Production of Biodiesel from Palm Oil by Extractive Reaction

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Process integration looks for the integration of all operations involved in the production of one specific product. This can be achieved through the development of integrated processes that combine different steps into one single unit. The reactive extraction is an integrated process simultaneously combining the chemical reaction and liquid-liquid extraction. The latter phenomenon allows the continuous removal of the reaction products favoring the direct conversion in the case of reversible reactions like the esterification of vegetable oils with methanol. The objective of this work is to evaluate the possibility of applying the integration principle to the biodiesel production by extractive reaction from palm oil. During the esterification of palm oil with methanol, the products formed (methyl esters and glycerin) generate two liquid immiscible phases. This fact makes possible the separate removal of two product streams: biodiesel-enriched (extract) and glycerin-enriched (raffinate) streams. In order to accomplish the assessment of the proposed simultaneous integrated process, the thermodynamic analysis of the liquid-liquid phase equilibrium was carried out based on the principles of the topological thermodynamics. Thus, the study of the interaction between the chemical transformation and the liquid equilibrium allowed determining that an extractive reaction process for biodiesel production is possible. Then, the set of operating conditions for the process was defined. Whit this information, the analysis of the integrated process was performed by using a process simulator. The outcomes obtained were compared to the conventional process where the reaction and the extraction are accomplished separately. The proposed methodology allowed clearly elucidating if an extractive-reaction process can be implemented. This analysis method makes possible the improvement of the rigorous simulation by delimiting the space of operating conditions and, consequently, achieving savings in the costly experimental runs. In this way, the energetic and economic advantages of the extractive reaction process for biodiesel production from palm oil are demonstrated.

1. Introduction

The biodiesel is a mixture of methyl or ethyl esters of fatty acids that can be used as a fuel for diesel engines. The ester group increases the oxygen content of diesel-biodiesel blends improving the efficiency of the combustion of the conventional fossil diesel. For producing biodiesel, the transesterification of vegetable oils with low molecular weight alcohols like methanol or ethanol is necessary. This reaction is accomplished with the help of acid, basic or enzymatic catalysts. Usually, biodiesel production in the world is carried out employing methanol and basic catalysts (mostly KOH). The most employed vegetable oils are rapeseed, soybean and sunflower oils. The oil from palm (*Elaeis guineensis*) is considered as an excellent feedstock for biodiesel production in tropical countries. The conventional technologies for biodiesel production employ reactors with acid or basic catalysts and a separation scheme that uses unit operations like distillation, centrifugation, flash evaporation, filtration, and decantation. The purification of this biofuel through the operation mentioned implies high capital investment and energy consumption leading to elevated production costs. Process design trends in chemical industry are related to the development of more efficient technologies. One of the most important approaches for the design of more intensive and cost-effective process configurations is process integration, which looks for the integration of all operations involved in the production of one specific product. This can be achieved through the development of integrated processes that combine different steps into one single unit. The reactive extraction is an integrated process simultaneously combining the chemical reaction and liquid-liquid extraction. The latter phenomenon allows the continuous removal of the reaction products favouring the direct conversion in the case of reversible reactions like the esterification of vegetable oils with methanol. The objective of this work is to evaluate the possibility of applying the integration principle to the biodiesel production from palm oil by extractive reaction.

2. Production of Biodiesel

Main feedstock for biodiesel production analyzed in this work is palm oil that is a mixture of triglycerides. The overall process for biodiesel production comprises the following steps: feedstock conditioning, reaction, separation, and product purification. During feedstock conditioning, the content of water and free fatty acids in the vegetable oil should be controlled in order to avoid undesirable reactions and products (soap). Thus, the conditioning strongly depends on the extraction method of the vegetable oil and on its origin. The reaction step includes the transesterification reaction between the triglycerides of the oil and low molecular weight alcohols (methanol or ethanol) in the presence of a catalyst (homogeneous or heterogeneous) to form fatty esters (biodiesel) and glycerol. The transesterification comprises three successive reversible reactions in which each one of the fatty acids linked to glycerol are to be esterified. The first step is the conversion of the triglycerides into diglycerides followed by the conversion of the diglycerides into monoglycerides and, finally, the conversion of the monoglycerides into glycerol producing one molecule of the ester per each glyceride in each step. The main products are the esters of the fatty acids (biodiesel) and glycerol. Due to the reversible character of this reaction, an excess of alcohol is employed to increase to a

decanter where two liquid phases are separated: biodiesel-enriched and glycerol-enriched phases. In general, for acid and alkaline processes, neutralization of the catalyst in each phase is needed after biodiesel separation in order to form salts that could be removed afterwards. After neutralization, the biodiesel phase undergoes washing with hot water to remove the salts and the non-separated glycerol. The glycerol is dried by distillation or flashing. If economically viable, the glycerol is refined to obtain a valuable co-product.

The application of extractive reaction is one of the integration approaches that can be utilized for the intensification of biodiesel production. This process consists in the combination of the chemical reaction and liquid-liquid extraction in the same unit achieving such synergistic effect, that the increase of selectivity, conversion, productivity, and purity of final product may be attained (Rivera and Cardona, 2004). Thus, two liquid phases are formed during the reaction. In this way, the principle of reaction-separation integration can be applied to the production of ethyl esters using palm oil and even castor oil. Biodiesel-enriched liquid phase is removed from the reactor-extractor and sent to a flash unit where ethanol is recovered. In order to obtain a high purity biodiesel, this stream is washed with hot water to extract the excess of NaOH or KOH and the soap that could have been formed during the reaction. Glycerol-enriched phase is directed to another flash unit where part of ethanol is recovered. If high purity glycerol is to be obtained, a distillation column working under vacuum conditions (0.2 atm) is required (Gutiérrez et al., 2009).

3. Short-cut Method for Liquid-liquid-reactive Equilibrium

The analysis of the statics is one of the thermodynamics-based approaches that has allowed the synthesis of integrated processes of the reaction-separation type (Pisarenko et al., 2001). This type of analysis is based on the principles of the topologic thermodynamics and has been widely used during the design of reactive distillation processes. Thus, the analysis of the statics provides the fundamentals and tools needed for the preliminary design of distillation, reactive distillation and, more recently, reactive extraction, extractive reaction and extractive fermentation processes through the development of short-cut methods based on a graphic representation that allows the visualization of the process trajectory. The application of this approach to biological processes has been very limited though is difficult to undervalue the potential of integration in the development of innovative biotechnological processes with a high performance. The thermodynamic properties of the system are not easy to find since the databases do not contain information on the thermodynamic properties of the components present in the vegetable oils. In this work, palm oil and anhydrous ethanol was employed as the feedstocks for biodiesel production. The reaction is catalyzed by NaOH. To avoid the saponification, the catalyst is fed to the process in the form of alkoxide.

For analysis purposes, the palm oil was considered to contain triolein, tripalmitin and trilinolein. Each fatty acid has a defined percentage content that characterizes the properties of the palm oil. Palm oil contains 42.8% (by weight) tripalmitin, 40.55 % triolein, and 10.1% trilinolein. It also contains small amounts of the following free fatty acids: lauric, myristic, stearic, and linolenic (Marchetti et al., 2007). As no information

on palm oil was available, the interaction parameters modified for UNIFAC equation developed by Batista et al. (1999). These authors modified the parameters mentioned to take into account the interactions of the triglycerides molecules with methanol or ethanol. In this way, it is possible to predict the liquid-liquid equilibrium behavior of the most representative system to be separated.

To simulate the liquid-liquid equilibrium, it was assumed that the palm oil was comprised by a mixture of triolein and tripalmitin. For these compounds, the group interaction properties were modified and this information was introduced into the *ModELL-R* software, which was described in a previous work (Sánchez et al., 2006). Practically, the same behavior can be observed for the system with ethyl palmitate.

This phase equilibrium behavior indicates the great possibility of implementing a reactive extractive process for biodiesel production. To preliminarily assess the viability of such a process, the chemical reaction surface was crossed with the phase equilibrium showing the interception of both types of equilibrium. Therefore, the reactive extraction process can be implemented. The software *ModELL-R* was employed to explore the possibility of this process. The software uses the thermodynamic information on the pure components of the mixture to predict the behavior of the system when it undergoes variations of the R_V ratio (the ratio of the volumes of both liquid phases). For this, the following assumptions were considered: a) the reaction is accomplished in a single phase; b) the reactor-extractor is well mixed; c) the reactor volume is enough to achieve the chemical equilibrium.
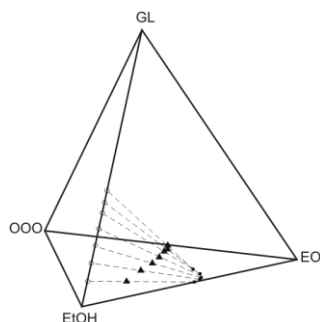

Figure 1: Liquid-liquid reactive equilibrium for the system ethyl oleate (EO) – glycerol (GL) – ethanol (EtOH) – triolein (OOO).
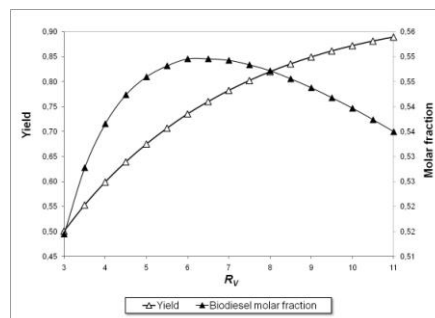

Figure 2: Steady states with maximum yield and biodiesel purity in the extract phase

The system behaviour is presented in Figure 1. The glycerol phase corresponds to the raffinate and the biodiesel (ethyl oleate) phase corresponds to the extract. The figure shows that the raffinate obtained is a mixture of glycerol and ethanol, and that the extract is a mixture enriched with biodiesel. Once the system is analyzed, the operating range of the variable R_V (the ratio of the volumes of the glycerol and biodiesel phases under batch regime) is delimited. For this work, the immiscibility occurs in the system spontaneously, i.e., there is no need to add any solvent to extract the product (biodiesel). This type of systems is called self-induced. As the ethanol should be fed in excess to the

reactor-extractor, the R_V ratio is controlled by the ethanol concentration in the feed. In order to find the limits of the process operation, the R_V ratio is varied from the minimum solubility limit to the maximum solubility limit. For this case, the reactive extraction process is possible from R_V values equal to 3 up to values higher than 11. Higher palm oil conversion and higher biodiesel purity in the extract can be obtained at higher R_V ratios. This indicates that the system should be operated with ethanol in excess to make the extractive effect to favor the process performance. In the batch process, the reactor is initially loaded with the reactants (triolein and ethanol). It is assumed that the system is initially stirred during certain time in such a way that the system remains homogeneous and, therefore, the reaction volume corresponds to the volume of the liquid medium inside the reactor. Then, the stirring is decreased and the separation of the two liquid phases occurs. The reaction volume is now the volume of the biodiesel phase where the palm oil is located.

The feasible steady states with the maximum yield and/or product purity are shown in Figure 2. As the triolein/ethanol ratio increases, the yield achieved increases and the biodiesel purity decreases in the extract phase (biodiesel stream). From the figure, a maximum of biodiesel purity in the extract can be observed for a specific reaction yield. Before assessing whether a higher yield is more suitable than higher product purity, it is necessary to corroborate if the steady state with maximum conversion is achievable in the practice. This can be determined by using the concept of trial trajectory. This trajectory is a line connecting the initial composition with the pseudo-composition. This is only possible if the extent of the reaction allows achieving this state. To confirm this, it is necessary to calculate the reaction extent at those R_V conditions corresponding to the point with maximum conversion and/or product purity. If the reaction extent corresponds to the composition of the pseudo-composition, then the trial trajectory can connect these two points. To complete the trajectory, it is needed to connect the pseudo-initial composition with the concentrations of the extract and raffinate. This requirement can be only accomplished if the pseudo-initial composition is located on the tie reactive line. Such point is evaluated through the LLRE. The maximum biodiesel purity in the extract phase corresponds to a R_V ratio equal to 6, i.e., 6 mol ethanol per each mol palm oil (triolein). For this ratio, the initial composition (in molar fraction) corresponds to the mixture of 0.1428 triolein and 0.8572 ethanol. The composition of the pseudo-initial composition should satisfy the mass balance of a tie reactive line. This solution means that this steady state is achievable in the practice. In other words, the trial trajectory satisfies the requirements to declare that state with maximum conversion and/or product purity as possible in the practice.

Once delimited the experimental space and selected the steady state with maximum conversion and/or product purity, the experimental evaluation of this point is needed. To do this, it is necessary to define the agitation rate of the system since this operating parameter plays a crucial role during the reactive extraction process. For the batch process, it is necessary to fix two agitation speeds: the first one, for mixing the reactants, and the second one, for the formation of two liquid phases in equilibrium. During different experimental runs, the first agitation speed was fixed using an agitation device Speed Control (Speed Control, Inc., USA), a 200 mL beaker, palm oil and ethoxide (mixture of ethanol and sodium hydroxide). The test was started with 10 rpm agitation and the agitation rate was varied by 10-rpm increments. The response of the

system was recorded. The ethoxide and the oil are immiscible. A homogeneous mixture is only achieved at 350 rpm. In this way, the minimum agitation speed needed to obtain a homogeneous mixture was fixed at 350 rpm. As the interest is the formation of two liquid phases between the biodiesel and the glycerol (the reaction products), the system was allowed to react for one hour and then the agitation speed was reduced until the formation of two liquid phases. This was attained at 210 rpm. At this speed, the two phases are formed and the reaction can be continued. For this specific case, the 200 mL beaker acts as a single-step reactor-extractor. The composition analyses for biodiesel were performed in a gas chromatograph Perkin Elmer (USA).

4. Conclusions

The employed methodology using the software *ModELL-R* allowed getting insight whether a process can be implemented by extractive reaction. This methodology saves calculation time and improves the rigorous simulation since it delimits the space of operating conditions. As a maximum conversion is assumed for the limiting steps, this powerful tool is able to determine the possibility of separation violating the constraint of thermodynamic equilibrium of the reaction.

Acknowledgements

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