

Modeling and simulation the process in a reactive dividing wall column for gasoline additive TAME synthesis in the oil refinery

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Tertiary ethers, as tert-amyl-methyl-ether (TAME), are formed in reactions between alcohols and alkenes and are used in reformulated gasoline as ecologic octane-enhancing agents. Catalytic distillation (CD), involving reaction and separation in the same unit, is possible and beneficial when both volatility of reactants is close each other, but quite different from the volatility of products, and the conversion is limited by chemical equilibrium. The reaction takes place on the surface and/or in the pores of the catalyst grains (e.g. cationic exchange resin amberlyst) in an excess of alcohols (1.1 or 1.2 the ratio between numbers of alcohol moles and isoamylenes). Fully thermal coupling design in a single column shell, the dividing wall column, is a very attractive solution for energy savings and for benefits both in term of reducing capital cost and operation costs. Operation of such arrangement involves very careful solutions (Mueller et al, 2004). This contribution aims to present a methodology to modelling and simulation of a dividing wall column to perform the separation and recirculation of unreacted alcohol and isoamylenes. Rigorous simulation was performed with ASPEN HYSYS[®]. The solution proposed is attractive from industrial point of view.

1. Introduction

Tert-Amyl-Methyl-Ether (TAME) is an oxygenated additive for gasolines. TAME is currently catalytically produced in the liquid phase by the reaction of isoamylenes 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B) and methanol (MeOH). TAME can be practically generated by the direct treating of the raw light gasoline with alcohol, in specific reaction conditions of temperature and pressure in the presence of acidic ion exchange resin catalyst as Amberlyst type. There are three simultaneous equilibrium reactions in the formation and splitting of TAME: the two etherification reactions and the isomerisation between isoamylenes:



These etherification reactions are typically chemical equilibrium limited and face challenges with product purification. They are carried out commercially using either large excess of one of the reactants, or by removing one of the products continuously in a reactive distillation column (RDC).

In this work, the possibility to operate the reactive distillation process in a dividing wall column (DWC) apparatus for TAME synthesis, using ion exchange resin Amberlyst 35, as catalyst, was studied using process simulator ASPEN-HYSYS. The main objectives in choosing of this operation is to get a high isoamylene-to-TAME conversion and a high purity of TAME product and also to recover and recirculate the excess of reactant MeOH.

2. Reaction Kinetics and thermodynamics

Main reactions for TAME synthesis were presented above. Keeping for the reaction zone certain operation conditions, secondary reactions can be avoided (e.g. intermolecular dehydration of MeOH, isoamylene hydrolysis). In this study we used a kinetic model published by Bumbac et al (2007), valid for Amberlyst 35 cationit as catalyst, and for the operating temperature in the interval 40 – 90°C and adequate adapted for using in ASPEN-HYSYS simulator.

Table 1. Kinetic model used

Reaction Rate Expression		Arrhenius parameters	
$v_{R1} = \frac{k_1(a_{2M1B} \cdot a_{MeOH} - a_{TAME}/K_1)}{(1 + K_{MeOH} \cdot a_{MeOH})^2}$		$k_1 = A_1 \cdot \exp(-Z \cdot E_1)$	
		$k_2 = A_2 \cdot \exp(-Z \cdot E_2)$	
$v_{R2} = \frac{k_2(a_{2M2B} \cdot a_{MeOH} - a_{TAME}/K_2)}{(1 + K_{MeOH} \cdot a_{MeOH})^2}$		$k_3 = A_3 \cdot \exp(-Z \cdot E_3)$	
		$K_{MeOH} = A \cdot \exp(Z \cdot E)$	
$v_{R3} = \frac{k_3(a_{2M1B} - a_{2M2B}/K_3)}{1 + K_{MeOH} \cdot a_{MeOH}}$		$Z = \frac{1}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right)$	
Parameters	$mole/(g_{cat,dry} \cdot h)$	Parameters	$J/mole$
A ₁	95.817	E ₁	45671
A ₂	0.22319	E ₂	40613
A ₃	5.9341	E ₃	65030
A	23.485	E	22853
T _m = 330 K; R = 8.314 J/(mole K)			

The kinetic model includes the chemical transformation and also the mass transfer (reaction components diffusion). The thermodynamic model is mentioned in the same source. A synthetic presentation of kinetic model is presented in Tables 1 and 2. The

mole fractions of the feeding mixture used in the simulated process scheme were: 0.6437 - isopentane (i-C₅), 0.0661 - 2M1B, 0.0756 - 2M2B, 0.0000 – TAME and 0.2146 – MeOH. Due to the MeOH presence in the liquid phase of hydrocarbon components mixture, the system shows strong non-ideal properties. The property package used to calculate the liquid activities of the considered components is based on NRTL model.

Table 2. Equilibrium constants data (Zang et al., 1997)

$$\ln K_i = \lambda_{1,i} + \frac{\lambda_{2,i}}{T} + \lambda_{3,i} \cdot \ln T + \lambda_{4,i} \cdot T + \lambda_{5,i} \cdot T^2 + \lambda_{6,i} \cdot T^3, \quad i = 1, 2, 3$$

Reaction	$\lambda_{1,i}$	$\lambda_{2,i}$	$\lambda_{3,i}$	$\lambda_{4,i}$	$\lambda_{5,i}$	$\lambda_{6,i}$
1	-39.065	5018.61	4.6866	0.00773	-2.635	1.547
2	-34.798	3918.02	3.9168	0.01293	-3.121	1.805
3	-4.159	1100.69	0.7698	-0.00521	-0.4865	0.258

3. Methodology for simulation

Analysis of RCM (built in ASPEN-DISTIL™) (Doherty and Malone, 2001) to find promising was used in process topology synthesis. Flowsheet simulation of RDWC is not very easy with commercial software (as ASPEN-HYSYS™) due to difficulties to adapt existing modules to needed topology. 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. 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. RDWC topology presented in Fig.1 could be in principle a candidate process structure to produce at industrial scale TAME (Bumbac et al, 2006). 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°C and 80°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 NRTL 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: TAME-MeOH-i-C₅, TAME-MeOH-2M1B and TAME-MeOH-2M2B to underline stable-instable-saddle nodes in these systems (Fig.2).

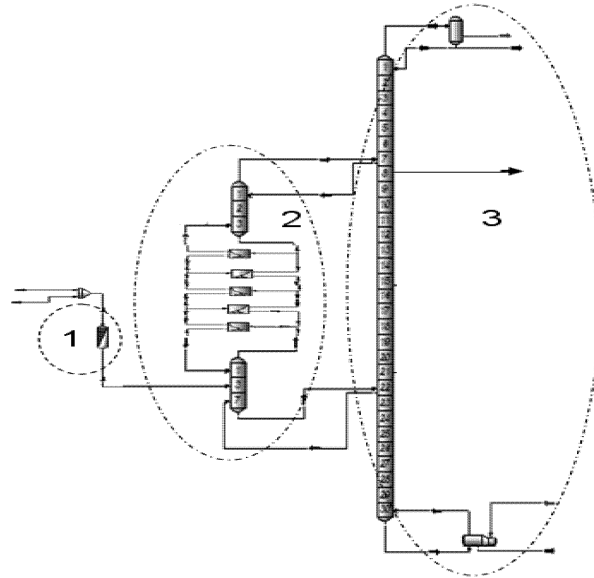


Figure 1 ASPEN-HYSYS flowsheet scheme for RDWC

Analysis of RCM indicated TAME as stable node, so TAME can be separated in bottoms. i-C₅, as saddle node, can be obtained as side product and binary azeotrope of MeOH - i-C₅ mixture as instable node, can be obtained as top product in RDWC.

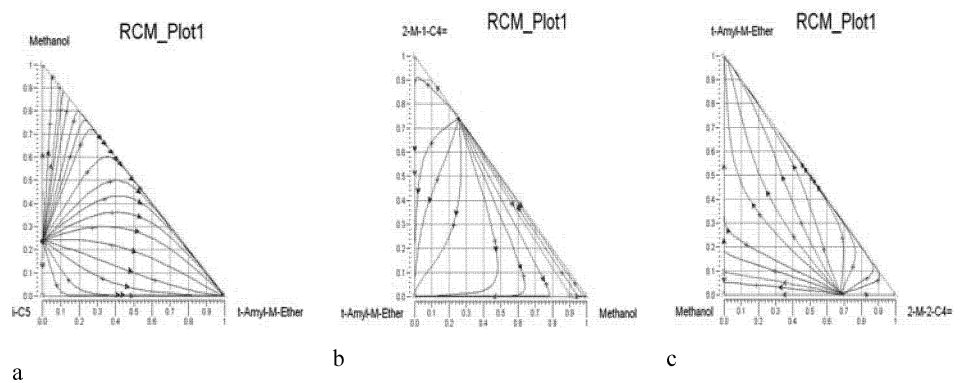


Figure 2 Residue curve maps for mixture components

ASPEN-DISTIL™ suggested topology for RDWC: 15 theoretical trays in pre-fractionator, and 30 theoretical trays (without reboiler and condenser) in right side of RDWC wall, and other detail as presented in Fig. 1

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. 3 which includes also reactive zone as BCM unit

Finally the prefractionator was equivalent to 15 theoretical trays (TT) and the rest of the column was 30 TT (without reboiler). 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 m³ catalyst.

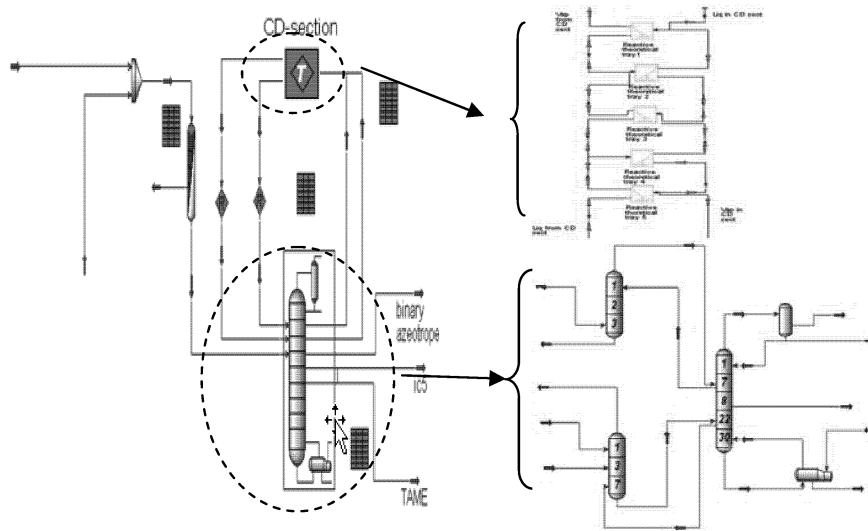


Figure 3. ASPEN HYSYS process flowsheet for TAME synthesis in RDWC

Similar calculations for separation zones were performed obtaining: prefractionator 0.12 m diameter for packing heights 0.6 m above reactive zone and 1.50 m below reactive zone, RDWC right zone 0.1 m diameter, situated between TT 7-22. The rest of column was 0.12 m diameter. Total height of separation zone was 3.8 m. In Fig. 4 ASPEN-HYSYS™ flowsheet is presented.

4. Results & discussions

Flowsheet in Fig. 4 presents an acceptable solution to proposed problem.

Product streams show good separation for targeted compounds (distillate 72% mol i-C, 27.3% MeOH and 0.7% isoamylenes), side stream 93.2% mol i-C5 and bottom stream 99.9% mol TAME). Isoamylenes to TAME conversion was 90.6%. Of course, further purification of products can be designed in other units. Maximum operating temperature in reaction zone was 70 °C at 2.5 bars.

Composition profiles in RDWC upper, right and bottom zones are presented in Fig. 4 showing targeting of separation objectives. i-C5 composition presented strong variation mainly in dividing wall right side neighbourhood, with maximum in that region. TAME was progressively accumulating in RDWC bottoms.

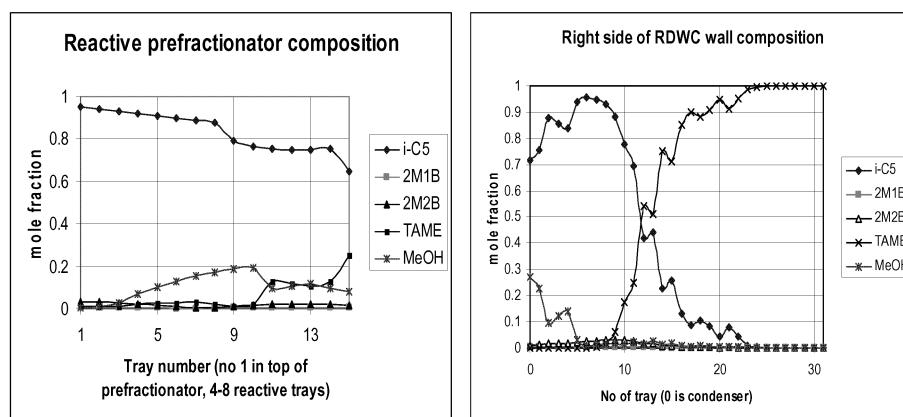


Figure 4. Liquid phase composition profiles in the RDWC

5. 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 TAME 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 TAME product purity and to increase the accuracy of the model.

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7. References

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