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An integrated reactive distillation process for biodiesel production

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ABSTRACT

An integrated reactive distillation process for biodiesel production is proposed. The reactive separation process consists of two coupled reactive distillation columns (RDCs) considering the kinetically controlled reactions of esterification of the fatty acids (FFA) and the transesterification of glycerides with methanol, respectively. The conceptual design of the reactive distillation columns was performed through the construction of reactive residue curve maps in terms of elements. The design of the esterification reactive distillation column consisted of one reactive zone loaded with Amberlyst 15 catalyst and for the transesterification reactive column two reactive zones loaded with MgO were used. Intensive simulation of the integrated reactive process considering the complex kinetic expressions and the PC-SAFT EOS was performed using the computational environment of Aspen Plus. The final integrated RD process was able to handle more than 1% wt of fatty acid contents in the vegetable oil. However, results showed that the amount of fatty acids in the vegetable oil feed plays a key role on the performance (energy cost, catalyst load, methanol flow rate) of the integrated esterification–transesterification reactive distillation process.

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1. Introduction

After a century where petroleum has dominated as the preferred energy source and as raw material for the production of organic chemicals, the continuous reduction of oil reservoirs, its increasing extraction cost, the emergence of new economies where oil demand is increasing exponentially and natural disasters in producing areas are forcing the oil consumer countries to redefine their energy strategies. In Europe, where oil demand largely exceeds domestic production, the search for new oil substitutes has been in the agenda of both the European Commission and the member state governments (Van Gerpen, 2007). Environmental concerns are also limiting petroleum based fuels consumption. We have been witnessing an intensification of air pollution and global warming problems due to the emissions of greenhouse gases and other air contaminants that are produced from the combustion of fossil fuels. As a result of all these issues, studies are nowadays being focused on reliable alternatives to conventional diesels. Biodiesel, a blend of fatty acid alkyl esters, is now seen as a sustainable short-term

substitute fuel. Biodiesel, made from vegetal oils or animal fats, has a renewable nature and a lower contribution to global warming due to its almost-closed carbon cycle. Analysis has shown that, with the use of biodiesel, CO₂ emissions can decrease up to 78%. This biofuel is conventionally produced through batch or continuous transesterification of highly refined vegetable oils with methanol by using homogeneous alkaline catalysts such as sodium or potassium hydroxides (Fukuda et al., 2001). Waste cooking oils can also be used for biodiesel production, reducing the related production costs and problems concerning the disposal of waste cooking oils that can cause environmental water contamination. However, the conventional technology is not compatible with oils which free fatty acids (FFAs) content exceeds a threshold value of about 1% wt. A possible solution to this drawback could be the development of new technologies enabling to employ waste raw materials such as fried oils or mixture of oils from various sources that cannot be treated in the conventional process due to their high content of free fatty acids (Kiss and Bildea, 2012). This perspective discloses the way towards the development of innovative biodiesel production processes such as those based on heterogeneous two-step reactive-separation process, supercritical processes, catalytic hydrodeoxygenation (HDO) processes and membrane technology (Yunus khan et al., 2014). Recently, Boon-anuwat et al. (2015) presented a study about the

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design of a continuous reactive distillation process for biodiesel production comparing the homogeneous and heterogeneous catalyst. They use sodium hydroxide as the homogeneous catalyst and magnesium methoxide as the heterogeneous catalyst for the transesterification of triglyceride with methanol into the reactive distillation column. The conclusions from their simulations are that the reactive distillation process with the heterogeneous catalyst offers advantages over the conventional process because it could eliminate the requirement of post-processing separation and purification at cost effective column design and operating conditions. Despite these relevant results, the above work is based only on the transesterification reactions, thus, a pure vegetable oil is assumed to perform the simulations and a wasted vegetable oil could not be managed. On the other side, Gomez-Castro et al. (2013) proposed a two-step modified Saka–Dadan reactive distillation process to produce biodiesel with supercritical methanol. They showed that, in terms of production costs and pollutant emission, the use of reactive distillation for biodiesel production at high pressure and temperature appears to be an interesting and convenient alternative. However, it is noticed at this work that the operating parameters of the reactive distillation column are ambiguously extreme for a reactive distillation column setup. Therefore, it is clear that additional research and analysis are required to determine if such system could be successfully operated in practice and industrial scale. Also, from the experimental point of view, Prasertsit et al. (2013) demonstrated that reactive distillation is a feasible, flexible and reliable alternative to produce biodiesel via the transesterification of palm oil with methanol. They used a 4 m long stainless steel column with inside diameter of 1–2 cm, connected with 2 L reboiler and found that, for an oil feed flow rate of 15 ml/min, the optimal condition is at reboiler temperature of 90 °C, methanol to oil molar ratio of 4.5:1 and the catalyst (KOH) amount of 1% wt, respect to oil. However, the excess liquid base catalyst should beware for the saponification to form soap in the process. Despite the interesting experimental results obtained, the work deals with a palm oil containing only approximately 0.3–0.6% free fatty acid and less than 1% moisture content, thus, a used vegetable oil with higher content of free fatty acid was not considered.

In the heterogeneous two-step reactive distillation process, the FFA in the feed is first esterified by acid catalysis to produce one type of mono-alkyl esters. This esterification step prevents soap formation during the second reactive separation step, which is the transesterification of the unreacted triglyceride with alkali or acidic catalyst to obtain alkyl esters. This two-step process may be able to reduce the overall processing time and it permits processing of feed stocks with high FFA content under normal pressure and temperature operating conditions. For both, the esterification and transesterification reactions researchers have explored the use of heterogeneous catalysts. Tesser et al. (2010) studied the transesterification of soybean oil with both basic and acidic heterogeneous catalysts. For esterification reaction the ion exchange resin Amberlyst 15 proved to be highly effective. On the other side, Dossin et al. (2006) proposed to use MgO as solid catalyst for the production of biodiesel heterogeneously in a continuous slurry reactor. They showed that the heterogeneous catalysts may allow good production levels and it presents an interesting alternative to homogeneous catalysts towards a more environment-friendly process. Besides, it is generally accepted that a process employing a solid acid catalyst, if technically feasible, would be preferred on economic grounds. Thus, in this work, an integrated heterogeneous two-step reactive distillation process for the production of biodiesel is investigated. Considering the above, the objective of this work is to develop an integrated reactive distillation process able to handle a raw material with high FFA content (wasted vegetable oil) to produce high purity biodiesel. In order to reach this objective a systematic procedure for designing of the integrated

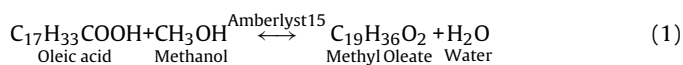
process is used, this is: (a) to perform an analysis of the reactive system in terms of thermodynamic properties, kinetics and catalyst available to design a feasible RD process; (b) to perform a conceptual design through the computation of reactive residue curve maps based on the *element* concept proposed by Pérez-Cisneros et al. (1997) for each occurring chemical reaction; and c) to perform intensive simulation to obtain a feasible and flexible reactive distillation column designs and to determine the operating conditions of the integrated process.

2. The reactive system

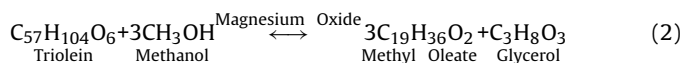
To describe the reactive system we incorporate the *element* concept in order to reduce the multicomponent composition space. Also, the appropriate thermodynamic model and kinetic expressions to obtain reliable simulation results are considered.

2.1. Chemical reactions and element representation

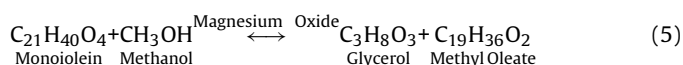
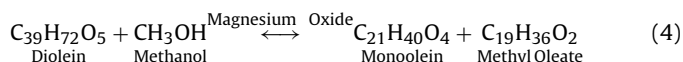
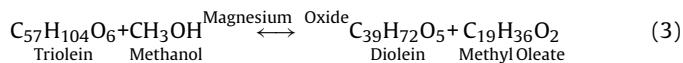
The generic esterification reaction of a carboxylic acid (oleic acid in our case) with methanol, producing methyl oleate (biodiesel) and water, is schematically shown below:



The global transesterification reaction of triolein with methanol to produce three moles of methyl oleate has been selected as a model system for the transesterification of a vegetable oil to produce biodiesel.



with the step by step transesterification reactions as:



By introducing the *element* concept proposed by Pérez-Cisneros et al. (1997) the esterification and transesterification reactions described in equations (1–5) can be represented in terms of *elements*. Table 1 shows the *elements* definition and the balanced reactions in terms of such *elements*. Also, Table 1 shows the *element* mole fractions which are given in terms of the different species participating in each reaction. It should be clear that, while the elements **A** and **C** are the same for both reactions, the element **B** for the esterification reaction means water and for the transesterification reaction means C₃H₈O₃, thus, it is necessary to use a separated *element* triangular diagram to represent each reaction in a triangular reactive space. Figs. 1 and 2 show the reactive space and the pure component location for the esterification and transesterification reactions, respectively. Note that the triangular *element* coordinates of the pure components can be straightforward obtained by using the *element* mole fractions definitions and it is done just assigning the unity value to the pure component mole fraction of each species.

2.2. Pure component properties

Due to the great variety of esters species and, in particular, triglycerides, group contribution and corresponding state approaches are the usual methods for the estimation of pure

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