Simulation and Process Integration of Clean Acetone Plant

Mădălina C.Tohăneanu*[a], Valentin Pleşu[a], Petrica Iancu[a], Gheorghe Bumbac[a], Alexandra Elena Bonet Ruiz[b], Jordi Bonet Ruiz[b]

[a]University POLITEHNICA of Bucharest, Centre for Technology Transfer in Process Industries (CTTPI), 1, Gh. Polizu Street, Bldg A, Room A056, RO-011061 Bucharest, România
[b]University of Barcelona, Department of Chemical Engineering, 1, Martí i Franquès Street, 6th Floor, Room 664, E-08028 Barcelona, Spain
pres2014@chim.upb.ro

Acetone is produced worldwide by cumene hydroperoxide process. Alternatively, free of aromatic compounds acetone is obtained by isopropyl alcohol (IPA) dehydrogenation. The feedstock is azeotropic mixture IPA-water (Luyben, 2011). This contribution aims to evaluate process feasibility both in terms of reaction engineering and separation by distillation. Rational use of energy is based on process integration A process flowsheet with better performance is proposed. The dehydrogenation reaction is endothermic with number of moles increase. Higher temperature and decreased IPA partial pressure using inert (water) are favourable. Reaction kinetics in vapour phase is simulated in Aspen HYSYS® with Langmuir-Hinshelwood-Hougen-Watson (LHHW) model, considering both direct reaction and reverse reaction terms, based on experimental data (Lokras, 1970). Such more realistic model is not considered in other papers (Luyben, 2011). The chemical reactor is simulated as an ideal CSTR. High volatile and non-condensable compounds from the cooled reactor effluent are separated into a flash unit. To minimize the loss of acetone in gas stream, an absorption column with water is considered. Possible separation schemes for liquid effluent (consisting of acetone, IPA and water) are evaluated with residual curves maps (RCM) built in SIMULIS® ver.1.3. This system has IPA-water azeotrope, a saddle node. The boundary, separes two distillation regions. Both direct and reverse separation schemes are possible. Two distillation columns are used to separate the components of flash unit bottom stream product and absorbtion column bottom stream product. As designed by RCM, for direct scheme, acetone separates in first column top product, and IPA-water azeotropic mixture separates as second column top product. This is recycled to meet plant feedstock stream. Water separated as second column bottom stream product is partly recycled, after cooling, to the absorption column. To minimise utilities consumption and to synthesize process heat exchangers network (HEN), maximum energy recovery (MER) methodology is used with SPRINT© software. The proposed HEN is included in process flowsheet. Energy saving is 35 % for hot utilities and 37 % for cold utilities, compared to non-integrated scheme.

1. Introduction

Clean acetone is used in pharmaceutical formulations and as solvent for biologic sensitive processes. A new process flowsheet based on IPA dehydrogenation is taken into account. The purpose of this paper is to simulate acetone from IPA process flowsheet. Systematic and realistic modeling, as well as energy savings by process integration, is considered with appropriate computer tools. The idea of the process flowsheet is based on block diagram given by Turton et.al (1998). Substantial improvement is considered both in reaction engineering aspects, and in separation feasibility. Systematic approach based on "onion diagram" is applied to develop the process flowsheet. Realistic reaction kinetic model, based on experimental data is considered. Separation scheme is obtained with RCM diagram, built in SIMULIS® ver.1.3. Process flowsheet data extracted is introduced in SPRINT© for process integration. Grand Composite Curve is used to select utilities. Energy saving solution for HEN synthesis is based on MER methodology.

2. Process Description

The azeotropic fresh feed (0.65 mole fraction IPA-0.35 mole fraction water) and the recycled unreacted mixture IPA/water are mixed feedstock. To reach reactor temperature of 598.15 K a preheat train is used, as the reaction is endothermic. The reactor effluent, containing acetone, hydrogen, water and unreacted IPA is cooled severely and then a flash unit separates phases. The non-condensable gas stream is absorbed with water to recover entrained acetone. With reasonable effort, about 67 % is recovered from gas stream. Absorber bottom stream product and flash unit liquid stream are mixed before the separation section. As indicated by RCM diagram, for direct scheme, the first column separates acetone as top product and the second column separates IPA-water azeotropic mixture as top product. The azeotrope obtained from the second column is recycled. Second column bottom product (water) is partially recycled to absorption column. Keeping in mind physical-chemical processes, more fluid packages are used. For vapor phase processes, as reaction, Peng-Robinson Twu fluid package is used. For liquid phase processes, the nonideality is described with NRTL fluid package. Binary coefficients are given by Aspen HYSYS® data bank.
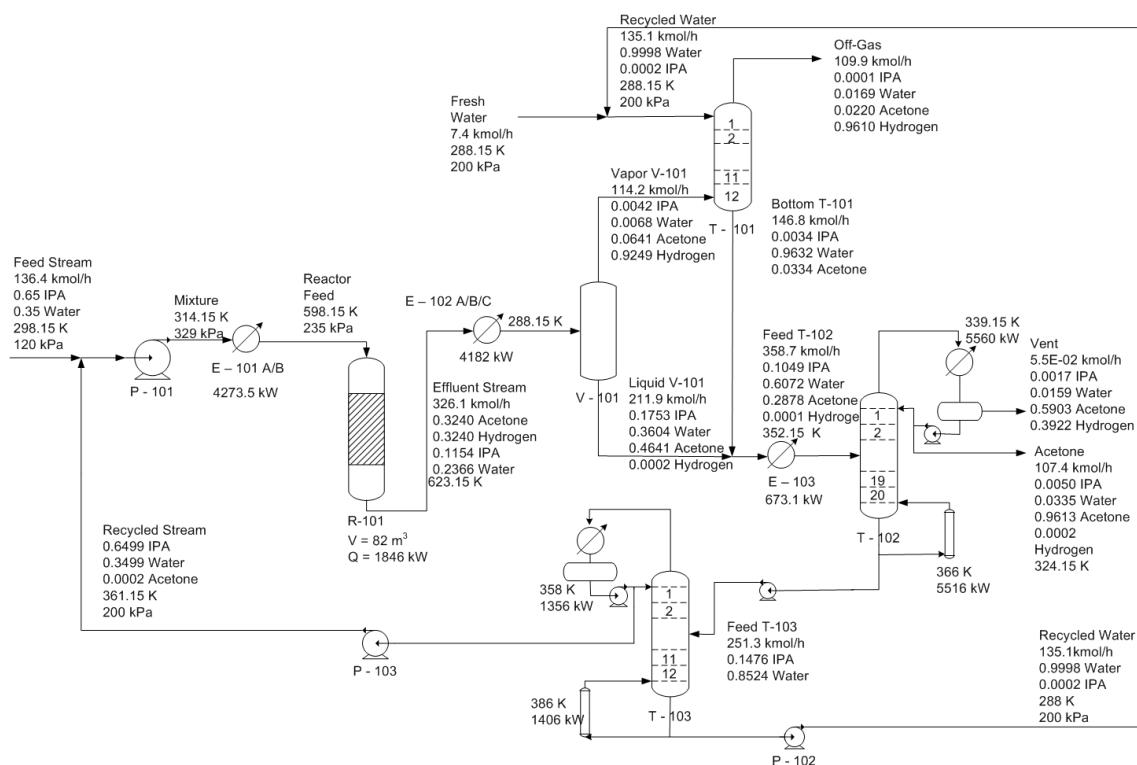

Figure 1. Process flow diagram for acetone production

3. Reaction kinetics

An onion diagram approach involves the reactor as starting point for flowsheet development (Klemeš et al, 2010). The temperature values for the inlet (598.15 K) and outlet (623.15 K) streams are proposed in literature for catalyst optimal operation (Turton et al, 1998). The dehydrogenation reaction is endothermic, with a standard heat of reaction of 56 MJ/kmol. For this reason the reactor heating is needed (heating oil is used). The pressure, assumed to be constant, is 235 kPa. A CSTR reactor model is used to predict the performance of a fluidized-bed reactor for IPA dehydrogenation. Single-pass conversion of 90 % is typically indicated in literature (Turton et al, 1998), under above mentioned conditions. Reactor simulation provides 80 % conversion for the process flowsheet developed in this paper. The reaction is kinetically controlled and occurs over catalyst surface. Reaction kinetics is modeled with (LHHW) model, containing both direct reaction term and reverse reaction term. In Table 1 main catalyst characteristics (SiO_2

supported Cu) from experimental data (Lokras, 1970) are shown. The reaction rate expression and kinetic model parameters are given below (Lokras, 1970):

$$r = \frac{k \cdot \left(C_{IPA} - \dfrac{C_H \cdot C_{AC}}{K_p}\right)}{1 + K_{IPA} \cdot C_{IPA} + K_H \cdot C_H}, \text{ kmol/(m}^3 \cdot \text{h)} \tag{3}$$

$$k = 230.4907 \cdot \exp\left(-\frac{3606.6}{T}\right), \text{ reaction rate constant, kmol/(kg·h)} \tag{4}$$

$$K_{IPA} = 0.1688 \cdot 10^{-2} \cdot \exp\left(\frac{2685.7}{T}\right), \text{ adsorption equilibrium constant for alcohol, m}^3\text{/kmol} \tag{5}$$

$$K_H = 9.9536 \cdot 10^{-12} \cdot \exp\left(\frac{12666.7}{T}\right), \text{ adsorption equilibrium constant for hydrogen, m}^3\text{/kmol} \tag{6}$$

Table 1. Catalyst characteristics

Surface area	31.01 m^2/kg
Apparent density	2481.80 kg/m^3
Bulk density	850.10 kg/m^3

Reactor feedstock and effluent composition are given in Table 2.

Table 2. Reactor feed and effluent stream composition

Composition	Reactor Feed Stream	Effluent Stream
x_{IPA}	0.6500	0.1153
x_{Water}	0.3500	0.2365
x_{AC}	0.0000	0.3240
x_H	0.0000	0.3240

4. Feasibility Thermodynamics of Separation by Distillation

A systematic approach aimed to propose innovative topology for separation scheme is used, based on advanced tools (Garcia Jurado et al, 2013). Detailed analysis of physical behaviour is accomplished. Effluent stream (consisting of acetone, IPA and water) separation in high purity fractions is suppressed by IPA-water azeotropic mixture. Using RCM built in SIMULIS$^®$ possible separation schemes are evaluated. The system presents a saddle node for IPA-water azeotropic mixture. From RCM shape it is obvious that both direct and reverse separation schemes are feasible. Presenting distillation columns position, in Figure 2 and Figure 3 those possibilities are illustrated. However, the direct scheme looks more favorable, because the top product of the first column is a quite pure (96 %) acetone, and the top product of the second column is the azeotropic mixture IPA-water. Consequently, in this paper, the direct scheme is considered for process flowsheet systematic development. The second column, as shown in Figure 2, separates two streams: the azeotropic mixture as top product and water as bottom product.

5. Separation section

5.1 Flash Unit (V-101)
Reactor effluent stream components are separated based on flash vaporisation as volatilities are very different. Flash unit is assumed to be isothermal. The inlet and outlet temperatures are 288.15 K. The pressure assumed constant is 185 kPa. Flash separation is essentially for this case, because the effluent stream is split into two streams: hydrogen enriched gas stream, and acetone enriched liquid stream.

5.2 Absorber unit (T-101)
Inlet streams temperature is 288.15 K. Column pressure is considered constant. To recover entrained acetone from non-condensable gas stream 142.5 kmol/h water is needed. Fresh water flowrate is 7.4 kmol/h, the rest is provided by recycled water from bottoms of second distillation column. Outlet streams composition of flash unit and absorber are given in Table 3.
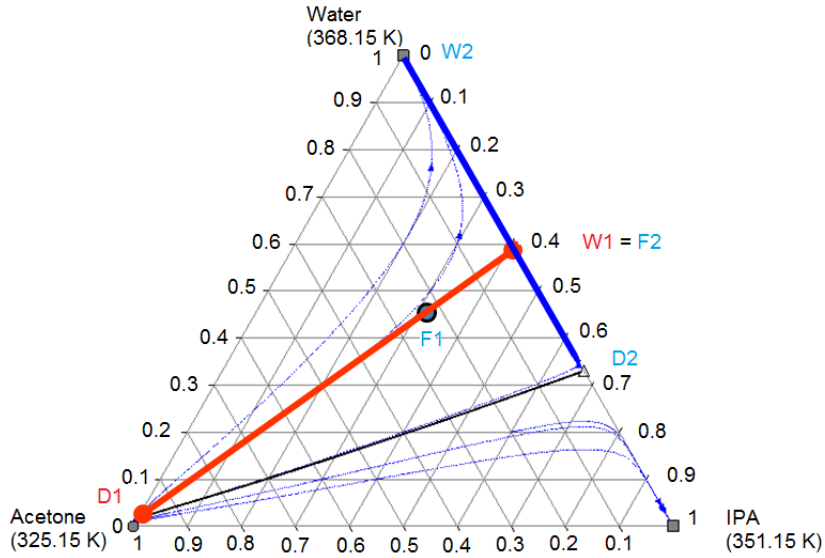
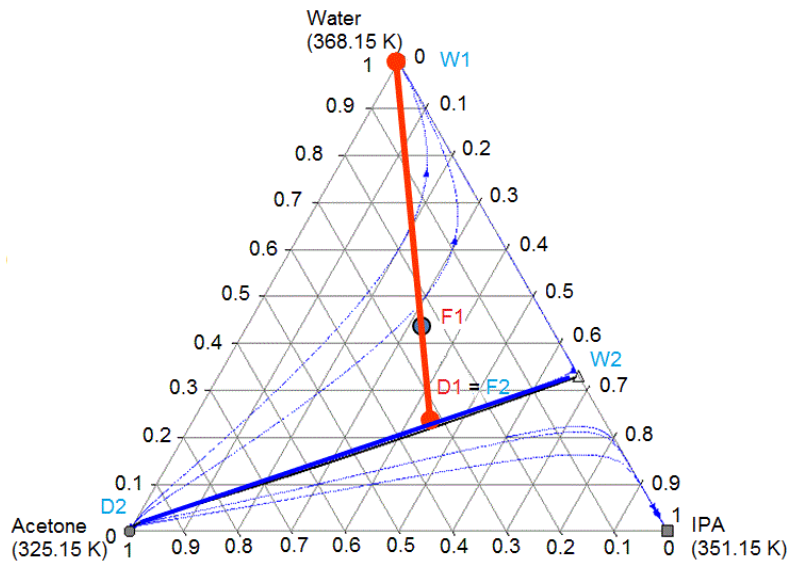Figure 2. Direct separation scheme

Figure 3. Reverse separation scheme

Table 3. Flash unit and absorber outlet streams composition

Composition	Vapor Stream (Flash)	Liquid Stream (Flash)	Off-Gas (Absorber)	Bottom Product (Absorber)
x_{IPA}	0.0042	0.1753	0.0001	0.0034
x_{Water}	0.0068	0.3604	0.0169	0.9632
x_{AC}	0.0641	0.4641	0.0220	0.0334
x_{H}	0.9249	0.0002	0.9610	0.0000

5.3 Distillation columns (T-102 and T-103)

Absorber bottom stream product and flash unit liquid stream are mixed. As resulted from Figure 2, two distillation columns are used to separate the resulted ternary mixture. As the first column has partial

condenser, three specifications are needed: acetone recovery degree in distillate, reflux ratio and hydrogen molar flow in gaseous distillate stream. The column produces 96 % acetone purity, for 50,000 t/y acetone productivity. The bottom product contains IPA (0.1476 mole fraction) and water. This stream is then separated into IPA-water azeotrope and water streams in the second column. Two specifications are needed for the second column : IPA recovery degree in distillate, and distillate composition of water. The second column waste product is partially recycled as absorption column feed.

6. Recycle and Adjust

Recycling contributes to raw materials consumption decrease. Waste products or unreacted feed recycling has become an important element of process sustainability. Two recycle operations are considered: IPA-water azeotropic mixture recycle and water recycle. Water recycle stream is adjusted as target variable meet required specifications. In this case, water recycle stream is set at 135.1 kmol/h and the target variable, the absorption column inlet water, is set at 7.4 kmol/h. Another *Adjust* operation is required on fresh feed stream. Raw material mass flowrate is adjusted to 136.4 kmol/h. Therefore, entire azeotrope amount is recycled.

7. Process Integration

Pinch analysis is used to determine potential for energy saving. Heat exchanger network synthesis is based on MER methodology. The first step is data extraction from non-integrated process flowsheet. Data is introduced in SPRINT©. The minimum difference temperature value is set to 10 K, based on heuristics.
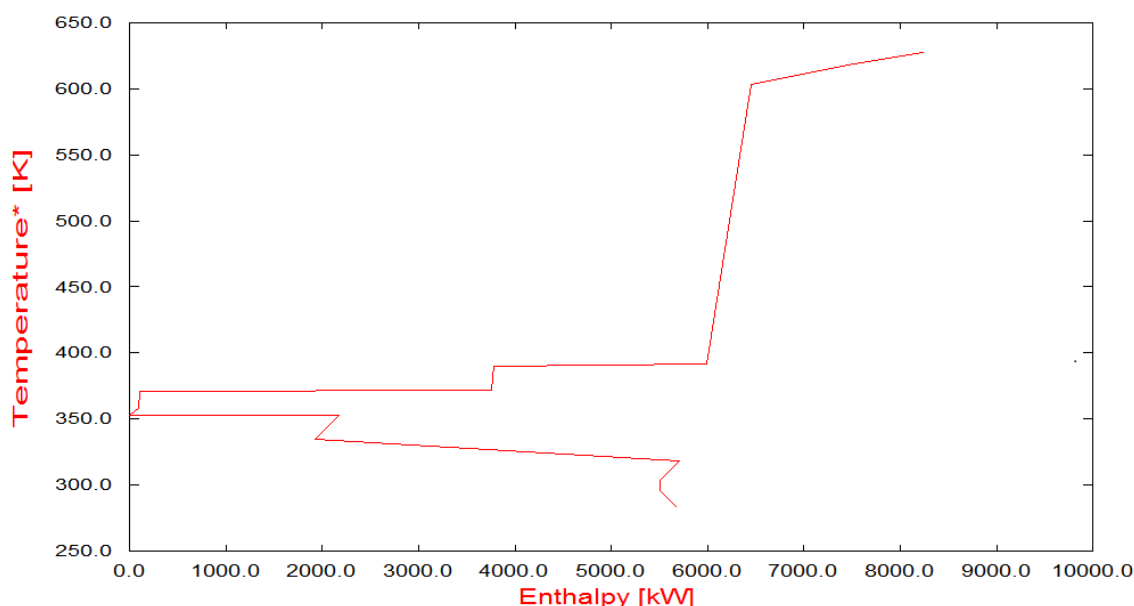

Figure 4. Grand Composite Curve

Utilities selection is based on Grand Composite Curve. Figure 4 illustrates suitable utilities: heating oil and low pressure steam are used as hot utilities, boiling feed water, cooling water and shaft water as cold utilities. New HEN is presented in Figure 5, temperatures are in °C, built for better economic feasibility. The proposed HEN is included in process flowsheet. Table 4 presents utilities consumption in four different situations.

Table 4. Utilities consumption analysis

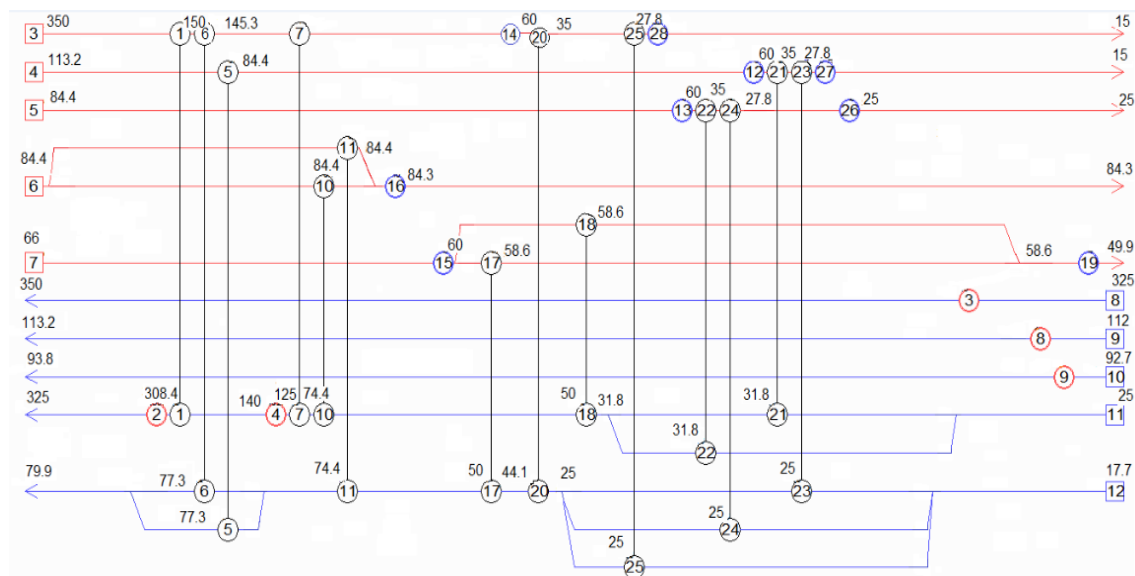| Utility	Minimum consumption	New HEN	Simulation of Integrated Scheme	Simulation of Non-Integrated Scheme
Hot	8.01 MW	8.23 MW	10.26 MW	13.70 MW
Cold	5.45 MW	5.67 MW	7.14 MW	11.38 MW

Figure 5. New heat exchangers network

8. Conclusion

This paper presents the results of isopropanol dehydrogenation process simulation. Study of designing a two-column distillation configuration to separate acetone, IPA and water is accomplished. The proposed scheme (direct scheme) provides good purity acetone. Unreacted feedstock is recycled. Bottom water from second distillation column is recycled to absorption column. Acceptable return amount of recycled water is determined with *Adjust* operation. Energy saving solution is found, based on Pinch analysis. Energy saving is 35 % for hot utilities and 37 % for cold utilities, compared to non-integrated scheme.

Nomenclature
C – molar concentration, kmol/m3
D - distillate product molar flow, kmol/h
F - feed molar flow, kmol/h
Kp - chemical equilibrium constant, kPa
W - waste product molar flow, kmol/h

Subscripts

AC - Acetone
H - Hydrogen

References

Garcia Jurado M.B., Pleşu V., Bonet Ruiz J., Bonet Ruiz A.E., Tuluc A., Llorens Llacuna J., 2013, Simulation of a hybrid reactive extraction unit. Biodiesel synthesis, Chemical Engineering Transactions, 35, 205-210, DOI:10.3303/CET1335034.

Klemeš J., Friedler F., Bulatov I., Varbanov P., 2010, Sustainability in the Process Industry: Integration and Optimization, McGraw-Hill Inc., USA.

Lokras S.S., Deshpande P.K., Kuloor N.R., 1970, Catalytic Dehydrogenation of 2-Propanol to Acetone, Ind. End. Chem. Process Des. Develop., 293-297.

Luyben L.W., 2011, Design and Control of the Acetone Process via Dehydrogenation of 2-Propanol, Ind. Eng. Chem. Res., 50, 1206–1218.

Turton R., Bailie R.C., Whiting W.B., Shaeiwitz J.A., 1998, Analysis, Synthesis and Design of Chemical Processes, 1st ed., Prentice Hall: Upper Saddle River, New Jersey, USA, 789-796.