REACTIVE DISTILLATION FEASIBILITY

FOR METHYL ACETATE SYNTHESIS

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Introduction

Process Intensification nowadays is the most trending concept in chemical technology and engineering field. PI is similar to process improvement also. Briefly, PI consist of novel equipment, processing techniques, process development methods, providing substantial benefits to chemical technologies and manufacturing. PI not only facilitates the process but also provides many advantages to industries other than reducing equipment size. PI can not solve all the problems but can give you a better result than the conventional processes. Still PI is unfolding and researches are going on to improve the existing methods & create new ones. American Institute of Chemical Engineer's (AIChE) Rapid Advancement in Process Intensification Deployment (RAPID) Manufacturing Institute could solve many problems that existed earlier. RAPID has abled to boost the efficiency and productivity of manufacturing industries like pulp and paper, oil and gas, other manufacturing industries.

Define Process Intensification?

Different authors have different definitions of PI. But the common threads that you will in all their definition are innovative process and equipment design, improvement in production and efficiency, reduction in cost and expenses, safer and sustainable technology etc. The well-known researcher in the PI, Stankiewicz and van Gerven introduced four guiding principles, through which most processes have been studied are

- Maximize the effectiveness of intermolecular and intramolecular events
- Provide all molecules with the same processing experience
- Optimize driving force and maximize the specific surface area
- Maximize synergic effect from conventional process

According to them applying all major principles of PI along with one or more approaches enables a completely intensified process.

Many PI equipment is available in which a static mixer is a classic example. And other types are centrifugal contactors, spinning-disk reactor, microchannel reactor, compact heat exchangers, diving-wall column etc. The Dividing-wall column is one type of process intensification which helps in the separation of three-phase systems.

What is the need for Integrate?

Integration of processes is the most promising idea to improve chemical processes. This can be done by combining reaction and separation to the single unit which is called reactive separation or two or more separations can be united to form a hybrid separation unit. These two technologies are highly efficient and also used on an industrial scale.

Reactive separation is a hybrid method in which both reaction and separation are carried out simultaneously. Because of a single unit, it reduses energy use, increases productivity & selectivity, use less solvet for extraction There are various types of reactive separation technologies such as reactive distillation, reactive absorption, reactive adsorption, reactive extraction, reactive crystallization etc. These integrated technologies provide advantages as earlier mentioned with the reduction in the number of equipment and cost of land and capital.

Figure 1. Use of Process Intensification in industries

In this review, we will see some research work that has been done for the synthesis of methyl acetate using a reactive distillation column (RDC). RD has various applications nowadays. It is used widely on a commercial scale to improve their conventional process.

Why Reactive Distillation?

As we see earlier reaction and separation will be carried in a single column, from our b.tech study we know that unit operation and unit process are the key technologies to convert raw materials into products. And Distillation is one of the separation processes used for the components having relative volatility greater than 1.5. RD is not a new concept, before 19s it is been mentioned in various European articles. But not commercialized at that time. In 1980 Eastman Company first synthesized methyl acetate using a reactive distillation column by the heterogeneously catalyzed reaction. RD has also a long story in its evolution. After Eastman Company, it was categorized into non-hybrid RD and hybrid RD. RDC has various sections, non-hybrid RDs don't have separate sections for reaction and separation but hybrid RDs have. Special structured catalytic packing for reactive distillation column has been developed by Sulzer Chemtech. Chemical synthesis which requires recovery of reactants uses RD, liquid-phase homogeneous catalyzed reaction having cation-exchange resin uses RD. It is used in the transesterification synthesis of biodiesel from raw materials like palm oil and mustard oil. But these are not commercialized. Chemical process industries are there which synthesize ethyl, methyl, butyl acetate, hydrolysis of methyl acetate etc. RD has various benefits over the distillation column:

- Increased rate of operation
- Reduced equipment size and energy use, handling being easy
- Fewer by-products hence less waste
- Less heat requirement which reduces degradation

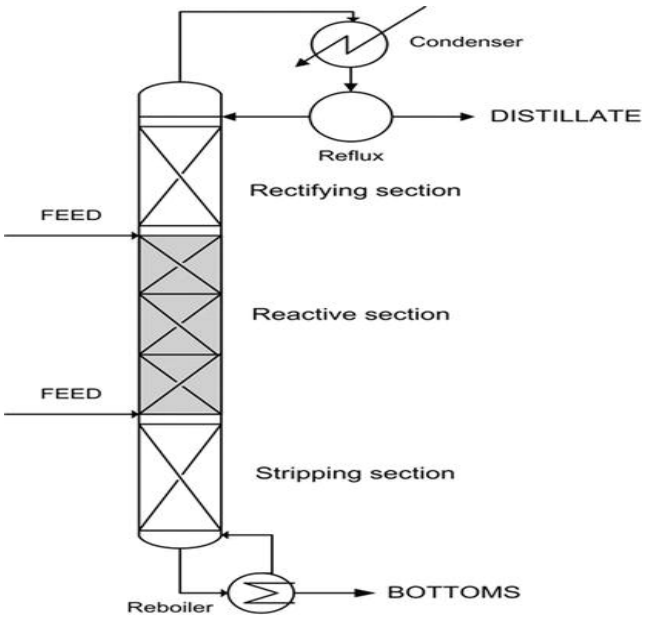
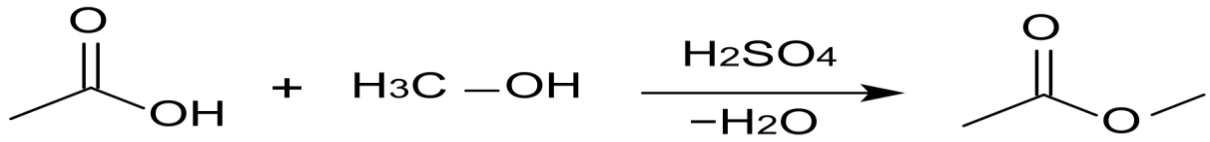


Figure 2. Schematic of reactive distillation column

Esterification Process

The reaction of an organic acid with an alcohol in presence of some catalyst is known as the esterification process. Acetic acid is organic acid and methanol is taken with a sulfuric acid catalyst to synthesize high purity methyl acetate by Eastman Company in 1980. Esters find many applications in our daily life. The most basic one is used in the synthesis of flavour & essence, they have a pleasant fruity odour, used as solvents for gum, fat, oils & resins and also used for plasticizers. RD is used for the esterification process, due to lower yield in conventional methods because of the formation of low boiling azeotropes.



Esterification reaction of acetic and methanol with a sulfuric acid catalyst.

What is Methyl Acetate?

Methyl acetate is also known as methyl ethanoate, Tereton, Devoton. It is a carboxylate ester with a molecular formula of $C_3H_6O_2$. It is a clear, colourless liquid that has a typical ester odour similar to glues and nail polish removers. It is commonly found in fruits like apples, grapes, bananas. It is soluble in alcohols, ketones, glycols, esters, organic solvents and soluble in water with elevated temperature.

Technical Properties of Methyl Acetate

Molecular Formula	CH3COOCH3
Molecular Mass	74.079 $gmol^{-1}$
Flash Point	-10 ^oC
Boiling Point	56.8 ^oC at 760 mm Hg
Melting Point	-98.0 ^oC
Vapour Pressure	170 mm Hg at 20 ^oC
Water Solubility	25% (20 ^oC)
Density	0.932 g/cm^3

Two major processes are there to produce methyl acetate, one is carbonylation in which carbon monoxide substrates are brought together. And another type methanol is heated alongside acetic acid in presence of sulfuric acid.

Methyl acetate has an NFFA rating of 2 and a flammable rating of 3, it causes temporary injury when comes in contact with skin and eye. Always use personal protective equipment while handling the chemical. When contacted with skin or eye immediately wash with water and seek medical attention. MeOAc finds major use in the industrial and commercial field, used in carbonylation to produce acetic anhydride, paints and coating adhesive, lubricants, intermediates, processing aids, solvents in paints, used as a chemical intermediate in the synthesis of chlorophacinone, diphacinone, fenfluramine, methyl cinnamate, methyl cyanoacetate and used in the manufacturing of cellulose adhesive & perfumes. Commercially used for flavouring agent in rum, brandy, whisky, in adhesive, cleaning products, personal care & cosmetics, lubricants, industrial coating, electronics product. The main end markets for this product are the paint, coating, cosmetics, textiles & motor industries.

How to Produce MeOAc?

The conventional process chosen by Eastman Company had one reactor and eight distillation columns in 1980. And the process was to react liquid methanol and liquid acetic acid in the presence of an acidic catalyst to form methyl acetate and water. The rate of reaction depends on temperature, the concentration of catalyst and the concentration of reactants & products. And reactor size is calculated using temperature, catalyst concentration, the ratio of acetic acid to methanol in feed and the required conversion. They aimed to optimize the process, reduce the size of the reactor and improve the yield. Computer simulations were used to implement those ideas, though process complexity was one major drawback at that time. The reaction is

$$CH_3COOH + CH_3OH \leftrightarrow CH_3COOCH_3 + H_2O$$

$$K_e = \frac{X_{MeOAc} * X_{H_2O}}{X_{HOAc} * X_{MeOH}}$$

Reasonably equilibrium constant was independent of temperature and the reaction is reversible also. From the stoichiometric equation, if one of the product feed in an excess amount we can have better conversion and more products we will get. Methyl acetate has higher volatility that's why in vapour-liquid equilibrium the ratio of product to reactant in the vapour is higher. Due to the reversible nature

of reaction in liquid phase reactor if one of the products is removed preferentially then the reaction will shift towards the product side. One more concept applied, flashing two reactants in countercurrent sequence to have better conversion. In conventional process purification of products was a major problem, refining required extractive agents to extract water and methanol. Acetic acid is such an extractive agent, if reactants flow counter currently in a sequence of flashing reactor then it would be beneficial. Two minimum boiling azeotropes are a form of acetic acid & water (5 wt%) at a boiling temperature of 56.1 ^{o}C and methyl acetate & methanol (18 wt%) at a boiling temperature of 53.9 ^{o}C which is near to bp of MeOAc.

Process development – Pilot plant development

For the actual design of a large commercial plant, they came up with a small model to check the desired requirement. They made a piot plant producing 100 lb/h of MeOAc, having 8 in diameter for stripping and reaction section, 6 in diameter for extraction and rectification section with 100 ft high. For the high hold up reverse flow, bubble trays are being used for the reaction & stripping section, pall ring packing is used in the extraction & rectification section. The plant confirm their feasibility and controllability and provided design data and reactor column design & system for the removal of intermediate boiling impurities. Successfully they got the production of methyl acetate with 99.5% MeOAc, 0.33% water, 0.15% MeOH, 0.01% HOAc [5].

Figure 3. Pilot plant reactive distillation column

The pilot plant consists of a total of 10 no. stages including reboiler and condenser, stage 1-2 for stripping, 3-6 for reactive section, 7-8 for rectifying section, packing used is amberlyst 15, acetic acid fed at 6 and methanol at 3 stages with a flow rate of 0.03 L/min at 50 ^{o}C and atmospheric pressure, reflux ratio maintained is 5 [3]. The temperature of rectifying zone lies between 30 & 45 ^{o}C, the stripping section lies between 50 and 59 ^{o}C and the reactive zone 50 and 70 ^{o}C which is favourable for the production of methyl acetate. The reboiler temperature is set at 70 ^{o}C and pressure varies between 249-300 mm Hg. Top stage pressure varies between 108 and 163 mm Hg and 96% composition can be obtained experimentally [3].

Feasibility Evaluation of Reactive Distillation for Methyl Acetate Production

Now, let us calculate the feasibility of reactive distillation for the synthesis of methyl acetate using methanol and acetic acid [6]. We will check the process is technically possible and economical attractive or not. We will through the steps described by Boodhoo and Harvey (Ed.s) in Process Intensification for Green Chemistry (Ch. 9).

RD Technical Constraints-

- The reaction is reversible and heterogeneous catalyzed
- Stoichiometry: 1-mole each of acetic acid and methanol gives 1 ole each MeOAc and water
- Reaction kinetics: $r = k_o e^{\frac{-E}{RT}}\{C_{MeOAc}C_{water} - C_{HOAc}C_{MeOH}/K_e\}$

Step 1. Number of products < 2

The number of products in the reaction is 2. Methyl acetate and water. Hence the condition is not satisfied.

Step 2. Check temperature, $|T_D - T_{R\_main}| < 120\ ^{o}C$

T_D = 30-70 ^{o}C, T_{R_main} = main reaction temperature = 50-70 ^{o}C. Codition is satisfied.

Step 3. Check Critical Properties ($T_{R\_main} < T_c$) & ($P_o < P_c$)

P_o = 1 atm, T_c ~ 200 ^{o}C, P_c = 45 bar, P_o = 1 bar. Condition satisfied. Yes.

Step 4. Is equilibrium constant acceptable? $K_{EQ} >= 0.01$

K_{eq} = 5.2 > 0.01. Satisfied. Yes.

Step 5. Check kinetics of the main reaction. $k_F >= 20\%\ k_R$

k_F = 0.001386 L/ min mol, k_R = 0.0002767 L/ min mol. Condition satisfied. Yes

Step 6. Side reaction present? No.

Step 7. Check relative volatility. $\alpha >= 1.1$

The relative volatility of methyl acetate and methanol is 2.57. MeOAc and acetic acid are easily separable. Yes.

Step 8. Is relative volatility temperature-dependent? Independent of temperature.

Step 9. Check if RD is economically attractive. Yes, it is economical.

Step 10. Are inerts present? No.

Step 11. Check the heat of the reaction. $\Delta H_{vap} > \Delta H_R$

The reaction is exothermic. Heta of vaporization for MeOH is 35.21 KJ/mol, HOAc is 39.1 KJ/mol and MeOAc id 33 KJ/mol.

The heat of the reaction is 29.99 KJ/mol. Yes.

Step 12. $|T_D - T_{R\_main}| < 50\ ^oC$. Yes.

Step 13. Production rate higher than 0.5-1 KTPA.

Production of pilot-scale RD is 100 lb/h. It is around 390 KTPA on a small scale. So it is possible to manufacture greater than 1 KTPA. Yes.

Hence reactive distillation is technically possible and economically attractive also.

Conclusion

PI does have an exact definition to understand, it is a vast subject to study and research. US patent has more than 500 publications in reactive distillation till 1999 and this number now may have increased to above 6 to 7 hundred. PI in simple words to improve the existing process and design new technologies to maximize the yield with a safer and sustainable process. Then we looked at integrating the reaction and separation process into a single unit called reactive distillation which added major benefits to conventional one. Esterification is the first process industrialized by the Eastman Company. Methanol is heated along with the acetic acid in the acidic catalyzed process to form methyl acetate. Synthesis has been done using the pilot plant to get 100 lb/h of product and composition of 99.5% MeOAc. For the feasibility evaluation, reaction validated all conditions for the deployment of the reactive column. The process is carried out at 50-70 ^oC and at atmospheric temperature. High purity methyl acetate is synthesized to greater yield using a reactive distillation column.

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