DME synthesis via catalytic distillation: experiments and simulation

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Abstract

This paper regards the field of the chemical engineering that is commonly identified as Process Intensification (PI). The main objective of PI is to improve processes and products to obtain technologies more safe and economic. ENI and the University of Pisa are partners in the European project INtegrating SEparation and Reactive Technologies (INSERT) that considers the integration of the two key steps common to conversion processes (reaction and separation), to develop new configurations with advanced performances respect to the conventional ones. It has been chosen to apply Catalytic Distillation, the most promising application of the intensification principles, to the synthesis of dimethyl ether (DME) from methanol. This is one of the seven industrial case studies being investigated to test and validate the INSERT methodology.

Keywords Process intensification, reactive distillation, rate-based approach, Katapak™
1. Introduction

Catalytic distillation has become in few decades very popular as demonstrated by the increasing application of this technology to new and old production processes and by the numbers of investigations carried out on this subject [1]. The attractiveness of this intensified process is based on the demonstrated potential for capital productivity improvements, selectivity enhancement, reduced energy and polluting solvent consumption. These advantages are greatest when the combination of reaction and separation implies a reciprocal synergetic effect, however limiting the application field only to processes whose reactive requirements are compatible with distillation conditions. Several projects have been successfully carried out with the aim of identifying the feasibility of this technology and of optimising the conditions and the necessary equipment [2]. Nowadays, the industrial companies urgently require a comprehensive methodology enabling to proceed from the design phase to the working process. This is the main objective of the large European Project INSERT (INtegrating SEparation and Reactive Technology), involving ENI and the University of Pisa together with other industrial and academic partners. INSERT activities comprise both theoretical and experimental work. The main goal of the theoretical part is to develop an integration methodology and software tools, whereas the experimental part is mainly directed to provide necessary data for the models development and validation. The models and methods developed will form the basis of generic computer-aided process-engineering tools for synthesis and optimisation of reaction-separation sequences [3]. In the framework of the project, ENI and the University of Pisa are investigating the synthesis of dimethyl ether (DME) via dehydration of methanol. The study comprises both theoretical aspects and laboratory and pilot-plant experimental investigations. This paper describes the approach as well as the results obtained so far.

2. DME production via reactive distillation in an experimental pilot plant

DME is a gas at ambient temperature and atmospheric pressure with physical properties similar to GPL. It is gaining attention as a promising alternative clean fuel thanks to its low toxic index and the versatility of its use. Its production starting from methanol represents one of the routes for technological innovation in natural gas valorisation. Besides the industrial production advantages, the catalytic distillation synthesis of DME has some peculiarities particularly useful for the validation of the INSERT methodology. In fact the conventional process is well known in literature [4] and a direct comparison between the industrial configuration and the innovative reactive distillation approach can be directly done. Moreover, at the selected operative conditions, no side reactions is expected and the only side product is water.
For this reason, a pilot plant has been built up to investigate experimentally the rate of integration between the separation and the reaction in a continuous process behaviour. The pilot plant can work in two different configurations sketched in Figure 1(a). In the first one the reaction takes place inside the pre-reactor while the column works as a common distillation column. In the second configuration, the reactor is bypassed while the column works as a reactive distillation column. The pre-reactor is a fixed bed of 50 mm internal diameter and 2 m height, filled with the commercial sulfonic resin Amberlyst 35 wet (by Rohm and Haas) as catalyst. The column has an internal diameter of 50 mm, is equipped with an internal reboiler and has an effective packing height of 4 m comprising four sections of 1 m each. The rectifying zone at the top and the stripping zone at the bottom are filled with Sulzer BX\textsuperscript{TM} packing while the two middle sections can be equipped with either the BX\textsuperscript{TM} packing or the Sulzer Katapak\textsuperscript{TM}-SP11 reactive packing, according to the working configuration. The catalyst used to fill the bag of the reactive packing is Amberlyst 35 wet.

The main operative condition for both the configurations are reported in Figure 1(b). It is important to highlight that a pressure of 50 bar inside the reactor has been chosen in order to ensure that the reaction takes place in the liquid phase. The collected data are used for the validation of the modelling approach.
3. The INSERT methodology

3.1. Modelling approach

The simulation of integrated processes is still a difficult task [5]. Reactive separation processes are always characterised by a multi component nature and by the coupling of thermodynamic and diffusional phenomena that are accompanied by complex chemical reaction. A physically consistent way to model a reactive distillation column is known as the rate-based approach [6,7]. This approach has been used in this work as a modelling basis. The developed models have been implemented into the simulation environment Aspen Custom Modeler™ (ACM) [8]. The hierarchy of the column model is shown in Fig. 2.

![Figure 2 Schematic representation of the reactive distillation column model.](image)

Briefly, the assumption has been made that the reaction takes place only in the liquid phase. Moreover, the compositions and the temperatures present in the mass and heat transfer equations depend on the hypotheses made for the flow behaviour at each stage. For the vapour phase, the hypothesis of plug flow behaviour has been made, while a plug flow with axial dispersion has been used for the liquid phase, that is equivalent to consider a series of CSTR.

Besides the computational difficulties due to the complexity of the model, the main problem concerning the simulation of a reactive column is related to the estimation of the model parameters. For the thermodynamic and transport parameters, the whole database of the Aspentech commercial simulator Aspen Plus™ can be used in ACM. On the other side, the fluid dynamic behaviour and the kinetic parameters depend on the type of packing and the considered process. For the distillative packing chosen (Sulzer BX™) several validated models are present in literature [9], while for the catalytic packing (Sulzer Katapak-SP11™) data and models are lacking. For this reasons to determine a detailed fluid dynamic and kinetic description of the problem, a combined theoretical and experimental analysis has been undertaken.
3.2. Experiments for the estimation of kinetic and fluid dynamic parameters

Few data are present in literature about the kinetic of catalytic dehydration of methanol to DME in the liquid phase over a sulphonic resin of the Amberlyst type [10,11]. Therefore, the catalytic dehydration has been studied over the sulphonic resin Amberlyst 35 in a stainless steel plug flow reactor. A single site mechanism (Eley-Rideal type) model has been developed in ACM and good agreement has been found between calculated data and experimental measurements [12].

As mentioned above, the other information needed for predictive design and scale-up models are fluid dynamic related parameters. For the INSERT project, partners decided to perform reactive distillation experiments in column equipped with Katapak-SP11™, the last generation of Sulzer Chemtech structured catalytic packing [13]. To this scope, pilot columns were set up for the measurement of the needed parameters, mechanistic based models have been developed and implemented in ACM [14].

3.3. Validation of the methodology

A first run of experiments carried out in the pilot plant with the reactive distillation configuration has been completed and a preliminary model validation is reported in Figure 3 where the temperature and composition profiles along the column height are sketched.

![Figure 3. Calculated vs. experimental (a) temperature and (b) composition profile along the column heights.](image)

This run has been carried out at a fixed reboiler duty of 3 kW, a column pressure of 8 bar with a reflux ratio of 15.1. The distillate flow rate was 0.84 kg/h while the bottom one was 2.16 kg/h. Despite the fact that no parameters
have been adjusted the model shows a good agreement with experimental data. Further experimentation is running nowadays and the different performances with or without process integration are under analysis. The complete set of results will be soon available for the final model validation and scale up criteria implementation.

4. Conclusions and future work

DME synthesis via catalytic distillation is one of the test systems under investigation in the framework of the European Project INSERT. The study is carried out in collaboration by ENI and the University of Pisa and it covers both the theoretical aspects to develop mechanistic models and an extensive experimental programme useful to develop the necessary scale up knowledge and to validate the INSERT methodology.

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