Heterogeneously Catalyzed Free Fatty Acids Esterification in (Monophasic Liquid)/Solid Packed Bed Reactors (PBR)

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Biofuels are key products for the sustainability of the world energy consumption in the next years. Biodiesel in particular is a non-toxic, biodegradable, environmentally friendly alternative diesel fuel. Nowadays, the main problem for the commercialization of biodiesel is its final cost, that is strongly dependent (about 85 % of the total) by the feedstock used. A possible way to lower the biodiesel production costs is using raw oils, which contain a higher amount of Free Fatty Acids (FFA) that should be eliminated before the transesterification reaction to avoid soaps formation. In this work the deacidification of raw sunflower oil in both batch and PBR reactor was conducted. Heterogeneous catalyst Amberlyst 46 was used in its dry form and all the experiments were executed using an amount of methanol higher than the stoichiometric but preserving the mono-phasic liquid phase. Different operative conditions, i.e. different methanol/FFA ratios and temperatures in both the reactor configurations, were tested. The robust techniques for kinetic parameters estimation and simultaneous discrimination of rival models were adopted and combined with a dedicated differential-algebraic equation (DAE) model that characterizes the PBR reactor. The main kinetic parameters were regressed using kinetic models other than literature models (a pseudo-homogeneous and an adsorption based one) in considering the components molar fractions (ideal system). The kinetic parameters were obtained using equilibrated resins, i.e. using the catalyst after having let it to adsorb reactants and products at the operative conditions. From the regression results, it could be concluded that the pseudo-homogeneous model is slightly better for fitting the experimental data.

1. Introduction

Biofuels are key products for the sustainability of the world energy consumption in the next years (Andrade, 2005). Biodiesel, in particular, is a fatty acid methyl esters (FAME) mixture and can be obtained by transesterification of highly refined vegetable oils with methanol in homogeneous based catalysed processes (Ma et al, 1999). The starting oils are mainly constituted by triglycerides (about 90-98 % of total mass) and Free Fatty Acids (FFA), linear carboxylic acids in the C14-C22 range, with different unsaturation levels. As of today, the main problem for the commercialization of biodiesel is its final cost, that is strongly dependent (about 85 % of the total) by the feedstock used. Using unrefined or waste oils as a feedstock represents a very convenient way in order to lower biodiesel production costs. Some examples of low cost raw materials for biodiesel production are crude vegetable oil (Pinto et al, 2005), waste cooking oil (Bianchi et al, 2009, Ceclan et al, 2012) and animal fat (Pirola et al, 2010). The main problem associated with the use of these type of low-cost feedstock lies in their high content of FFA, leading to the formation of soaps during the transesterification reaction. Esterification of FFA in presence of either homogeneous or heterogeneous acid catalysts allows, at the same time, to lower the acid content and to obtain methylesters, i.e. biodiesel, already in this preliminary step. A remarkable advantage of

heterogeneous catalysis is the easier separation and recovery of the catalyst after the reaction. One of the most studied kind of heterogeneous catalysts are the sulphonic acid exchange resins, characterized by a gel structure of microsphere that forms a macroporous polymer (generally copolymers of divinylbenzene and styrene) with sulfonic SO_3H Brønsted acid groups as active sites. Due to the fact that FFA esterification is an equilibrium reaction, the addition of a methanol amount higher than the stoichiometric one is common in order to shift the equilibrium towards the products. However, the formation of two liquid phases has got two main drawbacks: firstly, part of the catalyst inside the reactor will be wetted by this second phase and then it won't work in the reaction, due to the high affinity between the resins and methanol and secondly the repartition of FFA between the two liquid phases contributes to lower the final biodiesel yield even if the oil at the end results deacidified. The aim of the present work is the study of the esterification reaction of the FFA contained in crude sunflower oil (CSO) in a packed bed reactor (PBR), which offers the possibility to operate at pressures higher than the atmospheric one and thus at temperatures higher than the normal boiling point of methanol (64.70 °C, i.e the operative limit of a batch reactor, because when it is reached, the temperature remains constant with only a waste of duty) and thus to obtain faster FFA conversion. PBR reactor was charged with a particular kind of sulphonic acid exchange resin: the sample Amberlyst 46 (A46) from Dow Chemicals. The choice of this resin was based on its peculiar properties; in fact, unlike all other Amberlyst type resins, this catalyst is not internally sulphonated but it only has surface acid groups. Consequently, it is not subject to any internal adsorption-desorption phenomena for both reactants and products. A total of six operative temperatures (ranging between 54 °C and 105 °C) were tested for the esterification reaction of a monophase liquid mixture of acid oil and methanol. The experimental results obtained were used to regress the kinetic parameters taking into account two different models (Popken et al, 2000), a pseudohomogeneous one and an adsorbed based one, which accounts the different affinity toward the polymeric matrix for all the species involved in the reaction and the solvent (triglycerides).

2. Experimental

Sunflower oil was purchased from TopAgri (Verona, Italy). Methanol (>99.8 %) was purchased from Sigma Aldrich and KOH 0.1 N in ethanol was purchased from Fluka. Amberlyst 46 (wet) catalyst was used for all the experiments. It was kindly provided by Dow Chemicals Company. The main characteristics of this resin are summarized in Table 1.

Table 1: Amberlyst A46 physical characteristics

Surface Area $(m^2 g^{-1})$	Average pore Diameter (Å)	Total pore volume $(cc\ g^{-1})$	Acidity $(meq\ H^+\ g^{-1})$	Max working Temperature (°C)	Fines Content (%) <0.425 mm
75	235	15	> 0.4	120	<1

The exchange capacity of the catalyst in its wet form was evaluated by total exchange with sodium chloride solution and subsequent titration. A weighted amount of catalyst was put in a saturated NaCl solution overnight in order to let the Na^+ cations to substitute the H^+ at the catalyst surface. A precise volume of 10 mL of this solution was then sampled and titrated using KOH 0.1 N and phenolphthalein as indicator. A value of $0.43 \pm 0.01\ meq_H^+\ g^{-1}$ was obtained which is consistent with the manufacturer data. Due to the high hygroscopicity of the resin a determination of the exchange capacity was conducted also on the dried catalyst. After the Amberlyst 46 was put in a oven at 80 °C for a night the procedure was repeated obtaining an exchange power of $0.80 \pm 0.01\ meq_H^+\ g^{-1}$. This difference is due to the preferential adsorbtion of water on the active sites of the catalyst. For this reason it was chosen to use for the first run the dried catalyst to avoid the water desorption in the reactor. The determination of the FFA weight percentage was carried out using a colorimetric titration. An amount of oil was sampled from the reactor after the stop of the stirring for 1 minute, then it was weighted and 20 mL of 2-propanol was added to dissolve FFA and facilitate the titration. KOH 0.1 N was used as titrant and phenolphthalein as indicator. FFA weight percentage was calculated using the following equation:

$$FFA\ [\%w] = \frac{Volume\ *0.1*\overline{MW_{FFA}}}{sample\ weight} * 100 \tag{1}$$

here $\overline{MW_{FFA}}$ is the molecular weight of oleic acid (considering the average sunflower oil FFA composition it is a good compromise using this value). The value of residual acidity is compared to the initial value, and the percentage acidity conversion was calculated as follows:

$$FFA_{conversion} \, [\%] = \frac{FFA_0 - FFA_t}{FFA_0} * 100 \qquad (2)$$

where, FFA_0 is the initial acid value, and FFA_t is the acid value at contact time t.

2.1 PBR Reactor

The PBR reactor is shown in Figure 1. It is a stainless steel cylinder 20.3 cm long and with an internal diameter of 4.7 cm with 3 intermediate samplings. The catalytic bed is placed at 7.4 cm from the bottom of the reactor and it has a volume of 86 cm^3. The resins charged were used for all the experimental deacidification runs. In order to maintain a constant internal temperature, an electrical resistance band controlled by an internal thermocouple is used. This internal thermocouple was inserted in the middle sampling The oil is mixed with methanol using an FFA:MeOH molar ratio of 1:5 in a feeding chamber (FC) pressurized by compressed air up to 6 bar. This mole proportion corresponds to a weight methanol percentage of 1.5 %, far under the limit solubility value of 4-6 % (this limit value depends on temperature and type of oil), which means that all the experimental determinations were operated in a monophasic liquid, and this permits to avoid to consider the diffusion of the species between the two phases. The feed is fluxed into the reactor, heated by an external hot circuit and insulated using glass fibers. The whole system is thus under the same pressure of the FC while the flow is controlled by a suitable mechanical valve (V7). The esterification reaction were carried out at different operative temperatures, i.e. 54, 65, 75, 85, 95 and 105 °C at 6 bar. The main advantage of this reactor configuration is the possibility to perform deacidification reactions above the methanol normal boiling point (64.70 °C) because the system is under pressure. This means that the reaction is fastened both because the kinetic parameters are dependent on temperature and because the solubility of methanol increases with temperature, which means that a higher methanol/FFA molar ratio could be used avoiding the second phase formation. The most important configuration parameters of this reactor are reported in Table 2.
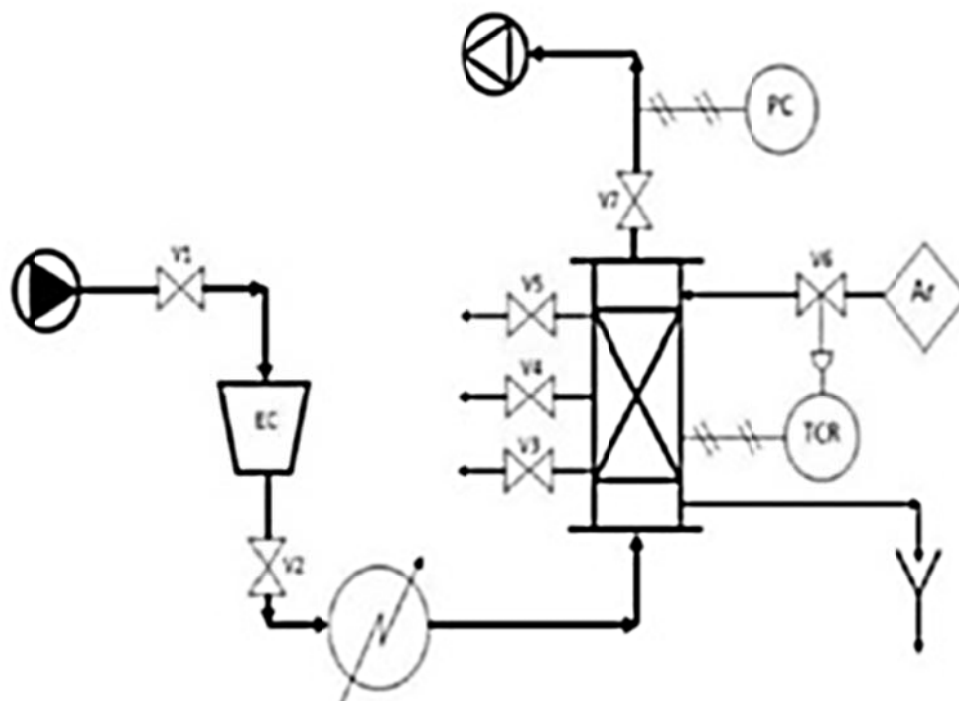

Figure 1: PBR reactor scheme: V= valves, FC= feeding tank

Table 2: configuration PFR reactor parameters

Reactor Volume	180 cm^3
Void fraction	0.36
Catalyst density	0.60 g/mL

2.2 Kinetic Modeling

All the experimental results, as previously described, were used to regress the kinetic parameters taking into account two different models: a pseudo-homogeneous one, a power-law equation which simply considers the reaction rate dependent on the bulk activities of the components, shown in the following equation:

$$r = \frac{d\xi}{d\tau} * C_{FFA}^o = \left(k_1^0 * e^{\left(\frac{-Ea_1}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right)} * x_{FFA} * x_{MeOH} - k_{-1}^0 * e^{\left(\frac{-Ea_{-1}}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right)} * x_{FAME} * x_{H_2O} \right) \quad (3)$$

where k_i^0 and Ea_i are the adjustable Arrhenius kinetic parameters, x_i are the components molar fraction, T_{ref} = 327.15 K while T is the absolute temperature. As previously explained, instead of considering all the fatty acids molecules, the oleic acid was chosen to represent all the oil FFA. The FAME then are represented by methyl oleate and the oil by triolein, a triglyceride constituted by three molecules of oleic acid.

The other model considered is the adsorption-based one, shown in the following equation:

$$r = \frac{d\xi}{d\tau} * C_{FFA}^o = \left(\frac{k_1^0*e^{\left(\frac{-Ea_1}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right)}*x'_{FFA}*x'_{MeOH} - k_{-1}^0*e^{\left(\frac{-Ea_{-1}}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right)}*x'_{FAME}*x'_{H_2O}}{\left(x'_{FFA}+x'_{MeOH}+x'_{FAME}+x'_{H_2O}+x'_{Oil}\right)^2} \right) \quad (4)$$

with

$$x'_i = \frac{K_i*x_i}{MW_i} \quad (5)$$

were K_i is the adsorption affinity constant for the i molecule, shown in Table 3, taken from the work of Popken (2000) and adapted considering

$$K_{FFA} = K_{FAME} = \frac{K_{MeOH}}{3.5} \quad (6)$$

as suggested in a work by Rehfinger et al. (1990)

Table 3: Adsorption parameters for the reacting components, see Eq. (5).

Component (i)	Adsorption Affinity (K$_i$)
Water	5.24
Methanol	5.64
FFA	1.61
FAME	1.61
Oil	0.00

It is important to observe that these modes do not consider the non-ideal behaviour of the liquid mixture because instead of activities the molar fraction are used. Also the binary adsorpition affinities were not regressed together with the kinetic parameters because in this way a good fit but a very poor prediction ability would have been obtained.

3. Results

3.1 Experimental deacidification RUNS

The experimental results collected in PBR reactor, expressed as FFA conversion percentage versus residence time, are reported in Figure 2. Since the PBR used for the esterification experiments has got

only three samplings (see Figure 1), for each temperature tested three different feeding flow rates have been used to obtain all the experimental curve reported. All the runs performed in PBR reactor are exclusively in (monophasic liquid)/solid system. In all the experimental curve after an initial step where the reaction rate is very fast, the FFA conversion tends to reach the thermodynamic plateau. Correctly, only the slope of the first step is highly dependent on the temperature. It is noteworthy to observe that, also working with a moderately quantity of methanol to form a new liquid phase the (monophasic liquid)/solid system allowed to reach very satisfactory FFA conversions suitable for the successive transesterification step in biodiesel production. No problems either due to extraction or liquid phase separation (the reaction produces water too) was observed and no additional tool (i.e. emulsificator or mixing chamber) was added to the plant before the catalytic reactor.
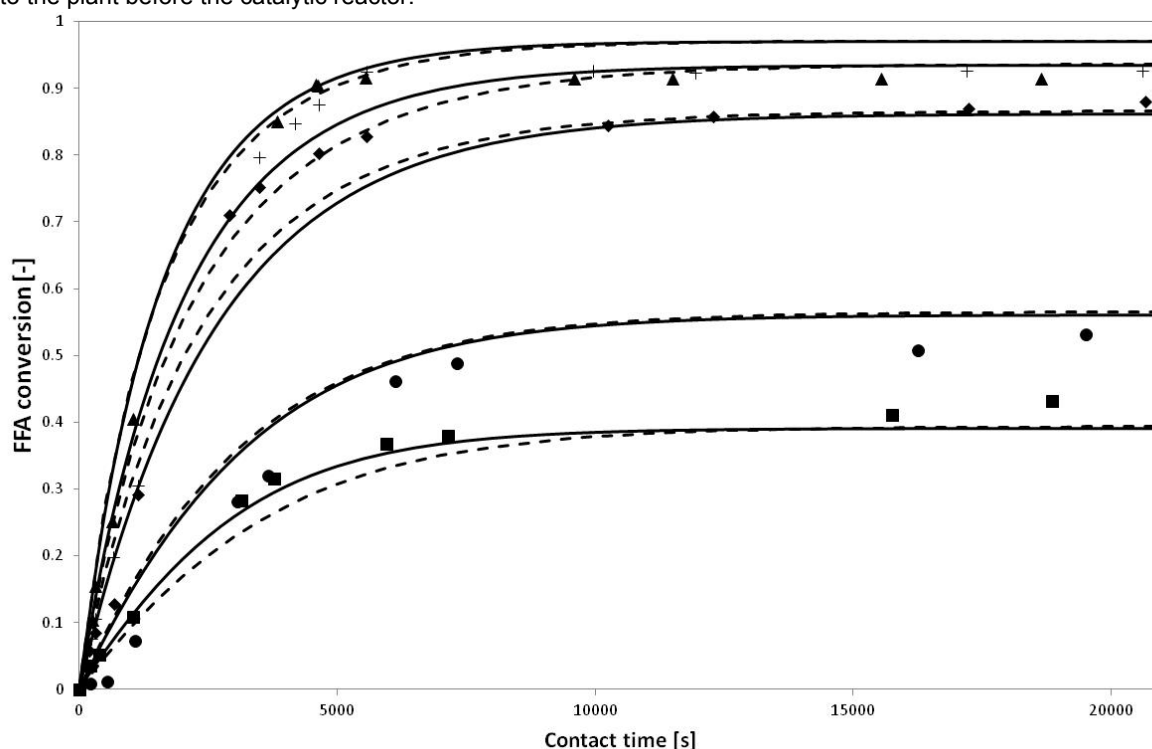

Figure 2: experimental values for FFA conversion and predicted course by pseudo-homogeneous model (dotted line) and adsorption-based model (solid line)

3.2 Kinetic regression

As explained in paragraph 2.2 the experimental data were used to regress the parameters taking into account two different models. These are reported below in Table 4 with the residual errors:

Table 4: Kinetic parameters regressed from the experimental data

Model	SSE	k_1^{0a} (mol*sec^{-1}*m^{-3})	k_{-1}^{0a} (mol*sec^{-1}*m^{-3})	Ea_1 (kJ*mol^{-1})	Ea_{-1} (kJ*mol^{-1})
Pseudo-homogeneous (eq 3)	0.131	0.657	12.100	32.268	-67.589
Adsorption-based (eq 4)	0.145	1.245	14.271	43.152	-57.229

a: kinetic constants are referred to the reactor volume. In order to express them specifically to the catalyst mass it possible to use the relation

$$mcat = V * d * (1 - \varepsilon) \tag{7}$$

where ε is the void space and d the catalyst density. Even if the pseudo-homogeneous model does not consider the adsorption of both reactant and products the optimized kinetic parameters permit to better calculate the experimental trends, especially for the runs performed at high temperatures.

4. Conclusion

The esterification of FFA in sunflower oil with methanol was studied in a PBR reactor. The experimental results permitted to regress the main kinetic parameters using two different models considering an ideal liquid phase behavior. From the regression results, it could be concluded that the pseudo-homogeneous model is slightly better to fit the experimental data. The regression of the kinetic parameters considering the non-ideality of the liquid phase, i.e. calculating the activity coefficient with suitable equations, is npt commonly found in literature, but, the activity coefficients calculation for the regression of the kinetic parameters is not commonly found in literature, but, especially for some kind of systems, like the one studied in this work that is highly non ideal, will be the object of a further work.

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