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Simulation of a Hybrid Reactive Extraction Unit. Biodiesel Synthesis

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Biodiesel is an alternative for existing diesel vehicles. This work focuses on the rigorous simulation of a hybrid reactive liquid-liquid equilibrium extraction as a novel alternative process for the production of biodiesel. In this study, the alkaline transesterification of vegetable oils, methyl oleate (triolein) being the major component, with methanol as short chain alcohol is considered. This process involves two zones in the extractive column: one reactive-extractive zone and another only extractive. The reactants are countercurrent thereby improving the separation and the formation of products, glycerin and methyl oleate, allowing a high purity of these. Part of the glycerol obtained from the reactive section is used as extractive agent in the extractive section. The simulation proves that reactive extraction achieves saving far more raw materials than other processes. It eliminates the need to use a large excess of methanol to shift the reaction equilibrium to the right and produce methyl esters (FAME) as a main product. The proposed process has been compared to other currently used processes.

1. Introduction

Biodiesel is chemically defined as mono alkyl esters of fatty acids, however it can contains several impurities from its synthesis process. Its quality is regulated by legislation in Europe EN14214 and in the U.S. by standard ASTMD6751. The currently most widely used technology for the production of biodiesel is a reactor where a homogeneous alkaline transesterification takes place between alcohol and oil, e.g. waste vegetable cooking oils (Ceclan et al, 2012), algae oil (Iancu et al, 2012) or non comestible seeds (Ng et al, 2012). The reactor is followed by several stages of product purification, neutralization and removal stages of the catalyst, recovery of methanol excess present in the product stream, and the possible formation of soaps (Kiss and Bildea, 2012). The soap formation, the neutralization and removal stages of the catalyst can be avoided by the use of heterogeneous alkaline catalysts. The energy requirements for methanol and glycerol recovery can be decreased with 27% by using a divided wall column (Ignat and Kiss, 2012) or 23% with an appropriate heat exchange network (Palmeira et al, 2012). But to really avoid the energy costly recovery of methanol and purification steps, a novel process is required. The overall reaction results of three consecutive reversible reactions, therefore an excess of alcohol (6:1) (alcohol: triglyceride) is usually used to shift the reaction towards the product side.

$$\text{Triglyceride} + 3\ \text{Methanol} \leftrightarrow 3\ \text{FAME} + \text{Glycerol} \qquad (1)$$

In European Union, Directive 2009/28/EC requires since 2008 by law that every year the production of biofuels increases with the aim that by 2020 10% of transport fuels to be biofuels. Given the increase in the demand for biofuels and the growth forecasts, new technologies are needed to optimize production, such as reactive separation units with heterogeneous catalyst (Kiss and Bildea, 2012). To avoid the methanol recovery, the reaction must be shifted towards the product side by continuous products removal instead of using an excess of methanol. The system shows immiscibility of the products, FAME and glycerin, and increased affinity glycerin – methanol (Komers et al, 1995). The products immiscibility shifts

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the reaction forward, but the affinity glycerin-methanol reduces the methanol concentration from the triglyceride/biodiesel phase, slowing down the kinetics. From this point of view, an excess of methanol is required for high triglycerides conversion. A qualitatively similar behavior is observed in case ethanol is used (França et al, 2011).

2. Proposed Process

In the present work, a novel continuous process is proposed, consisting of a single unit, a column of liquid-liquid extraction with two zones: a reactive-extractive zone and another extractive only (Figure 1). All along the column, the reactants flow in countercurrent. In this way, at one end of the reactive section, an excess of methanol is assured for high conversion of triglycerides and in the other end the excess of triglycerides assures a high conversion of methanol. Therefore, an excess of reactants can be achieved at both reactive section ends, meanwhile the overall reactant feeds to the system can be in stoichiometric ratio. Reaction and liquid-liquid separation have a synergy effect. Moreover, the process takes advantage of the affinity between methanol and glycerol, having a non reactive extractive section useful to recover the methanol present in FAME stream. The feasibility of this column is checked by rigorous simulation using Aspen Plus and the UNIFAC thermodynamic model.

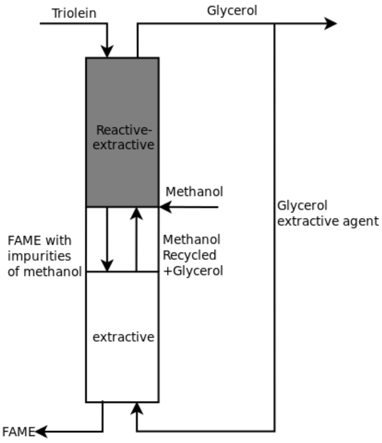

Figure 1: Diagram of the different sections inside the reactive extraction column.

At our knowledge, this kind of reactive extractive process has never been simulated before and, at the contrary of the reactive distillation, it is not readily implemented in the simulators. This equipment has been simulated using a set of reactors and decanters, as shown in Figure 2. An equivalent stage of reactive extraction column corresponds to the set of a reactor and a decanter in the arrangement simulated. In practice, this would be a section where the heterogeneous catalyst is found packed inside the column.

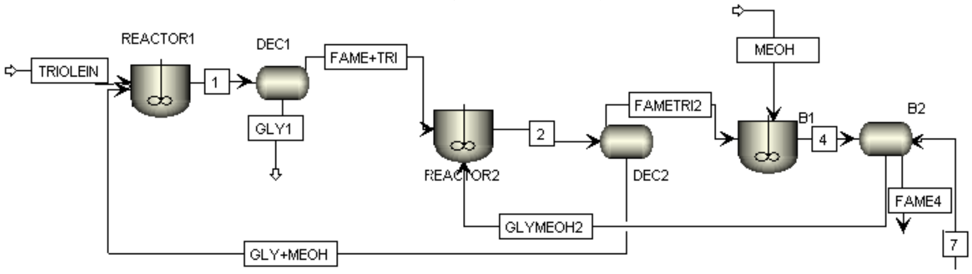

Figure 2: Simulation of the reactive-extractive section in an extraction L-L column.

The streams circulating in each stage from left to right (according to Figure 2) are rich in triolein and FAME (non-polar compounds with affinity) and from right to left are streams rich in methanol and glycerin (polar compounds with strong affinity). Although methanol is a polar compound, it is also rather miscible in esters; therefore part of methanol is present in the non-polar streams.

The number of stages required to obtain a final product suitable for marketing depends on the raw materials used, operation parameters and kinetics. The operation parameters used for the simulation are shown in Table 1. Both the residence time and temperature for each reactor were determined by sensitivity analysis, studying the effect of varying these parameters on the product stream FAME purity. Kinetic data of Vicente et al (2006) and Noureddini and Zhu (1997) were implemented, with a power law model, assuming a pseudo-homogeneous alkaline transesterification of B. Carinata and soybean oil as illustrative examples. However, it can be implemented for any new oil transesterification data, e.g. Urrejola et al. (2012). The calculation basis was taken as 28 kmol/h of triolein and 84 kmol/h of methanol (stoichiometric ratio 1:3).

Table 1: Operating conditions of the reactive extractive section

Raw material	$T_{reactors}$(ºC)	Residence time reactors (h)	Heat duty decanters (kW)	P(bar)	Nº Stages react-extract
B. Carinata oil	60	0.7	0 (adiabatic)	1	7
Soybean oil	60	0.4	0 (adiabatic)	1	4

The liquid-liquid extraction column without reaction is readily implemented in the commercial simulators (figure 3). The required amount of glycerin to recover the methanol present in FAME stream was calculated using sensitivity analysis, which studied the effect of this parameter variation on biodiesel quality. It was found that for a flow of 87.69 kmol/h were needed 32 kmol/h of pure glycerin, when the oil considered was B. carinata and 29.8 kmol/h in the case of soybean oil. The temperature and pressure conditions for this section are shown in Table 2.

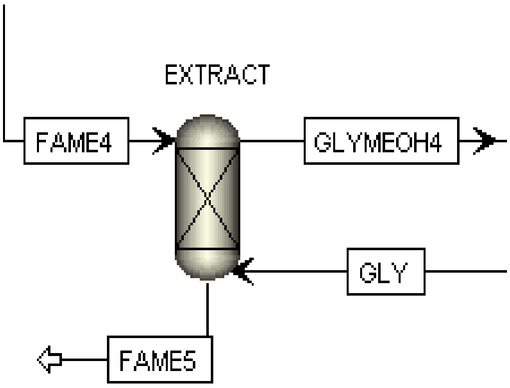

Figure 3. Simulation of the extractive section of the liquid-liquid extraction column

Table 2: Operating conditions of the extraction

Raw material	T_{feed}(ºC)	P(bar)	Heat duty (kW)	Nº Stages extraction	Total Nº Stages column
B. Carinata oil	60	1	0 (adiabatic)	7	14
Soybean oil	60	1	0 (adiabatic)	4	8

3. Process evaluation by rigorous simulation

The proposed process is compared to a nowadays standard process, where the reaction is carried out in a plug-flow reactor and the methanol excess recovery is performed with a distillation column.

3.1 Standard process

In the standard process (Figure 4), good quality of end product was possible to be attained only when using a ratio 6:1 (alcohol: triolein) of reagents, therefore 28 kmol/h triolein and 168 kmol/h methanol. It is important to note that temperature should not exceed 150 ºC to prevent biodiesel degradation, for this reason, the pressure in the distillation column is very low (Table 3). It can be seen in Table 4 that the energy requirements are high, especially in the distillation column and the reactor, due to the difficulty of maintaining a plug-flow reactor in isothermal conditions and extreme conditions of distillation. In reference to the streams results (table only shows the values of the most significant components), the quality of the products is high, but excess methanol, a higher number of stages in the RADFRAC distillation column model and a large reactor were required.

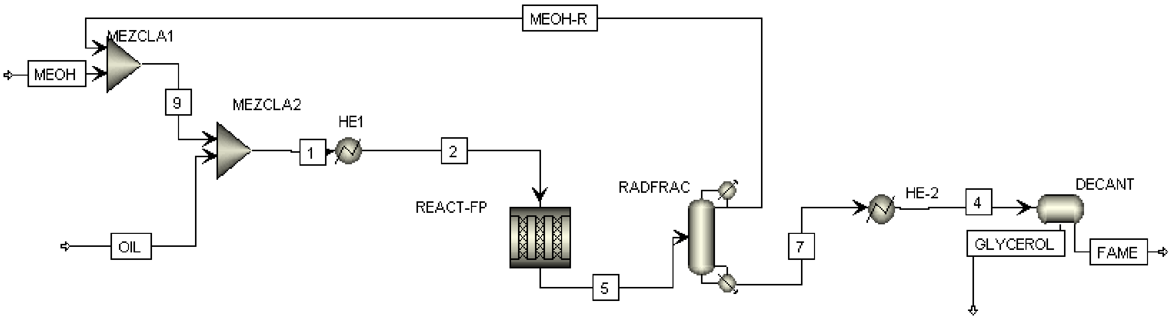

Figure 4: Continuous existing process with FP reactor and methanol excess recovery in distillation column.

Table 3: Operating conditions for existing process

Raw material	RFP dimensions	T reactor (ºC) isothermal	Nº Stages RADFRAC	P(bar) RADFRAC	T bottom RADFRAC (ºC)	T top RADFRAC (ºC)
B. Carinata oil	13.2 m x 0.8 m	60	10	0.07	125	9
Soybean oil	8 m x 0.3 m	60	10	0.055	130	15

Table 4: Mass fraction and heat duty results for the different raw material

Stream	Mass Frac *B. Carinata*		Mass Frac Soybean		Bloc	Heat duty (kW)	
	FAME	Glycerol	FAME	Glycerol		*B. Carinata*	Soybean
Methanol	2.73E-4	5.63E-3	2.32E-4	4.81E-3	Heat exchangers	-846.50	-737.75
Triolein	2.00E-3	0	7.70E-4	0	Decanter	-2.57E-06	1.29E-04
FAME	9.96E-1	2.47E-5	9.98E-1	2.46E-5	RADFRAC	4,307.81	1,298.83
Glycerine	1.75E-4	9.94E-1	1.73E-4	9.95E-1	Reactor	1,408.54	365.56
Mass flow (kg/h)	24,919.30	2,577.76	24,881.9	2,579.37	Total	4,869.88	4,853.3

3.2 Proposed process results

Figure 5 shows the overall simulated process. As seen in Table 5, the stream quality (mass fraction) of both FAME and Glycerol exceed established quality marked by the standards and required by market. These results are relevant, given that are achieved without an alcohol excess, requiring five times less energy than existing processes and the process being performed in a single unit (a hybrid reactive extraction column). As the triolein feed flow rate to both processes is the same, then the flow rate of FAME is very similar in both existing and proposed processes. Glycerol flow rate is different in the proposed process, due to its usage as extractive agent in the second section of the column. However, when the glycerol feed is substracted from the collected glycerol also becomes very similar in both processes. In this way, the necessary resources for carrying out the process are deduced per unit of product generated. The high purity achievable for glycerol makes it useful for a wide variety of applications or energetic valorisation of the stream. Figures 6 and 7 illustrate the composition profiles along the column for Brassica Carinata and soybean oil. The left side is for the reactive section and the right side represents the non reactive section. Glycerol is collected by the left end, biodiesel by the right end and in the middle between graphics is where methanol is fed. The overall number of stages necessary is the sum of reactive (left) and non reactive (right) stages.

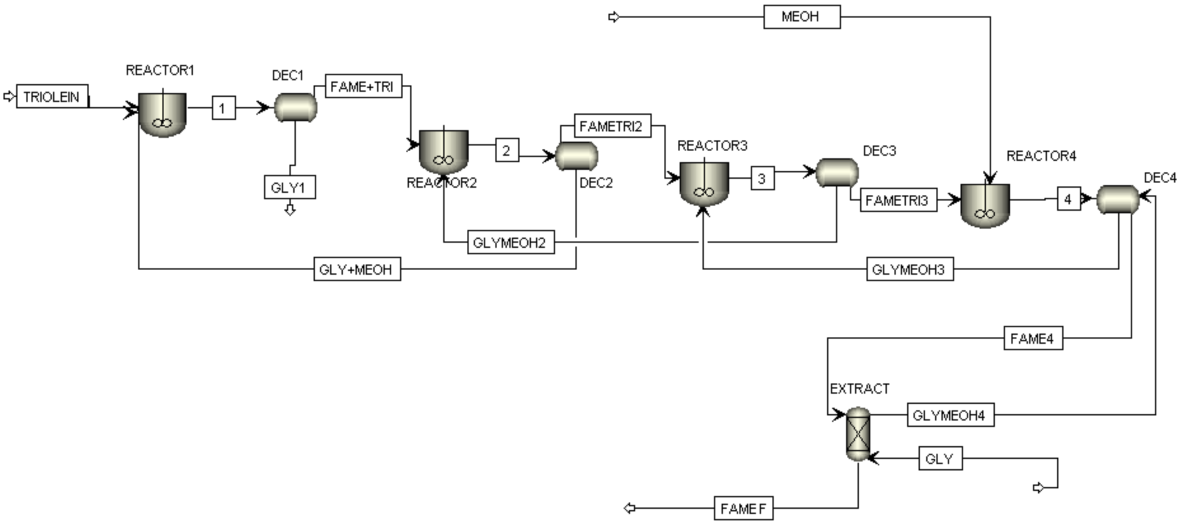

Figure 5: Simulation of the reactive extractive column with Soybean oil.

Table 5: Mass fraction and heat duty results for the different raw material

Stream	Mass Frac B. Carinata		Mass Frac Soybean		Section	Heat duty (kW)	
	FAMEF	GLY1	FAMEF	GLY1		*B. Carinata*	Soybean
Methanol	1.66E-4	4.96E-05	1.14E-04	4.65E-10	React-extract	1,004.73	934.04
Triolein	1.59E-3	3.38E-09	7.78E-04	3.45E-09			
FAME	9.98E-1	1.86E-06	9.99E-01	3.45E-09	Extract. only	-78.34	-7.53
Glycerine	1.78E-4	1.00	1.78E-04	1.00			
Mass flow (kg/h)	24,913.86	5,609.35	24,913	5,886.51	Total column	926.39	926.40

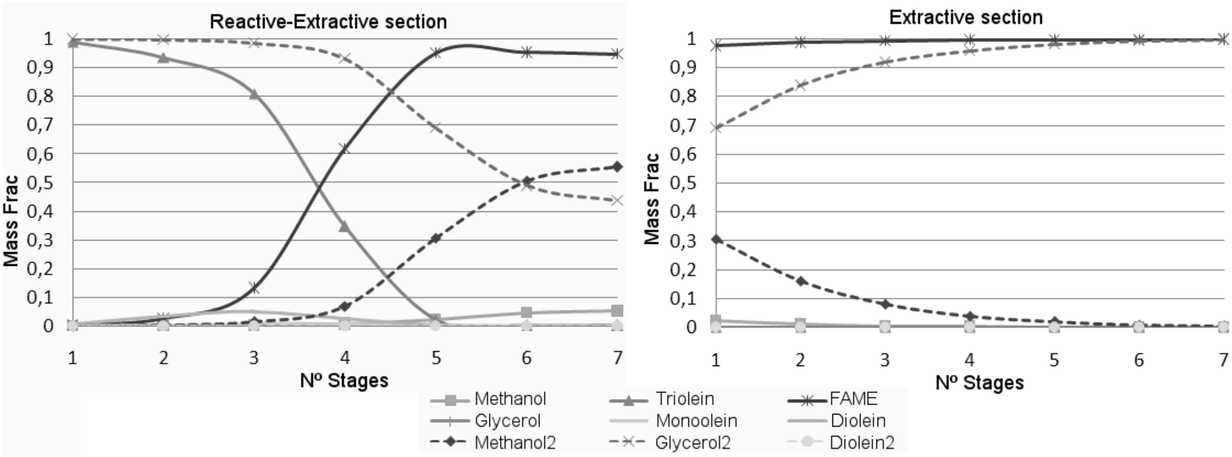

Figure 6: Composition profile in reactive extraction column. Raw Material: Brassica Carinata oil (2 indicates the composition of the higher density second phase).

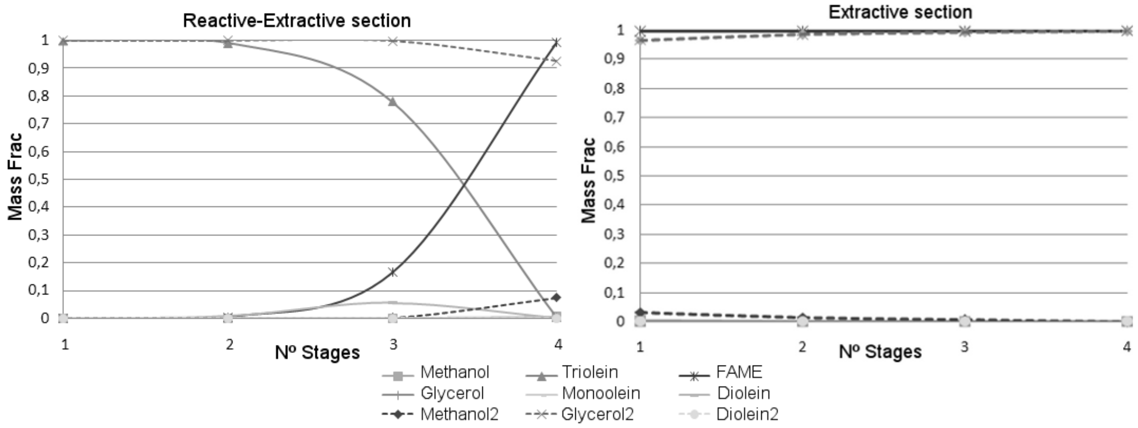

Figure 7: Composition profile in reactive extraction column. Raw Material: Soybean oil (2 indicates the composition of the higher density second phase).

4. Conclusions

A novel hybrid reactive extraction column for the biodiesel synthesis has been proposed and simulated, assuming pseudo-homogeneous kinetics of alkaline catalysts. A high conversion is achieved, without methanol excess to displace the equilibrium. The liquid-liquid equilibrium is used in synergy with the reaction, obtaining a very efficient separation. The energy consumption is greatly reduced; it is one-fifth of the energy required in existing processes, reducing operating costs and environmental impact. Similarly, as all stages are integrated in a single unit capital costs are also drastically reduced. Glycerol and biodiesel (FAME) are obtained in very pure mass fraction, therefore fully complies standards EN14214 and ASTMD6751. High purity glycerol is collected being useful for a high range of applications. Currently glycerol is a real waste problem in the synthesis of biodiesel, can not be used as raw material in many sectors because the purity rarely exceeds 70% wt.

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