Model Development and Validation of Ethyl tert-Butyl Ether (ETBE) Production Reactors Using Industrial Plant Data

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Introduction

The use of ethers as octane-rating enhancing additives began in mid 1970s, driven by the negative impact of lead on our health and on the environment [1].

ETBE is a clear, colourless to pale yellow liquid, produced by the reaction of isobutene and ethanol, which is catalysed by acid ion-exchange resins [2]. In order to carry out optimisation, as well as to evaluate the impact of catalyst deactivation on the design of alternative processes for ETBE production (e.g. reactive distillation), a validated kinetic model is necessary. Such a model, which considered both the formation of ETBE and coproducts, as well as catalyst deactivation, was lacking in the literature.

Objectives

- To validate a kinetic model, which can be used to predict the formation of both ETBE and coproducts (diisobutene and tert-butyl alcohol), as well as catalyst deactivation
- To develop and validate a model of the battery of process reactors

Process and Chemistry

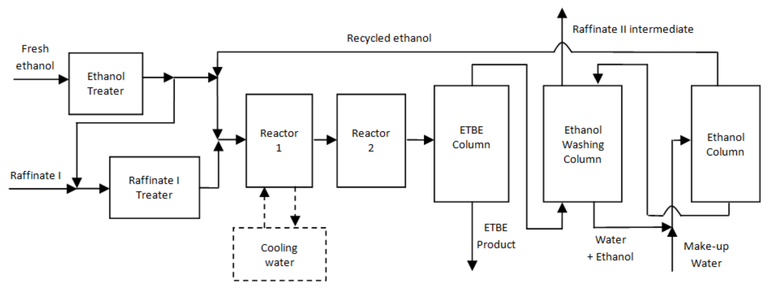


Fig. 1 – ETBE production process

Main reaction:

$$Isobutene + Ethanol \rightleftharpoons ETBE$$

Side reactions considered:

$$2\,Isobutene \rightarrow Diisobutene$$

$$Isobutene + Water \rightleftharpoons tert\text{-}Butyl\ Alcohol$$

Model Description

- Dynamic pseudohomogeneous plug-flow reactor model
- Presence of inerts (1-butene and n-butane)
- Reactor 2 operates adiabatically
- Only heat exchanged between the tube side and the shell

Rate laws used:

$$\Re_{ETBE,n} = \Phi_n \frac{k_{rate,ETBE,n} a_{EtOH,n}^2 \left(a_{IB,n} - \frac{a_{ETBE,n}}{K_{eq,ETBE,n} a_{EtOH,n}}\right)}{(1 + K_{A,EtOH,n} a_{EtOH,n})^3}$$

$$\Re_{DIB,n} = \Phi_n k_{rate,DIB,n} \frac{a_{IB,n}^2}{K_r a_{EtOH,n} + a_{IB,n}}$$

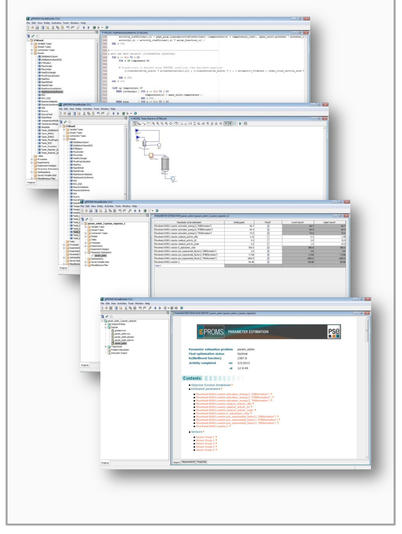
$$\Re_{TBA,n} = \Phi_n \frac{k_{rate,TBA,n} \left(C_{IB,n} C_{Water,n} - \frac{C_{TBA,n}}{K_{eq,TBA,n}}\right)}{1 + K_{A,TBA,n} C_{TBA,n}}$$

Due to the existence of feed treaters, desulfonation was assumed to be the dominant process of catalyst deactivation

$$\frac{\partial \Phi_n}{\partial t} = -k_{0,d} \exp\left(-\frac{E_{a,d}}{R}\left(\frac{1}{T_n} - \frac{1}{334.42}\right)\right) \Phi_n^{\alpha}$$

$$\Phi_n = \frac{[acid\ sites]}{[acid\ sites]_{t=0}} \quad ; \quad reactor\ n\ (n = 1,\ 2)$$

Model was implemented using **gPROMS Modelbuilder 3.3.1**



Parameter Estimation

Parameter estimation was carried out using industrial plant data, and the *Parameter Estimation* functionality of gPROMS Modelbuilder 3.3.1. Further details in [3].

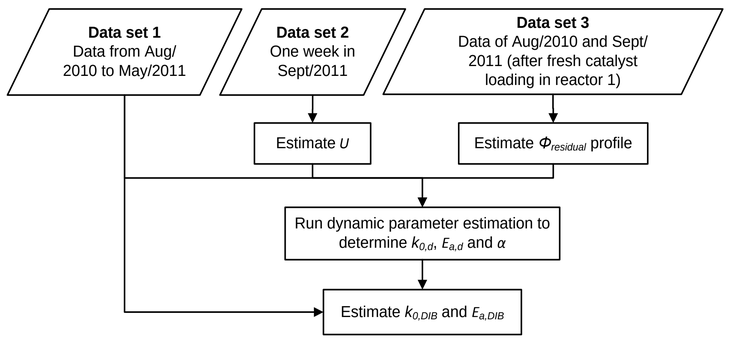


Fig. 2 – Flow diagram of the methodology used for parameter estimation.

Available data consisted of:

- Inlet mass flowrate and compositions for reactor 1
- Temperature profiles for reactors 1 and 2

Results

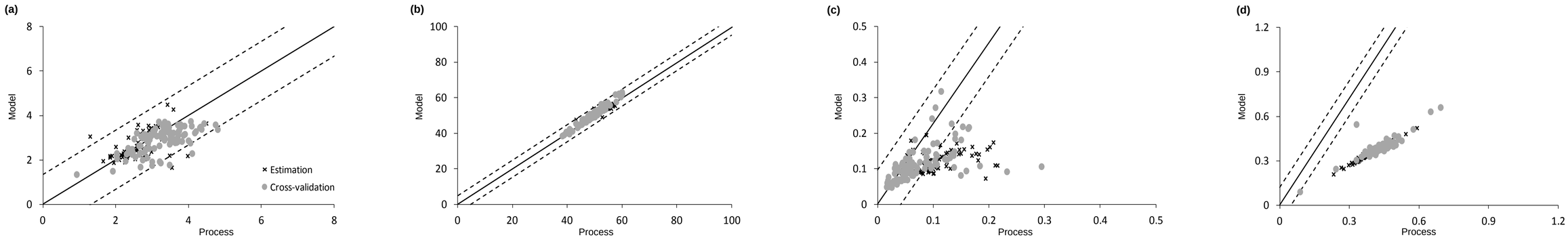


Fig. 3 – Parity diagrams obtained for reactor 2 outlet mass fractions (wt %) of: (a) Ethanol; (b) ETBE; (c) Diisobutene; (d) tert-Butyl Alcohol [3]

Tab. 1 - Parameters estimated using gPROMS Modelbuilder 3.3.1 [3]

Parameter	Units	Value
$k_{0,d}$	s^{-1}	$6x10^{-8}$
$E_{a,d}$	kJ/mol	92
α	-	2.8
U	$W/(m^2.K)$	70
$k_{0,DIB}$	mol/(kg.s)	0.2
$E_{a,DIB}$	kJ/mol	75
Φ_{res} (Aug/2010)	-	0.46
Φ_{res} (Sept/2011)	-	0.41

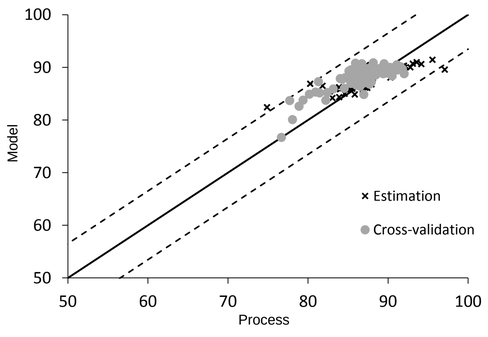


Fig. 4 – Parity diagram for isobutene conversion (%) at the outlet of reactor 2 [3]

Conclusions

- The model is able to accurately predict the outlet mass fractions of reactor 2 for all species, including the main product ETBE
- gPROMS proved to be an effective tool for model implementation and validation
- The kinetic model is fit to be used in future studies

References

[1] Kirk-Othmer Encyclopedia of Chemical Technology (5th Ed.), Vol. 10, New York, United States, John Wiley & Sons (2005).
[2] M G Sneesby, M O Tadé, R Datta, T N Smith, *Ind. Eng. Chem. Res.*, vol. 36, (1997) pp. 1855–1869.
[3] L Domingues, C I C Pinheiro, N M C Oliveira, J Fernandes, A Vilelas, *Ind. Eng. Chem. Res.*, vol. 51 (2012) pp. 15018–15031.

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