Chemical Engineering Journal 297 (2016) 35–44

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Theoretical study of the effect of trickle phase conditions on competitive adsorption in packed bed adsorption columns

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HIGHLIGHTS

- Model describes adsorption in trickle phase conditions in breakthrough experiment.
- Model accounts for phase transitions due to shifts in vapor–liquid equilibrium.
- Investigate the effect of trickle phase conditions on competitive adsorption.
- Determine how operational conditions affect selectivity of catalytic processes.
- Depending on conditions vapor and liquid fronts are observed.

ARTICLE INFO

Article history:
Received 2 October 2015
Received in revised form 29 January 2016
Accepted 20 March 2016
Available online 1 April 2016

Keywords:
Trickle phase conditions
Vapor–liquid equilibrium
Adsorption equilibrium
Breakthrough experiment

ABSTRACT

In several industrial catalytic processes the operating conditions cause the feed to be in trickle phase conditions. For example in the hydroconversion process the linear alkanes are converted in trickle phase reactor and it is well known that the presence of the vapor–liquid equilibrium has a determining effect on selectivity through changing adsorption behavior. In this paper a model is developed that describes adsorption in trickle phase conditions in an adsorption breakthrough experiment. Due to adsorption the composition in the column during breakthrough changes and local shifts in aggregation state can occur. The model allows to simulate both single and mixed phase conditions and transitions between these states. The composition of the vapor and liquid phase in trickle phase conditions is calculated using the Peng Robinson equation of state (PREOS).

The model shows how vapor–liquid equilibrium influences adsorption selectivity. Two cases are identified, adsorption of linear alkanes with nonspecific adsorption interaction and adsorption of polar and apolar compounds on an apolar adsorbent. Depending on conditions vapor and liquid fronts are observed and the effects of temperature and pressure are studied for both cases and different behavior is observed. From the simulation results it is concluded that accounting for the presence of vapor–liquid equilibrium in trickle phase adsorption columns is important since it has an effect on selectivity and the shape of breakthrough curves.

1. Introduction

The importance of adsorption in practical applications in industry and environmental protection cannot be underestimated. Adsorption plays a major role in separation of mixtures on laboratory and industrial scale and is the first stage in all heterogeneous catalytic processes [1,2]. Adsorption processes are typically conducted in tubular columns, packed with porous materials. Separation is achieved due to preferential enrichment of a specific component in the pores of the adsorbent at the solid/fluid interface, resulting in the depletion of that component from the mixture flowing through the adsorption column. This preferentially adsorbed component can be recovered from the adsorbent pores using various desorption methods, including pressure swing, temperature swing, displacement desorption etc. [3]. Adsorption has a wide range of applications and is used for the separation and purification of different types of feeds including both diluted and undiluted gas and liquid mixtures. The most important applications include water purification [4], separation of bulk chemicals (e.g. xylene isomers, *n*- and iso-alkanes) [5], separation of chiral mixtures in pharmaceutical production processes [6,7], gas drying [8] etc.

Because of the importance of the adsorption process, innumerable research is performed on this subject both by modeling and

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http://dx.doi.org/10.1016/j.cej.2016.03.100

List of symbols

Latin letters

C	species concentration/mol m^{-3}
D_c	column diameter/m
D	dispersion constant/m^2 s^{-1}
k	speed constant/s^{-1}
K_{ads}	Langmuir adsorption constant/m^3 mol^{-1}
k_{vap}	vaporization/condensation constant/mol (m^3 s)$^{-1}$
K_{vap}	vapor–liquid equilibrium constant
L_c	column length/m
P	pressure/Pa
q	adsorbed concentration/mol kg^{-1}
r	molar adsorption term/mol (m^3 s)$^{-1}$
R	gas constant/J K^{-1} mol^{-1}
t	time/s
T	column temperature/K
u	bed velocity/m s^{-1}
V_p	pore volume/m^3 kg^{-1}
x	distance/m
x	species molar liquid fraction/mol mol^{-1}
y_i	species molar vapor fraction/mol mol^{-1}
z	species molar mixture fraction/mol mol^{-1}

Greek letters

ρ	molar density/mol m^{-3}
ε	volume fraction in bed/m^3 (m^3)$^{-1}$
α	volume fraction in fluid/m^3 (m^3)$^{-1}$
γ	molar fraction in fluid/mol mol^{-1}
$\emptyset$	phase

Subscripts/superscripts

ads	adsorption
b	bed
comp	compound
eq	equilibrium
eff	effective
G	vapor
i,j	species
L	Liquid
mix	mixture
LDF	Linear driving force
s	solid phase
sat	saturation

experimental approaches; diverse aspects of the process are focused on. For example, molecular modeling is used to obtain a better understanding of the physical mechanisms of the adsorption process at the molecular level [9,10], transport models are developed that focus on the kinetics of the adsorption process where the different diffusion mechanisms are considered including diffusion in micropores, mesopores and macropores [11,12] while process/engineering models focus on the flow and heat transport through packed beds [13,14]. Such models have been developed for diluted and undiluted systems both in vapor and liquid phase. The investigation and modeling of adsorption processes in trickle phase conditions however is as good as absent in literature.

However, many heterogeneous catalytic processes are conducted in trickle phase conditions, in presence of a solid catalyst and a mixed gas/liquid feed and product stream [15–18]. As aforementioned, adsorption plays a predominant role in this process, as it is the first step in the catalytic conversion of the molecules in the feed mixture. Typically in the petrochemical sector, many catalytic processes are conducted in trickle phase conditions since these feeds are characterized by a mixture of components with a wide range of boiling points. In hydroconversion reactors for example, a paraffin feed is converted in the presence of H_2 gas at high temperatures. In these conditions, the vapor phase is enriched with the more volatile components, while the liquid phase is enriched with the heavy fraction. It is already recognized that the presence of both a vapor and liquid phase has an effect on the performance of the hydroconversion process [19–21]. It is often assumed that a liquid film, in thermodynamical equilibrium with the vapor phase, surrounds the solid phase particles. Molecules from this liquid film directly enter the pores of the catalyst before their catalytic conversion. Operating conditions (pressure, temperature) directly affect the composition of this liquid film through the vapor–liquid phase equilibrium and as a result have an impact on catalytic activity and selectivity. From several studies, it is observed that the heavy paraffin fraction is preferentially converted; only at a high degree of conversion the lighter fraction starts to be converted. This is partly ascribed to its higher enrichment in the liquid phase and subsequently higher concentration on the catalyst surface and thus higher conversion rate [20,21,24].

Apart from the effect of adsorption selectivity on reaction kinetics, it thus is interesting to study the effect of trickle phase conditions on the adsorption process and to verify how operational conditions can influence separation efficiency. From our previous experimental work on the adsorption of paraffinic mixtures, it follows that adsorption behavior is strongly dependent on aggregation state [22,23]. In vapor phase conditions (high temperature, low pressure), *n*-paraffins could be selectively adsorbed and efficiently separated on a packed bed of mesoporous silica-alumina according to differences in chain length. Longer *n*-paraffins are preferentially adsorbed and retained for a longer time in the adsorption column as compared to the shorter paraffins. In liquid phase conditions (high pressure, lower temperature), this adsorptive selectivity disappears and the short and long chain paraffins co-elute. The effect of the presence of trickle phase conditions on the separation of paraffinic mixtures was not yet studied in detail; adequate models are lacking. Recently, we developed a model that describes adsorption of dissolved n-paraffins in conditions where liquid conditions prevail in a part of the column while vapor conditions prevail in the other part [25]. Since the adsorbing species were considered as being diluted (present in only low concentration), their changing composition during the breakthrough experiment did not cause trickle phase conditions or shifts in vapor–liquid conditions.

In this paper, a more general model for adsorption processes in trickle phase conditions with non-diluted species (large concentration for all components in the mixture) is developed. This model accounts for phase transitions due to changing compositions during breakthrough and shifts in vapor–liquid equilibrium. It allows investigating the effect of trickle phase conditions on competitive adsorption behavior, for various types of feeds. This new model is then used to determine (1) how operational conditions affect the selectivity of catalytic processes through the effect of changes in vapor–liquid equilibrium on competitive adsorption and it is also used (2) to study the effect of trickle phase conditions on adsorption processes. Finally, it is evaluated if the presence of trickle phase conditions may contribute to more efficient separations of mixtures and if so, determine the optimal operational conditions.