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Reactive Distillation Process Analysis in a Divided Wall Column

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Abstract

This contribution aims to present a methodology to model and simulate the reactive dividing wall column (RDWC) using commercial software. Feasibility of separation scheme was established with ASPEN DISTIL™. Simulation of flowsheet configuration was performed with ASPEN HYSYS™, using the two columns model. The reactive zone hosted by the prefractionator was modelled and simulated as backward flow CSTR series. Proposed solution is attractive from industrial point of view. As case study isoamylenes (contained in fluid catalytic cracking-FCC-C_5-fraction) etherification with ethanol (EtOH), to obtain *tert*-AmylEthylEther (TAEE) in RDWC with structured packing was illustrated. Operation of such arrangement involves very careful solution of the model. Composition profiles demonstrated feasibility of proposed flowsheet.

Keywords Dividing wall column, computer aided process engineering, reactive distillation, process simulation, TAEE, gasoline additives, plant design.

1. Introduction

Performances of systems combining reaction and separation depend on some factors as level of integration and level of exploitation of synergy potential. It is well known that reactive distillation (RD) represents probably the most important application in intensification and thermal coupling between reaction and separation processes. The main advantages and disadvantages of RD are

well known [1]. Thermo-coupled process topologies as dividing wall column (DWC) proven to be very successful in reducing energy costs compared to conventional arrangements. Now, the main question is: which can be the role of DWC in RD (catalytic or non catalytic) process? They represent two different ways of process integration which can be combined again to improve the global process performances, featuring very high degree of integration. The configuration of RD system leads to additional synergy effects and very strong interactions between mass&energy transfer and chemical reaction.

2. Problem Statement, background

The suitability of RDWC for a particular reaction-separation system depends on various factors such as volatility of reactants and products, reasonable reaction and distillation temperatures, feedstock and product characteristics. In this respect feasibility domain of RDWC is rather restricted. The question is "How can be decided quickly whether RDWC is a good process technology?" Based on thermodynamic and kinetic behaviour of envisaged system Computer Aided Process Engineering (CAPE) tools create framework for solving the problem.

3. Paper approach

Conceptual design, based on study of residual curve maps (RCM) generated by appropriate CAPE tools, allows to establish tentative system structures, considering reaction, feedstock and product specifications. For more than three component systems, different topologies can be generated and compared using the RCM analysis of included ternary systems. Selected topologies were simulated with ASPEN HYSYS™ using adequate kinetic and process models and parameters. TAEE synthesis by etherification of iso-amylenes: 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B) contained in FCC-C_5 fraction with ethanol was considered for methodology illustration.

3.1. Methodology for simulation

Analysis of RCM to find promising topologies is well known and quite standard [1] using different CAPE tools as ASPEN-DISTIL™ [1] or ICAS [2]. Flowsheet simulation of RDWC is not very easy with commercial software (as ASPEN-HYSYS™) due to difficulties to adapt existing modules to needed topology. However Aspen CM™ (ACM) offers an alternative of modelling and simulation [3]. Our approach is attractive from practical point of view, as offers a robust solution with common CAPE tools for process engineers. There are several papers presenting this subject [4, 5]. RDWC was modelled considering four zones: the prefractionator, hosting reactive packing, (modelled with back flow cell model (BCM) with forward flow of liquid and back flow of vapour), upper separation zone in prefractionator (modelled as absorber standard unit),

separation zone in the prefractionator below the reaction zone (modelled also as absorber standard unit) and finally upper, right side and lower DWC separation zone (modelled together as standard distillation column), as in Fig. 1.
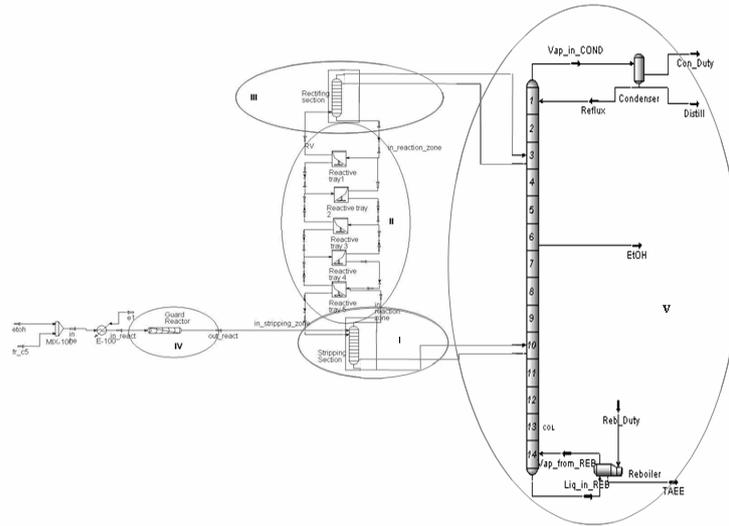
Figure 1 ASPEN-HYSYS flowsheet scheme for RDWC

The flowsheet included as well as some additional units for mixing and conditioning of feedstock streams and pre-reactor. Reporting system of this CAPE tool allowed performance assessment of each analysed topology.

3.2. Case study

TAEE synthesis from isoamylenes (2M1B and 2M2B) contained in FCC-C$_5$ fraction and EtOH (in excess 15%) represent direct generation of the oxygenated additive in light gasoline. Specific reaction conditions (temperature and pressure) should be chosen to ensure good activity of catalyst (acidic ion exchange as Amberlyst, Purolite or Lewatit). These etherification reactions are typically chemical equilibrium limited. Main reactions for TAEE synthesis are presented below.

$$EtOH_{(liq)} + 2M1B_{(liq)} \leftrightarrow TAEE_{(liq)}$$
$$\text{ethanol} \quad \text{2−methyl−butene−1} \quad \text{tert−amyl−ethyl ether}$$

$$EtOH_{(liq)} + 2M2B_{(liq)} \leftrightarrow TAEE_{(liq)}$$
$$\text{ethanol} \quad \text{2−methyl−butene−2} \quad \text{tert−amyl−ethyl ether}$$

$$2M1B_{(liq)} \leftrightarrow 2M2B_{(liq)}$$
$$\text{2−methyl−butene−1} \quad \text{2−methyl−butene−2}$$
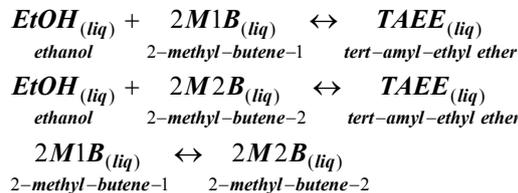
The main objective was to get good isoamylenes to TAEE conversion and TAEE separation, while recovering and recirculating the excess of ethanol. RDWC topology presented in Fig.1 could be in principle a candidate process

structure to produce at industrial scale TAEE. From analysis of thermodynamic data given by the specific CAPE tools resulted that both etherification reactions are exothermic, i.e. equilibrium conversion decreases with temperature. Therefore temperatures between 40 $^{\circ}$C and 80 $^{\circ}$C (to keep reasonable catalyst activity) and pressure between 2.5 bar and 4.0 bar were chosen. Property package used in activity coefficient calculations was based on UNIQUAC-UNIFAC model. Therefore in this paper only separation in RDWC was analysed with ASPEN-DISTIL™ to find conditions for targeting above mentioned objectives. In this respect RCM were drawn for systems: TAEE-EtOH-i-C$_5$, TAEE-EtOH-2M1B and TAEE-EtOH-2M2B to underline stable-instable-saddle nodes in these systems (Fig.2). Analysis of RCM indicated TAEE as stable node, so TAEE can be separated in bottoms. Ethanol, as saddle node, can be obtained as side product and i-C$_5$ as instable node, can be obtained as top product in RDWC.

a   b   c
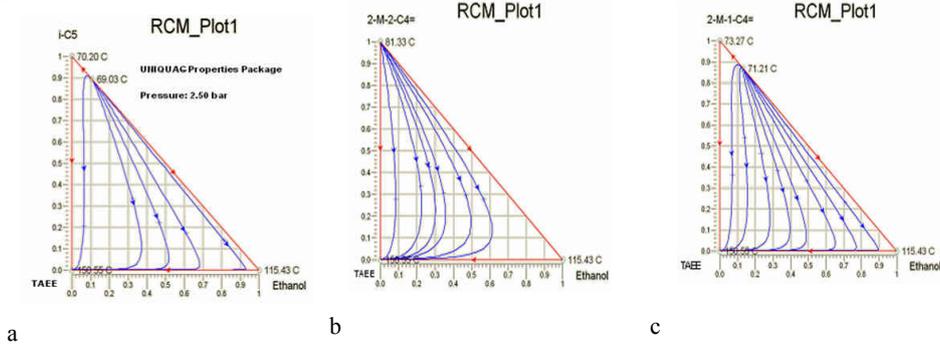
Figure 2 Residue curve maps for mixture components

ASPEN-DISTIL™ suggested topology for RDWC was presented in Fig.3.
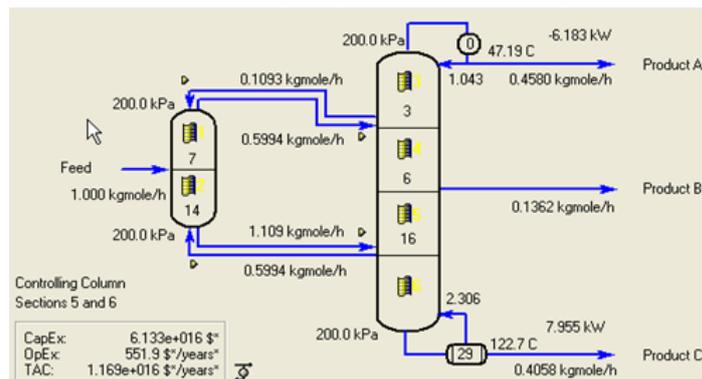
Figure 3 Chosen alternative for TAEE synthesis in RDWC

In next step ASPEN-HYSYS™ was used to find acceptable flowsheet for RDWC to target specified objectives. More attempts of simulation gave final topology presented in Fig. 4 which includes also reactive zone as BCM unit.

Finally the prefractionator was equivalent to 14 theoretical trays (TT) and the rest of the column was 31 TT. Sulzer structured packing Melapack/Katapack was considered for column capacity calculations. From flooding calculations column reactive zone (left side) was 0.15 m diameter for 0.57 m^3 catalyst.
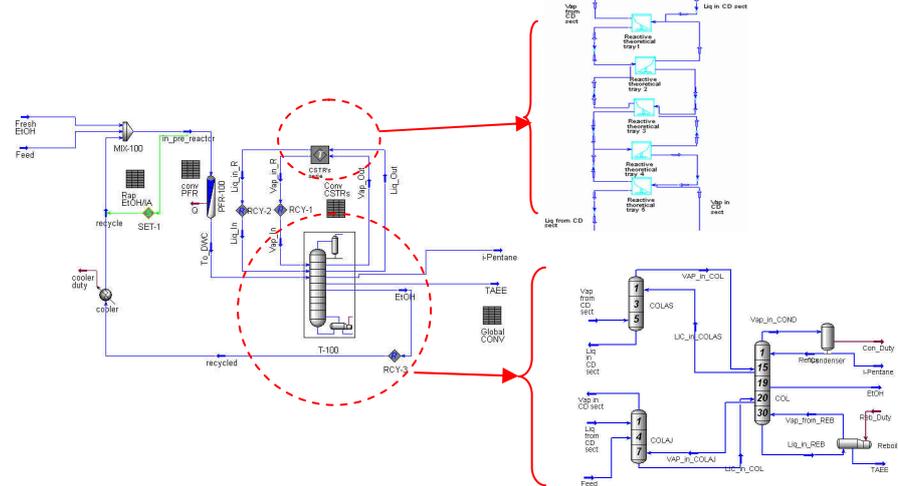
Figure 4. ASPEN HYSYS process flowsheet for TAEE synthesis in RDWC

Similar calculations for separation zones were performed obtaining: prefractionator 0.15 m diameter for packing heights 0.76 m above reactive zone and 1.10 m below reactive zone, RDWC right zone 0.09 m diameter, situated between TT 15-20. The rest of column was 0.15 m diameter. Total height of separation zone was 4.6 m. In Fig. 4 ASPEN-HYSYS™ flowsheet is presented.

3.3. Results & discussions

Flowsheet in Fig. 4 presents an acceptable solution to proposed problem.
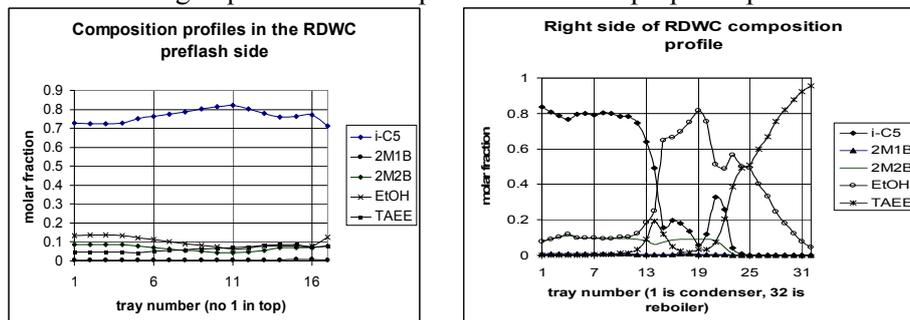
Figure 5. Liquid phase composition profiles in the RDWC

Product streams show good separation for targeted compounds (distillate 86% mol i-C_5, side stream 82.7% mol EtOH and bottom stream 80% mol TAEE). Isoamylenes to TAEE conversion was 80.6%. Of course, further purification of products can be designed in other units. Maximum operating temperature in reaction zone was 70 ^{o}C at 2.5 bars. Composition profiles in RDWC upper, right and bottom zones are presented in Fig. 5 showing targeting of separation objectives. Ethanol composition presented strong variation only in dividing wall right side neighbourhood, with maximum in that region. TAEE was progressively accumulating in RDWC bottoms.

4. Conclusions and Future Work

The methodology presented in this paper proves to be applicable to solve reactive-separation problems using RDWC. CAPE instruments used were satisfactory and allow process engineer to investigate easily such complex type problems. The case study illustrated the methodology allowing to obtain acceptable solutions for TAEE synthesis in industrial conditions, using RDWC. It was recommended to place the reaction zone as close as possible to the prefractionator top and to have column feed below reaction zone. The quality of results was limited by the hypothesis introduced in model building. The authors had foreseen additional studies to optimise RDWC topology for increasing TAEE product purity and to increase the accuracy of the model.

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