

Development of an Industrial Multitubular Fixed Bed Catalytic Reactor as CAPE-OPEN Unit Operation Model Applied to Ethene Production by Ethanol Dehydration Process

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The ethene production by ethanol dehydration has been established as a promising production route. In this work a computer software simulation written in FORTRAN 95 for an industrial multitubular fixed bed reactor (MTR), applied to this production route, is embedded in process simulation environment through a C#/NET wrapper code. This wrapper code was developed in agreement with the CAPE-OPEN standards, allowing the MTR simulator to be used as a native unit operation component in any CAPE-OPEN compliant simulation environment.

1. Introduction

Nowadays, due to the recent instability of petroleum prices, perspectives of resource scarcity, geopolitical risks derived from petroleum dependence on political unstable countries and the most solid commitments with environmental issues, attention to alternative sources of energy have been drawn increasingly. This situation puts alcoholchemistry, the chemical industry segment that uses ethanol as feedstock, in evidence again, since it could be a feasible alternative or even a substitute for petrochemical industry, with ethanol assuming the place of petroleum as a raw material resource in near future. In this new scenario, attentions drawn to ethanol are not only restricted to ethanol fuel, but also incorporate ethanol as a raw material to be used in many sectors of transformation industry as, for example, in the manufacture of ethene. Ethene is obtained from steam-cracking of raw materials such as petroleum and natural gas, as well as from ethanol catalytic dehydration, which has recently been established as a promising production route, becoming more and more competitive. Bearing this in mind, in this work a FORTRAN 95 simulation software for an industrial MTR for dehydration of ethanol to ethene over alumina (Al_2O_3) catalyst was developed and embedded as a native unit operation module in a process simulation (Aspen Hysys®). Chemical process simulation has long been used as a design tool in the development of chemical plants, and it has been considered a means to evaluate different design options (Barrett Jr. and Yang, 2005). However, the process simulator softwares typically come

with a built-in set of generic unit operation models, but for many purposes, more specialized unit operation models are required. Thus, the CAPE-OPEN interface standards were developed to allow process modeling components to be used in any compliant process modeling environment (Barrett Jr. and Yang, 2005). The CAPE-OPEN standards have chosen to adopt an object-oriented approach for developing software components. As consequence, original softwares written in procedural languages as FORTRAN should be wrapped in an appropriate object-oriented computer language in order to be linked with the rest of the components that are in agreement with the CAPE-OPEN standards.

2. Ethene Production by Ethanol Dehydration

The ethene is produced by the passage of ethanol or diethyl ether over heated alumina or silica catalyst (Winter and Eng, 1976). Until the mid-1940s, a significant portion of the ethene produced industrially was derived from ethanol dehydration. Nowadays, with the shortage of natural resource and energy, and also with the recent increase in the prices of crude oil, catalytic dehydration of ethanol to ethene has become a more and more competitive and promising route, and therefore has been drawing much attention (Guangwen *et al.*, 2006).

In the present work, the kinetic model proposed by Butt *et al.* (1962) for dehydration of ethanol to ethene over alumina (Al_2O_3) catalyst was considered as case study. This reaction mechanism is composed of four reactions in series and parallel, and is based on their studies using pure alumina as catalyst in a differential reactor incorporated in a recycling system. The reaction system is represented by:



3. Multitubular Fixed Bed Catalytic Reactor Design

The ethanol dehydration process is highly endothermic and requires an elevated amount of energy. Therefore, the reaction temperature control appears as a key factor to maintain a good selectivity level. In fact, diethyl ether is formed over oxide catalyst mainly bellow a temperature of 300 °C and ethene is formed above this temperature. As consequence, the reactor choice and its design become extremely important. In this case, the use of a MTR, with a large number of tubes, may be the appropriate choice. These kinds of reactors are usually designed to carry out reactions that require good temperature control. To achieve high performance operation in these systems, a thermal fluid circulating through the tubes is required to avoid occurrences of hot and/or cold spots in the reactor, otherwise thermal efficiency is reduced.

In this work, a detailed mathematical representation of a MTR for dehydration of ethanol to ethene over alumina (Al_2O_3), which account for changes and interactions for

both tube-side and shell-side domains, was developed. This means that two sets of equations need to be considered, i.e., the tube-side (where heat production and/or absorption due to chemical reactions is occurring), and the shell-side (where heat transfer between tubes and thermal fluid takes place). The link between them is determined by the overall heat exchange. More details about the mathematical models can be found in Stankiewicz (1989a,b), Maciel Filho and McGreavy (1993), Maciel Filho and McGreavy (1998), Vasco de Toledo et al. (2002).

4. CAPE-OPEN Standards

To be embedded as a native module in process simulation environments the legacy codes written in procedural languages should be wrapped in an appropriated computer programming language. In this approach, the FORTRAN code is treated as a *black box*. An object-oriented shell around this black box is provided to integrate the system into the component based framework (Pérez, 2005). This shell could be implemented using an object-oriented language such as C# or C++. One way to do this is using the Dynamic Link Libraries (DLL). Creating a DLL allowed us to call a FORTRAN subroutine from C# without additional source code. In this study the MTR simulation software originally written in FORTRAN 95 were wrapped in a C#.NET shell in order to be in agreement with the CAPE-OPEN standards.

5. Results and Discussions

In this section, the steady-state simulation results for MTR are presented. The case study reactor is a MTR composed by 10634 tubes involved in a 3.5 diameter shell with co-current flow. The reactor operates with a mass feed rate of $6719.36 \text{ kg.h}^{-1}$ of ethanol and, 1 atm pressure for an inlet temperature of $375 \text{ }^\circ\text{C}$. The Figure 1 shows a simplified process simulation flowsheet for the ethene production by ethanol dehydration with the MTR software simulator embedded as a native unit operation module.

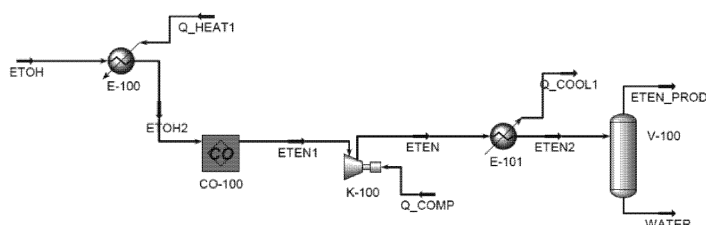


Figure 1: MTR embedded as a CAPE-OPEN unit operation module in a dehydration of ethanol to ethene process flowsheet

The operating parameters and the process streams composition are presented in Tables 1 and 2. These results are intended to show the applicability of the methodology used in developing applications (legacy simulation software) compatible with CAPE-OPEN standards.

Table 1: Operating parameters in process streams

	ETOH	ETOH2	ETEN	ETEN2	ETEN_P ROD	WATER	ETEN1
Vapour fraction	0.0	1.0	1.0	0.6	1.0	0.0	0.5
Temperature (°C)	24.9	374.9	374.8	29.9	29.8500	29.8500	492.700
Pressure (kPa)	101.3	101.3	100.9	304.0	304.0	304.0	304.0
Molar flow (kmol.h ⁻¹)	154.9	154.9	285.4	285.4	159.5	125.9	285.4
Mass flow (kg.h ⁻¹)	6720.0	6720.0	6720.0	6720.0	4450.0	2270.0	6720.0
Volumetric flow (m ³ .h ⁻¹)	8.4	8.4	13.8	13.8	11.6	2.3	13.8

Table 2: Molar composition of process streams

Molar Fraction	ETOH	ETOH2	ETEN	ETEN1	ETEN2	ETEN_PROD	WATER
Ethanol	0.9	0.9	0.0	0.0	0.0	0.0	0.0
Diethyl ether	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ethene	0.0	0.0	0.6	0.6	0.6	0.1	0.0
Water	0.1	0.1	0.4	0.4	0.4	0.01	0.1

Figures 2 and 3 show the cross-flow and parallel flow fractions distribution inside the MTR shell. The variations in the cross-flow fractions between the cells 3 and 6 are due to existence of parallel flow through the annular gaps present in the reactor baffles (Figure 2) resulting from the pressure differences between the reactor sections. Although these streams are not noticeable in Figure 3, their cumulative effect along the radial direction significantly reduces the cross-flow fractions, resulting in different thermal fluid temperature profiles in different regions of the MTR shell (Figure 5). It can also be observed in Figure 3 that there is a non-uniform parallel flow distribution in the window regions, since it occurs mainly close to the baffles edges (cells 2 and 7) rarely reaching the outer regions of the reactor shell (cells 1 and 8). This characteristic reduces the heat transfer coefficients in these regions, influencing negatively the thermal efficiency of the MTR. Therefore, a very special attention should be done to these regions in order to guarantee the MTR operational stability (Figure 4).

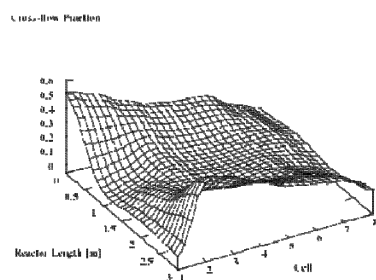


Figure 2: Spatial distribution of thermal fluid cross-flow fractions inside the MTR shell

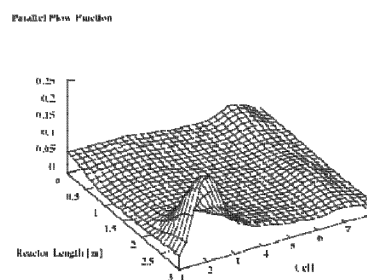


Figure 3: Spatial distribution of thermal fluid parallel flow fractions inside the MTR shell

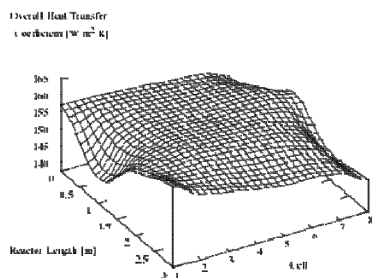


Figure 4: Spatial distribution of overall heat transfer coefficient inside the MTR shell

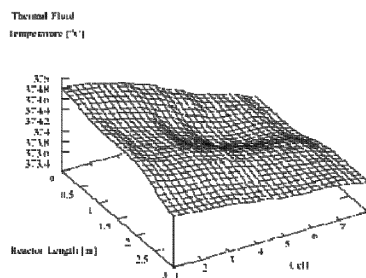


Figure 5: Spatial distribution of thermal fluid temperature inside the MTR shell

The reactants temperature and ethene concentration profiles inside the tubes for different regions of the MTR are shown in Figures 6 and 7. While the qualitative features are the same, differences in the location and value of the cold spot temperature can be observed in each cell (Figure 6). The differences in cold spot temperature values refers to the tubes located in the cells 1 and 8, and are due to the presence of the window regions. In these regions there is a reduction in the overall heat transfer coefficient (Figure 4) due of the presence of parallel flow and the reduction in the thermal fluid velocity, resulting from changes in the flow direction (Figure 3). These results highlight again the critical role that the window regions play in the behavior of the MTR. There were no differences in the ethene concentration profiles, but a high concentration level for ethene is observed (Figure 7). This result was favored by the use of a higher temperature (Figure 6).

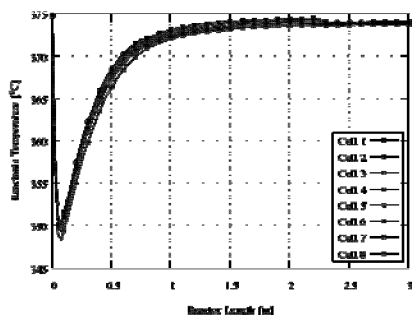


Figure 6: Reactants temperature profile along the reactor length

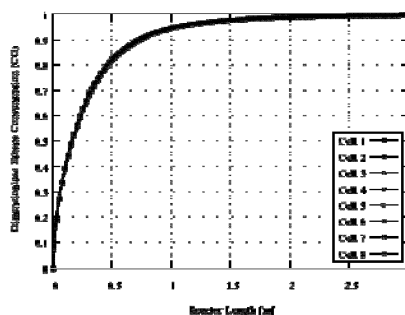


Figure 7: Dimensionless ethene concentration profile along the reactor length

6. Conclusions

The adherence to the CAPE-OPEN standards allowed the integration of the developed MTR simulator in a simplified process simulation flowsheet for the production of ethene by ethanol catalytic dehydration. The methodology described here can be easily extended to more complex and specific cases. Furthermore, more detailed analysis can be performed, since it is possible to develop more rigorous unit operation modules that

permit to reproduce the system more realistically. For the case study considered in this work, was possible to analyze the thermal fluid flow distribution in the shell side of the MTR, allowing to highlight the most critical areas of flow (window regions) that negatively influence the thermal efficiency of the MTR, compromising its operational stability. These analysis are not normally available in the generic unit operation modules (e.g. reactors) presented in the various existing process simulators. Thus, the strategy used here may be of fundamental importance for the integration of models that predict specific chemical processes.

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