyzed by acidic or some heterogeneous catalysts.

Enzymatic process, on the other hand, has important advantages which include mild reaction conditions and the possibility of using feedstock with high free fatty acid content, but generally presents kinetics limitations. Mangas-Sánchez and Adlercreutz [10] recently proposed the use of silica particles, which permitted a larger surface area in the interphase, overcoming mass transfer limitations and thus increasing the rate of the triacylglycerol and free fatty acids conversion process to biodiesel. The authors used *Thermomyces lanuginosus* lipase as catalyst in an aqueous/organic two-phase system and a high oleic acid content starting material in order to simulate low-quality oil obtaining a biodiesel yield of 96%, with 2% monoacylglycerols and 2% diacylglycerols remaining after 5 h under the mild conditions used (37 °C), but further increases in the efficiency of the enzymatic process are desired to make it attractive and suitable for large-scale applications.

Transesterification reactions in supercritical and subcritical thermodynamic conditions have been described in the literature, using methanol or ethanol and avoiding most of the above-mentioned problems [11,12], or trying to find, by mathematical modeling, the best thermodynamic conditions to produce biodiesel from triglycerides using methanol, subcritical or supercritical [13–21]. Generally, under subcritical thermodynamic conditions, short reaction times are sufficient to achieve conversion yields above 90% in the absence of catalysts. Compared to the alkaline and acid reaction mechanisms, the proposed mechanism for the supercritical (and perhaps subcritical) transesterification reaction [22] indicates a direct attack of the alcohol to the triglyceride's carbonyl groups, forming an intermediate diglyceride and then the methyl or ethyl esters of fatty acids. High yields and very low reaction time (about 5 min) have been achieved, in which the major critical factors are the optimization of the mix between the reactants and the characteristics of the supercritical fluids. Water use in subcritical conditions is a technologically cleaner alternative that has been successfully applied in various processes such as extraction, hydrolysis [23,24] and wet oxidation of organic compounds, including glycerol [25,26]. Recently the production of biodiesel by transesterification using methanol and water in subcritical condition was described with conversion rates above 90% and reaction time of 4 h [11]. The main problem of this process is the huge energy demand. Some authors of the same research group showed that wet activated sludge may be converted directly into biodiesel using only subcritical water as catalyst [24], but the long reaction time (24 h) at 175 °C also implies in huge energy demand. More recently, they showed again that subcritical water act as a catalyst for esterification with methanol of fatty acids obtained from low quality feedstock oil [27], at 175–205 °C and 2.0–2.8 MPa. A catalyst-free two-step process has been proposed, with hydrolysis of triglycerides to fatty acids in subcritical water and subsequent methyl esterification of these acids in supercritical methanol [23]. This process presents some advantages, as glycerol is removed away prior to methyl esterification, avoiding backward reaction; moreover, because the fatty acids act as acid catalysts, smaller amounts of methanol are used. All these aspects may contribute to higher energy efficiency.

A key point for the production of any fuel is that the energy produced per product unit must be greater than the energy expended to obtain this product (which, in the present case, is biodiesel). The metrics used here to evaluate the energetic feasibility of the process is the net energy ratio (NER), which can be defined as "the ratio of the total energy production to the primary non-renewable energy requirements" [28].

In Brazil, the main feedstock used for biodiesel is soybean oil, varying between 70% and 85% of the total biodiesel matrix each year, but animal fat corresponds to 10% in average, and reached 25% in 2008. Animal fat is abundant in Brazil, as this country is the second meat producer in the world, but many biodiesel industries limit the addition of animal fat to 30 wt.% of the total feedstock, generally combined with the soybean oil, due to its high acidity and high viscosity, which may cause clogging of pipes and equipment. To achieve this ratio of 30 wt.% in the mixture, a pretreatment is required to remove the free fatty acids from the animal fat. This treatment is made through a reaction with sodium hydroxide, followed by centrifugation and neutralization with hydrochloric acid, and all these steps generate more fatty acid residues. The process presented here has no such limitations, as it can use raw animal fat as feedstock, with no need for mixtures, and generates almost no effluents and residues, compared to the all traditional processes. This process has other intrinsic advantages due to the absence of catalysts, as homogeneous alkaline catalysts causes the undesirable saponification reaction, and the homogeneous acid catalysts may cause corrosion problems, and both led to the intrinsic generation of effluents. Moreover, solid catalysts implies on mass transfer limitations between phases and within the pores of the catalyst itself, resulting in lower conversion of the feedstock. Enzymatic catalysts also have limitations; mass transfer of substrate and products between the phases constitutes a bottleneck to overcome in these bioprocesses.

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