REACTIVE DISTILLATION: AN INTERESTING INTENSIFICATION PROCESS TECHNOLOGY

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SUMMARY – Processium, a French company newly implemented in Brazil, is an expert in industrial process engineering. We design, develop and improve processes for chemical, petrochemical and biotech industries. CAPEX and OPEX are key criteria to effectively operate a process. Reactive distillation is a process intensification technology particularly suitable to reduce these costs. We present a design study of an ester hydrolysis process in which different reactive distillation configuration are compared. The process specification on low residual ester content implies a very high rate of conversion. Reactive distillation achieves this goal without recycling and consequently allows the utilization of compact equipments. Thermodynamic and kinetic data are measured and modeled to develop reliable process simulation models. After process optimization, the economic optimum is determined for each process. The next step is experimental validation in a pilot-scale reactive distillation column.

1. INTRODUCTION

Recent economic and environmental considerations lead to technologies development based on process intensification. Reactive distillation is a process intensification technology which combines reaction and distillation. Reactive distillation is particularly adapted for equilibrium-limited reaction such as esterification, and hydrolysis. The works of Jan Harmsen (2007) reports more than 150 industrial scale units. The major benefit of reactive distillation is CAPEX and OPEX reduction. Reduction by 5 can be achieved for methyl acetate production (Eastman's process) (Siirola, 1996 and 1998). Heterogeneous or homogeneous catalysis reaction can be implemented. Heterogeneous catalysis encounters difficulties with catalytic resin installation in the column. Cdtech, Sulzer or IFPEN provide solutions to install catalytic resin in distillation column. Nevertheless, simulate, and predict performance for such kind of device is complex and resin replacement in the column (depending on life time) is expensive. An alternative to heterogeneous catalysis consists in using a homogeneous catalyst and applying a temperature increase by a pressure raise. The benefits of this solution are a classical trays design (bubble cap) and no maintenance for resin replacement.

Esterification and hydrolysis are widely studied in literature, with heterogeneous catalysis (Lai *et al.*, 2007; Hung *et al.*, 2006; Arpornwichanop *et al.,* Huang *et al.*, 2005). The main lack in these

studies is about the technology ensuring resin stability in trays. Assumptions are done about resin fraction in trays, but the device ensuring this fraction is not described, so it is not suitable for industrial design.

Processium develops a hydrolysis process, with reactive distillation. To ensure a robust and cost efficient process a homogeneous catalysis is used. Homogeneous catalysis is achieved by acid formed during the reaction. Pressure, liquid hold-up and number of trays are investigated. Also economic evaluation is done.

2. PROCESS DESCRIPTION

The process flow sheet is given by Figure 1. The feed stream comes from an industrial process and contains ester, alcohol, water and acid (60.9 / 29.1 / 2.2 / 7.7 % in mass). A steam stream feeds the column at the bottom. The reaction (ester + water $\rightarrow$ alcohol + acid) occurs in reactive trays. A rectification section purifies the alcohol. The industrial specifications are: 200 ppm (mass) of ester in acid (acid can contain water) and a purity of 99.5 % (mass) for alcohol. The reaction is catalyzed by acid. In order to increase reaction rate the column is run under pressure. The aim of the study is to determine the optimal process from an economic point of view.
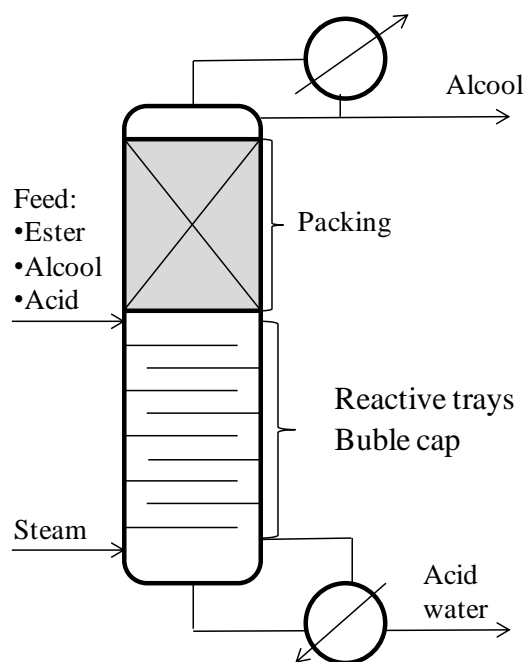

Figure 1 – Process flow sheet

3. THERMODYNAMICS AND KINETICS DATA

3.1. Thermodynamics data

Liquid-vapor equilibria are modeled with NRTL model. Existing equilibrium data are collected from technical literature and Processium databases. Unavailable data are obtained through experimental measurements: e.g. measurements for the quaternary system are carried out in Processium's laboratory. Then NRTL coefficients are fitted with ASPEN Tech software by Processium's thermodynamic experts. The binary ester-alcohol equilibrium is also measured. Figure 2 shows equilibrium data for ester-acid and ester-alcohol mixtures at 4 bar.
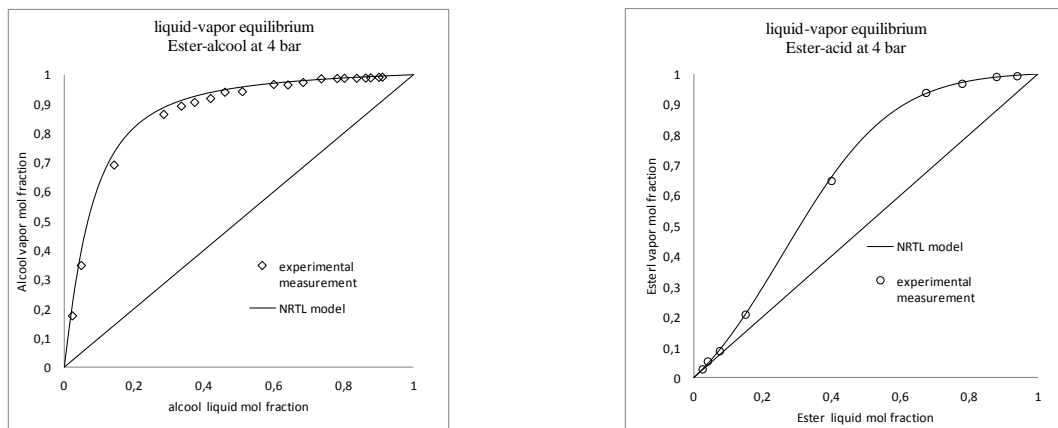

Figure 2 – Liquid-vapor equilibria

3.2 Kinetic data

Kinetic measurements are carried out in Processium's laboratory in a static cell with online analysis. Three temperatures are investigated. The mixture composition is 18.5 % (mol) ester, 74 % water, 7.5 % acid. The kinetic model is:

$$\frac{dC_1}{dt} = -r = -k_1 \exp\left(\frac{-E_a}{R \times T}\right)\left(a_1 a_2 - K_{eq} a_3 a_4\right) a_4^{\alpha} = mol.m^{-3}.s^{-1} \quad (1)$$

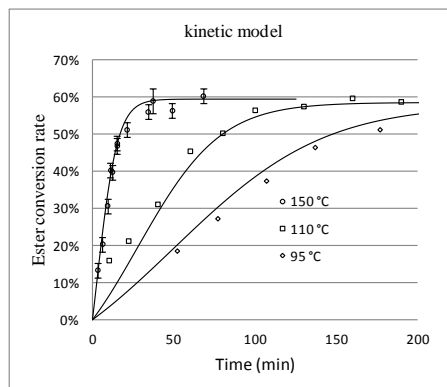$$K_{eq} = \frac{a_1 a_2}{a_3 a_4} \quad (2)$$

Figure 3 – Kinetic model and Static cell

4. METHODOLOGY

Methodology used to identify the best process from an economic point of view is presented in the figure 4.
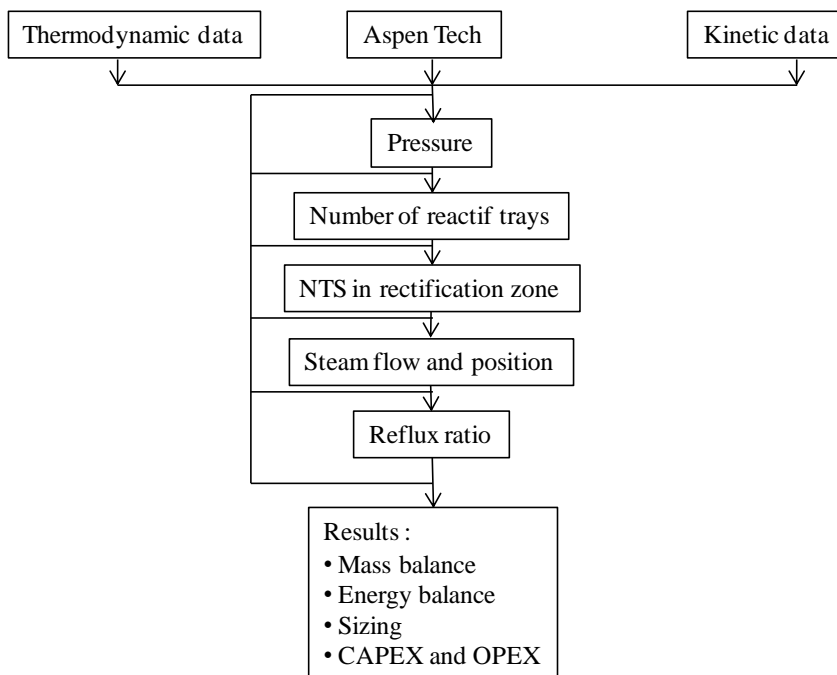

Figure 4 – Methodology

Thermodynamic and kinetic data are implemented in ASPEN. Kinetic rate is calculated via Fortran, because ASPEN does not support the kinetic model. Then simulations are run and design parameters are optimized. The final results are CAPEX and OPEX estimations for each configuration.

5. ASSUMPTIONS

Assumptions for column sizing are as follow. They are collected from suppliers and/or based on Processium expertise in separation technologies

- Thermodynamic and kinetic models are fitted with experimental data;
- Temperature limit at the bottom is fixed;
- Bubble cap trays hold-up is calculated by the supplier. The height of cap is 19 cm;
- Trays efficiency: 50 % (Murphree efficiency);
- CAPEX are estimated with (Chauvel *et al.*, 2001) and CEPCI index. Trays prices are from a quotation;
- Materials are made in stainless steel 316 L;
- The gas load in rectification section is fixed to 1.5 Pa 0.5;
- Steam price is 25 €/t;
- Electricity price is 50 €/MWh.

6. RESULTS

Impact of NTS in rectification section and number of trays in reactive section are presented in figure 5. The pressure at the top is set at 3.6 bar, and the reflux ratio is roughly constant for each case at 3.5. Steam feeds the column in the reboiler. Figure 5 shows that the NTS in rectification section has a big impact on the residual fraction of ester at the bottom. Increase NTS in rectification section leads to alcohol fraction decrease at the column bottom. Thus the reverse reaction (esterification) is very slow. Number of trays in reactive section also impacts the residual fraction of ester. Indeed, liquid hold-up and residence time increase, so the rate of conversion increases.
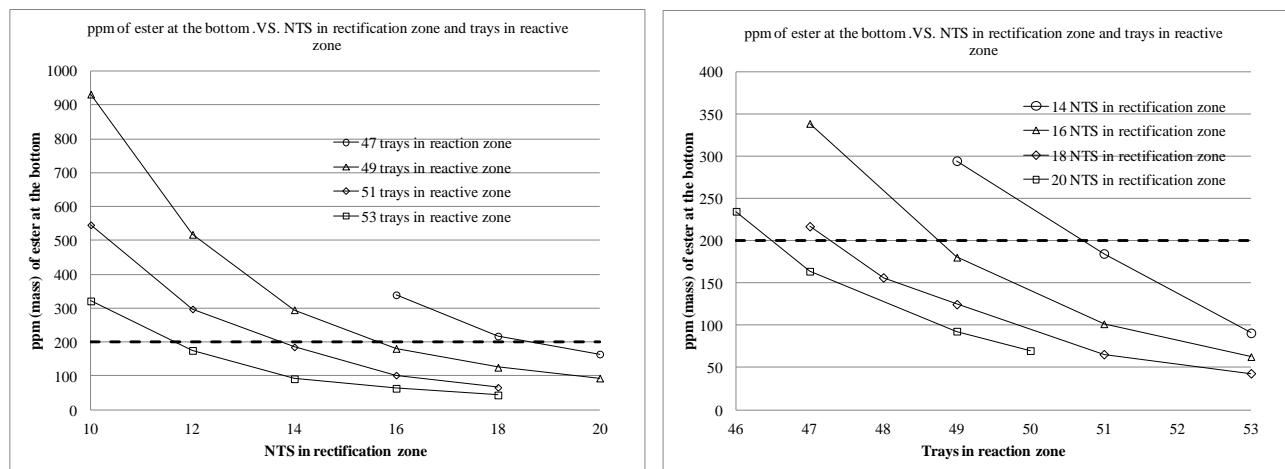

Figure 5 – Results

Figure 5 shows that different configurations lead to the target of 200 ppm of ester at the bottom. Economic evaluation allows to select the best configuration. Results of economic evaluation are

presented in table 1.

Table 1: Economic evaluation

NTS in rectification section	Trays	Residual fraction of ester ppm	CAPEX k€	OPEX k€/an
14	51	185	981	45
16	49	181	974	45
18	48	156	976	44.5
20	47	177	977	44.2
20	50	70	1003	44

Table 1 shows that the CAPEX are roughly identical (reboiler, condenser and column diameter are roughly identical). So, to keep a safety margin, Processium and the industrial company decided to industrialize the design with 20 NTS in rectification section and 50 trays in reactive section.

Simulations and sizing are also done for an alternative process with a pre-reactor. Pre-reactor is a CSTR (6 m^3), it runs at 8 bar and 150 °C and it converts 34 % of the ester. Pre-reactor leads to reduce reactive trays by 30 % and the height of the column by 25 %. But overall the CAPEX increases by 14 % and OPEX stay constant. So the most efficient process is the reactive distillation.

7. FUTURE WORKS

The next step consists in experimental trials in Processium's laboratory. The aim is to validate the sizing and performances (mass and energy balances). Our reactive distillation is customized to represent the industrial column.

8. CONCLUSION

PROCESSIUM's methodology for sizing a reactive distillation leads to the best configuration selection from an economic point of view. Our methodology consists in several points:

- Thermodynamic measurements and modelisation
- Kinetic measurements and modelisation
- Column simulations, with supplier data for trays
- Optimisation (pressure, reflux, NTS, feed position etc...)
- Economic evaluation
- Sizing validation with experimental trials in our lab
- Industrial implementation

This paper presents an esterification reactive distillation. The simulation result is several designs which reach the target of 200 ppm of ester at the column bottom. The economic evaluation shows that

CAPEX and OPEX are roughly identical for each design. So to keep a safety margin, PROCESSIUM and the industrial company select the design leading to ester fraction minimization at the bottom (70 ppm). The next step of the study is to run trials in Processium's laboratory.

7. NOMENCLATURE

a: activity coefficient
c: volumetric molar concentration [$mol.m^{-3}$]
CAPEX: Capital expenditure
CSTR: Continuous Stirred-Tank Reactor
Ea: activation energy [$J.mol^{-1}$]
k: pre exponential constant
K_{eq}: equilibrium constant
NRTL: Non Random Two Liquids
NTS: number of theoretical stages
OPEX: Operational expenditure
r: reaction rate [$mol.m^{-3}.s^{-1}$]
R: Ideal gas constant [$j.mol^{-1}.K^{-1}$]
t: time [s]
T: Temperature [K]

Greek letter
α: exponent for autocatalysis

Indices:
1: ester
2: water
3: alcohol
4: acid

6. REFERENCES

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