A Feasible Route for Producing Ethylic Biodiesel

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Introduction

Nowadays the industrial production of biodiesel is based on the methylic route. This occurs due to the advantages and simplicity of this route in relation to the reaction kinetics and to the purification steps and in spite of the fact that methanol is obtained from petrochemical sources. Although ethanol has the advantage of being a renewable alcohol produced at competitive costs, at least in Brazil, the ethylic route for producing biodiesel has some drawbacks. The reaction kinetics is slower and the purification steps used in the methylic route can not be directly transferred to the ethylic one. Ethanol enhances the mutual solubility of the hydrophilic and lipophilic substances that occur along the production process and makes more problematic all purification steps. The literature on biodiesel production focuses on the methylic route, emphasizing the evaluation and development of catalysts. Along the reaction path two liquid phases are formed, the upper one contains mainly monoalkyl esters (biodiesel) and the bottom one is rich in glycerol. The traditional approach uses basic homogeneous catalysts, such as sodium hydroxide or methoxide. These catalysts are preferred due to their low cost and higher catalytic activity. But their use also generates soaps, impairing the process efficiency and increasing the requirements for the purification steps. In any way, the use of alternative approaches for the reactive step, such as biocatalysis, heterogeneous catalysis or supercritical conditions, will also generate a two-phase reaction system and require an amount of alcohol in excess. This means that, even if the reactive step is changed, phase splitting and alcohol recovery will remain as required procedures for purifying biodiesel and its byproducts and also for recycling the reactant in excess. Nowadays biodiesel purification involves phase splitting and a sequence of water washing procedures, so that residues of catalyst, methanol, glycerol and soaps are extracted to the aqueous phase. Subsequently methanol is recovered from the washing water by distillation. As informed above, the sequence of purification steps used in the methylic route can not be directly transferred to the case of ethanol as the alcoholic reactant. For instance, in the present situation such an approach will necessarily require a specific and complete dehydration unity for recovering bioethanol, increasing the production costs of ethylic biodiesel. Note that, even if the addition of any and every amount of washing water is avoided, the problem of water accumulation in the recycled bioethanol persists. In fact, anhydrous bioethanol contains 0.5 mass% of water and, considering that it is used in a proportion around the double of the value required by the reaction stoichiometry, the amount to be recycled will contain around 1.0 mass% of water at the end of the process.

Results and Conclusions

A new approach must be developed for the ethylic biodiesel route and the present work presents such an approach based on the concept of using bioethanol in the whole sequence of biodiesel production, from the seed to the tank. This approach involves the following main steps: i) extraction of vegetable oils from oilseeds using bioethanol as solvent, ii) deacidification of the crude oil either by liquid-liquid extraction or by adsorption on a strong anion exchange resin, in both cases using bioethanol as solvent, iii) reactive steps applied to the deacidified oil miscela and to the second miscela containing free fatty acids, iv) purification steps with minimal addition of washing water and recovery of glycerol with very low water content, v) recovery of the excess of bioethanol contaminated with water by flash distillation, evaporation or rectification, vi) dehydration of bioethanol by extractive distillation using glycerol as dehydrating agent. The development of this ethylic route is being performed on the basis of three simultaneous investigations: the phase equilibrium related to specific processing steps, the mass transfer performance of the main processing steps and the simulation of the whole sequence of purification and reaction steps. In case of phase equilibrium, experimental measurements, correlation and prediction of equilibrium data are underway for systems involving oilseeds and bioethanol or ion exchange resins and fatty miscelas (SLE), or fatty

compounds, glycerol, bioethanol, and water (LLE or VLE). The equilibrium data are being correlated or predicted by empirical or semi-empirical approaches, such as the Langmuir, NRTL, UNIFAC or the Cubic Plus Association Equation of State (CPA-EoS) models. In case of specific purification steps the performance of solid-liquid extractors for oil extraction with bioethanol are being investigating. The oil deacidification by liquid-liquid extraction or ion exchange, in both cases in an ethanolic media, is also being evaluated via experiments conducted in continuous equipments (PRDC-extractor, breakthrough curves in fixed bed columns). The whole sequence of ethylic biodiesel production is being investigated using ASPEN PLUS, in this case with emphasis on the recovery and dehydration step of bioethanol. Following conclusions can be enumerated: i) an expressive amount of phase equilibrium data is already available, their correlation and prediction were successfully performed using empirical or semi-empirical approaches; ii) vegetable oils can be extracted using bioethanol, producing a concentrated oil miscela that can be conducted to the biodiesel production without requiring solvent evaporation; iii) oil deacidification can be performed either by liquid-liquid extraction or by ion exchange, generating two product streams, the first one rich in the deacidified oil and the second one rich in free fatty acids; iv) along the biodiesel purification steps, glycerol can be recovered with a very low level of contaminating water, so that it can be used for dehydrating bioethanol; v) the bioethanol to be recycled, as well as the new bioethanol stream that should be fed to the process, can be dehydrated by extractive distillation using glycerol, so that no specific dehydration unity or source of anhydrous bioethanol outside the biodiesel production process is required; v) the integration of bioethanol in the whole sequence of biodiesel production allows the reduction of production costs related to solvent evaporation, to crude oil refining and to feeding and/or recycling bioethanol in a anhydrous form. This reduction cost may have a significant impact on the economic performance of ethylic biodiesel production.

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