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Acid exchange resins deactivation in the esterification of free fatty acids

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ABSTRACT

In this work the deactivation of an ionic exchange resin, used as catalyst for promoting the esterification of fatty acids for producing biodiesel, has been studied. At this purpose, a dynamic mathematical model, suitable to describe the performances of a continuous tubular reactor containing the catalysts mixed with stainless steel springs as inert diluent, and its evolution with time due to the catalyst deactivation, has been developed. Experimental runs, performed in a pilot plant tubular reactor on fatty acid mixtures (oleins), are reported in the paper. The catalyst deactivation has been shown to depend mainly on the poisoning effect of iron that was present as impurity in the fatty acids used as feedstock. Some information about catalyst regeneration is also given at the end of the paper.

1. Introduction

The worldwide interest towards biofuels has recently grown significantly as a direct result of the renewed need of facing the global warming effect by reducing the greenhouse gases emissions that are related to the wide use of fossil fuels. With this respect, biodiesel represents a valuable alternative to petroleum-derived fuels due to both its renewable nature and its substantially null net carbon dioxide emission. Biodiesel is normally produced by transesterification of highly refined vegetal oils with methanol in the presence of homogeneous alkaline catalysts like sodium or potassium hydroxide or related alkoxides [1,2]. The use of the mentioned alkaline catalysts is not compatible with the presence of free fatty acids and moisture, because, the formation of soaps determining long settling time for separating biodiesel from the by-product glycerol. This is a drawback of this technology because many cheaper feedstock like waste or fried oils cannot be used for producing biodiesel. As a matter of fact, with the current technology the cost of biodiesel is affected for more than 85% by the feedstock supply [3]. At this purpose, new technologies have recently been proposed like: the use of supercritical methanol [4] and a two-stage process (esterification + transesterification) [5,6]. Esterification of free fatty acids (FFA) can be promoted by Broensted acid catalysts, both homogeneous [5,6] and heterogeneous. Many different heterogeneous acid catalysts have been proposed for this reaction but one of the most studied and used is the sulphonic acid exchange resin [7]. A recent review on the use and properties of exchange resins has been published by Alexandratos [8]. The exchange resins are subjected to remarkable swelling [9–12] in the presence of polar substances. This phenomenon must be carefully considered in a kinetic approach for either the liquid volume absorbed or the selectivity in absorption. The liquid composition inside an exchange resin particle could be quite different with respect to the liquid bulk. This is particularly true for the binary mixture water–methanol.

We have studied the importance of this aspect in a previous work [12] where we have shown the effect of neglecting the partition equilibria for runs performed in the presence of different amounts of catalyst. As water is more retained by the resin than methanol, the use of a greater amount of catalyst has the consequence of altering the reaction rate inside the particles. This aspect becomes dramatic in packed bed pilot plant reactor where the catalyst concentration is very high.

A first paper published by Tesser et al. [13] reported a simplified kinetics of the esterification reaction of oleic acid with methanol in the presence of triglycerides, catalyzed by an acid exchange resin in a batch reactor. Furthermore, Santacesaria et al. [14,15] have shown that the esterification reaction, performed in a continuous packed bed tubular reactor (PBR), is possible but, in order to achieve high conversions, a long residence times and consequently low volumetric flow rates are required resulting in very low Reynolds numbers at which the external fluid-to-solid mass transfer resistance becomes significant in comparison with the intrinsic kinetics. Tesser et al. [16] have shown that the kinetic regime can be reached by conducting the esterification reaction in a packed bed loop reactor (PBLR) operated in batch conditions. By adopting a sufficiently high recirculation flow rate, as expected, the PBLR operates near to

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Nomenclature

Ac	acidity wt% in oleic acid
a_s	specific interface area ($cm^2\ cm^{-3}$)
C	concentration ($mol\ mL^{-1}$)
C_{cat}	concentration of catalyst ($g_{cat}\ mL^{-1}$)
C_{Fe}	iron concentration ($mmol\ mL^{-1}$)
C_{titr}	concentration of titrant ($mol\ mL^{-1}$)
C_σ	concentration of active sites ($meqH^+\ {g_{cat}}^{-1}$)
d_p	particles average diameter (cm)
D_{eff}	effective diffusivity ($cm^2\ min^{-1}$)
E_A	activation energy ($kcal\ mol^{-1}$)
H	ionic exchange equilibrium constant
k	kinetic constant of uncatalyzed reaction ($mL^2\ mol^{-2}\ min^{-1}$)
k_{cat}, k_{-cat}	kinetic constants of the forward and the reverse reaction ($mL^{-1}\ {g_{cat}}^{-1}\ min^{-1}$)
k_d	deactivation kinetic constant ($g_{cat}\ mL\ min^{-1}\ {meqH^+}^{-2}$)
k_S	mass transfer coefficient ($cm\ min^{-1}$)
K	partition constant ($mL\ mol^{-1}$)
K^{eff}	effective partition constant
m_{sample}	weight of sample (g)
M	molecular weight ($g\ mol^{-1}$)
n	number of moles (mol)
N	number of experimental data
Q	volumetric flow rate ($mL\ min^{-1}$)
r_{cat}	rate of catalyzed reaction ($mol\ min^{-1}\ {g_{cat}}^{-1}$)
r_d	rate of deactivation ($mmol\ min^{-1}\ {g_{cat}}^{-1}$)
r_{uc}	rate of uncatalyzed reaction ($mol\ min^{-1}\ cm^{-3}$)
R	universal gas constant ($kcal\ mol^{-1}\ K^{-1}$)
Re_p	particle Reynolds number
RMS	root mean square error
Sc	Schmidt number
Sh	Sherwood number
t	time – for continuous run (h), – for batch run (min)
T	temperature (K)
U	linear velocity than tubular section ($cm\ min^{-1}$)
U_{bed}	linear velocity in the bed ($cm\ min^{-1}$)
V_{abs}	volume of adsorbed liquid phase per gram of catalyst ($mL\ {g_{cat}}^{-1}$)
V_C	volume of single cell (mL)
V_L	liquid volume (mL)
V_R	volume of tubular reactor (mL)
V_{swell}	total swelling volume (mL)
V_{titr}	volume of titrating solution (mL)
W_{cat}	weight of catalyst (g)
x	conversion
z	axial coordinate (cm)

Greek letters

β	deactivation factor
η_{mix}	viscosity of the mixture ($g\ cm^{-1}\ min^{-1}$)
ν	stoichiometric coefficient
ρ	molar density ($mol\ cm^{-3}$)
ρ_{mix}	density of the mixture ($g\ mL^{-1}$)

Subscript

A	fatty acid
E	fatty acid methyl ester
h	height of bed
i	index for i-th component
j	index for j-th cell
M	methanol
n	index for n-th experimental data
T	triglycerides
W	water
0	reactor inlet

Superscript

B	bulk-external of resin
C	cell
calc	calculated value
exp	experimental data
R	internal of resin
ref	reference temperature (373.16 K)
S	surface of catalyst
uc	uncatalyzed reaction

the chemical regime but without the negative effect of breaking the catalyst particles as it occurs in well stirred reactors and with performances higher than the continuous tubular reactor, operating at high conversions, that works in diffusional regime.

In the present work, the esterification with methanol of a mixture of free fatty acids (oleins) has been studied in the presence of an acid exchange resin catalyst of the type Resindion Relite CFS in a pilot-size continuous fixed bed tubular reactor operated for relatively long time-on-stream. The experimental runs have been shown a progressive deactivation of the resin that we have observed mainly due to the presence of iron dissolved in the feeding mixture. The experimental data have been interpreted with a kinetic model based on an ionic-exchange reaction mechanism, reported in more details in our previous work [12], that takes into account also for the physical partitioning effects of the various components of the reacting mixture between internal and external liquid phase of the resin. The catalyst deactivation mechanism has been studied and we have found that the kinetics of the resin acid sites poisoning was essentially due to iron contained in the oleins mixture fed to the reactor. This aspect has been appropriately introduced in the dynamic reactor model to describe the experimental data.

In the final part of the work a study of the deactivation and regeneration of the Relite CFS resin is reported, in which batch esterification runs have been performed on a model mixture represented by soybean oil artificially acidified with oleic acid (about 50% by weight of oleic acid). These runs have been conducted on samples of resin taken at different axial positions in the tubular reactor at the end of the continuous run when the reactor was opened and the resin discharged. The aim of this set of runs was the study of the catalyst deactivation along the reactor axis and its influence on the reactor performances.

2. Experimental

2.1. Reactants and methods

The reactants used in the investigation are the following: methanol (Aldrich, purity > 99%, w/w), oleic acid (Carlo Erba, purity > 90%, w/w), and a commercially available acidity-free soybean oil (acidity < 0.3%, w/w). The oleins have been furnished by a local company (Parodi s.r.l.) and their composition in fatty acids is shown in Table 1. The amount of iron and other metals dissolved in this mixture has been analyzed by atomic absorption spectroscopy and the result are reported in Table 2.

The resin Relite CFS has been purchased by Resindion. This resin is a macroreticular copolymer styrene-DVB in wet form and their characteristics, as reported by the technical data sheet from the