Journal of Basic and Applied Engineering Research
Print ISSN: 2350-0077; Online ISSN: 2350-0255; Volume 1, Number 13; October-December 2014 pp. 20-23

http://www.krishisanskriti.org/jbaer.html

Dynamic Behavior of TAEE Synthesis Process in Membrane Assisted Reactive Distillation

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Abstract: *Octane number is an expression for the antiknock property of a gasoline which can be increased by adding a certain percentage of oxygenates. Tertiary Amyl Ethyl Ether is an excellent oxygenate of ether family because of its non carcinogenic nature and availability of raw material as the byproduct of other industrial processes. Reactive distillation is a technique in which chemical reaction and distillation are integrated into a single unit which is explored as an energy efficient and cost effective technique. Thus TAEE is synthesized in reactive distillation column. However, the yield of TAEE as found from reactive distillation column is further improved by taking side streams withdraw to a pervoporation unit. The composition obtained using this novel module is found to be 62%. The integration of reaction and separation into single unit makes the process highly nonlinear hence we have explored a novel technique of applying dynamic control for a combine module of pervoporation with RDC using PID controller.*

1. INTRODUCTION

The octane number of gasoline can be increased by adding a certain percentage of oxygenates such as Methyl tertiary-butyl ether, Ethyl tertiary-butyl ether, Tertiary amyl methyl ether, or Tertiary amyl ethyl ether. Oxygenated chemical compounds contain oxygen as a part of their chemical structure.

Among the various ethers present in literature as fuel oxygenators, it was observed that MTBE can pollute underground waste [1]. The production of higher tertiary ethers such as tert-amyl methyl ether (TAME) and tert-amyl ethyl ether (TAEE) have been present interest to replace MTBE [2-5]. TAEE is excellent blending component due to its low volatility, high octane number and they do not contain aromatics and olefins. So the use of TAEE as environmental friendly and economic oxygenates is increasing in recent years. TAEE is more favorable choice compared to TAME as one of the reactant ethanol can be derived renewably from agricultural product such as sugarcane and potatoes while the other reactant TAA is a main component in fuel oil is a byproduct of fermentation process for ethanol production, and can be alternative reactant instead of iso-amylenes. Therefore the synthesis of TAEE from TAA and ethanol can be promising route as both reactants are derived from renewable resources [6]. Most of the previous work considered the production of TAEE from iso-amylenes and ethanol in a reactive distillation. (Linnekoski etal 1997)[7-9]. Reactive distillation is a technique in which chemical reaction and distillation are integrated into a single apparatus. Various researchers have explored RDC to produce TAEE and have done its simulation using Aspen plus process simulator [10].In a certain paper author summarized the kinetic study and the modeling equations were developed which were implemented in Matlab to see the behavior of the process. Simulation was also performed in HYSYS and the gap remained was to find the optimal design and optimization of the process[11] In the cases in which the reactive distillation technology is applied, the reactants are firstly transformed up to a concentration close to the equilibrium one, in one or more pre-reactors [12] . The yield of TAEE as found from RD column is further improved by taking a side stream withdraw, to a pervoporation unit consisting of a zeolite membrane tube, thus a novel technique of combined pervoporation module and a reactive distillation column has been explored. Under suitable conditions, the pervoporation tests have shown higher than 99.9% water mole fraction in permeate. The experimental study at standard conditions has shown a gain of 10% in tert-amyl ethyl ether (TAEE) yield when the zeolite membrane tube was inserted inside the distillation column. Further improvements in TAEE yield were realized when the feed location was separated and the time factor or the reflux ratios was increased [13]. A cellulose derivative membrane (30 wt. % cellulose acetate butyrate (CAB) combined with 70 wt. % cellulose acetate propionate (CAP)) was prepared, and its properties were evaluated by the pervoporation separation of mixtures of ethyl tert-butyl ether (ETBE) and ethanol [14].

The experimental conditions must be carefully selected, because TAEE decomposition and a high by-products formation occurred if high pressures or D/F ratios were used during the column operation [15].

Some methods are applied to determine the optimal column configuration and operating conditions for the synthesis of tert-amyl ethyl ether from ethanol and iso-amylenes [16]; the temperature–composition cascade strategy was proposed to control the reactive distillation (RD) process for the synthesis of tert-amyl ethyl ether. In those optimized conditions, the proposed control strategy was introduced to manage the RD process by changing the sensitive variables. From results of the dynamic simulation, it can be known that the proposed strategy was able to handle disturbances while maintain the tert-amyl ethyl ether product purity and quickly reach the steady state.

In this research work we have explored a novel technique of applying dynamic control for a combine module of pervoporation with RDC using process simulator. The yield of TAEE in a side stream withdraw to the pervoporation unit is improved using PID controller. The Ziegler Nicolas tuning rule is used to estimate the actual behavior of system.

2. SIMULATION

In Aspen Plus to study the behavior of any process, the first step is to make the flow sheet converged in steady state so as to define and obtain the characteristic of the process. Once this flow sheet is converged, then it is imported to Aspen plus Dynamics so as to control and study nonlinearity of the system.

Simulation of TAEE etherification is carried out in Aspen Plus. Firstly, the reactive distillation column is simulated by the module, Radfrac, using NRTL property method. For this purpose, ASPEN PLUS requires the specification of components, property method, feed conditions (flow rate, composition and thermal state), operating pressure, column configuration (number of stages, feed location, reaction stage, types of condenser and reboiler), two operating parameters, and reaction type. The reaction type can be chosen from kinetic, equilibrium and conversion. The product purity is attaining a highest value at the bottom stage. The operating and feed conditions are shown below in table 1

Table 1: Operating Condition Used In Aspen Plus

PARAMETERS	CHARECTERSTIC	
1.Feed flow rate	TAA	Ethanol
	0.02litre/min	0.02litre/m
2.Feed temperature	50˚C	50˚C
3. Feed Pressure	Atmospheric	
4.Feed Location	Top of reactive zone (segment 6)	Bottom of reactive Zone (Segment 3)
5. Feed location	Middle of reactive zone in case of mixed feed.	
5.Reboiler Duty	1KW	
6.Reflux Ratio	1	
7.Packing	• Rectifying & Stripping Section: KATAPAK-S • Reactive Section: Amberlyst-15	

Figure below shows the simulation diagram.

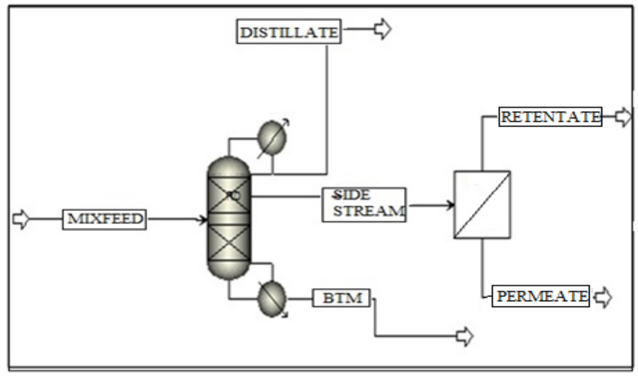

Fig. 2: Schematic Diagram of Steady state simulation in Aspen Plus

3. DYNAMIC SIMULATION

Aspen plus steady state simulation files are indispensable for dynamic simulation. So first steady state simulation is done and these files are exported to Aspen dynamics.

In preparation for exporting the steady-state flow sheet into Aspen Dynamics, all equipment is needed to be sized. Column diameters are calculated by Aspen tray sizing. The converged steady state flow sheet with degree of freedom zero is imported to Aspen plus dynamics. Three PID controllers are added additionally to this flow sheet which is pressure controller, reflux level controller, and composition controller for maximizing the purity of side stream withdrawn from RD to the pervoporation unit.

The equation below shows the PID algorithm as discussed in the previous PID Control section.

$$u(t) = K_c((\varepsilon(t)) + (1/T_i \int \varepsilon(t) dt) + (T_d d(\varepsilon(t))))$$

u is the control signal

ε is the difference between the current value and the set point.

K_c is the gain for a proportional controller.

τ_i is the parameter that scales the integral controller.

τ_d is the parameter that scales the derivative controller.

t is the time taken for error measurement.

The sluggish behavior of these controllers is studied with respect to time. For pressure control of the column the condenser duty is taken as variable, for reflux level controller flow rate of reflux is taken as the variable, and for composition control of the TAEE from pervoporation unit in the retentate, side stream flow rate is taken as the control variable. The simulation diagram is shown in figure 3.

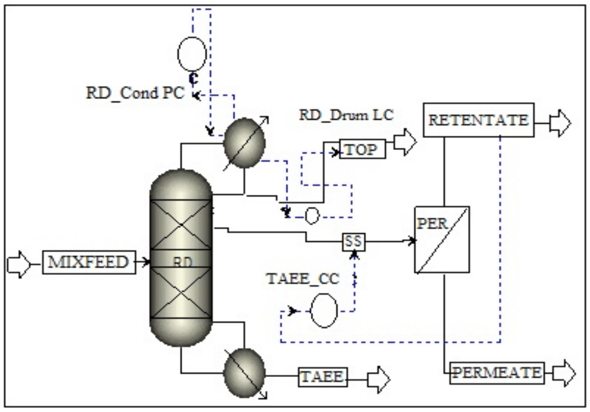

Fig. 3: Control Configuration using Dynamic Control

The Ziegler-Nichols closed-loop tuning method allows you to use the ultimate gain value, K_u, and the ultimate period of oscillation, P_u, to calculate K_c .

It is a simple method of tuning PID controllers and can be refined to give better approximations of the controller. The tuning parameters are tabulated in table II.

Table 2: ZN Tuning Parameters

	K_c	T_I	T_D
P	$K_u/2$		
PI	$K_u/2.2$	$P_u/1.2$	
PID	$K_u/1.7$	$P_u/2$	$P_u/8$

4. RESULT AND DISCUSSION

4.1 Simulation using Aspen Plus

The highest purity of TAEE was achieved at the bottom of column of RDC and is found to be 62%. However a side stream has been withdrawn at the eight plate and is taken to a pervoporation unit where the retentate stream is found to have a TAEE purity of 60% and permeate consist of water.

The temperature and composition profile of RDC using Process simulator is shown in figure 4 and figure 5.

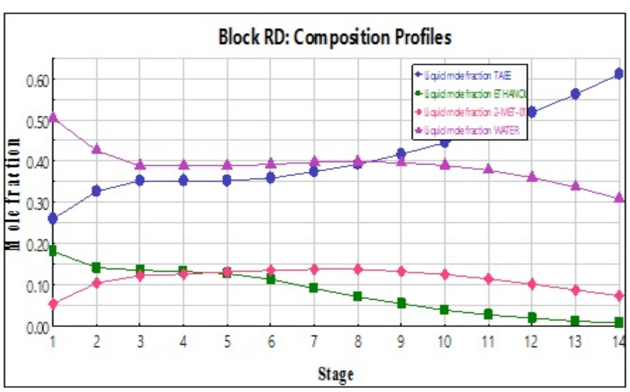

Fig. 4: Composition profile in Reactive distillation column using Aspen Plus

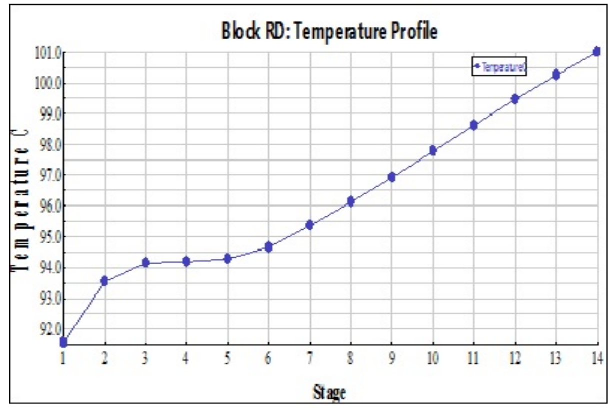

Fig. 4: Temperature profile in Reactive distillation column using Aspen Plus

4.2 Dynamic Control

The converged flow sheet is exported to Aspen plus dynamics and the resultant graph are shown for condenser pressure control with corresponding duty, reflux level control to the corresponding reflux rate and composition control of TAEE in retentate for the side stream flow rate from RD to pervoporation unit. It is observed that for the purity control in retentate, making a change in the side stream flow rate, results into a very small error leading to the overshoot.

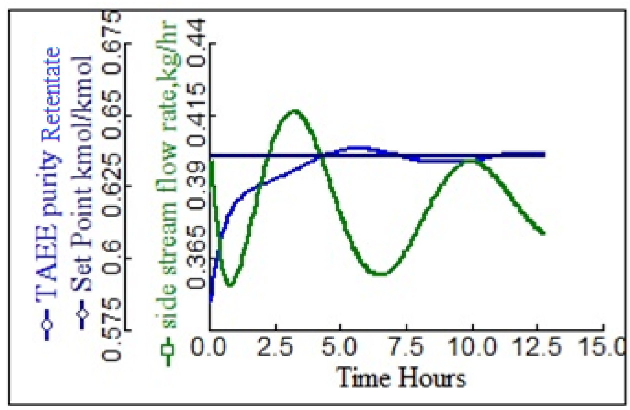

Fig. 5: Composition control using PID controller

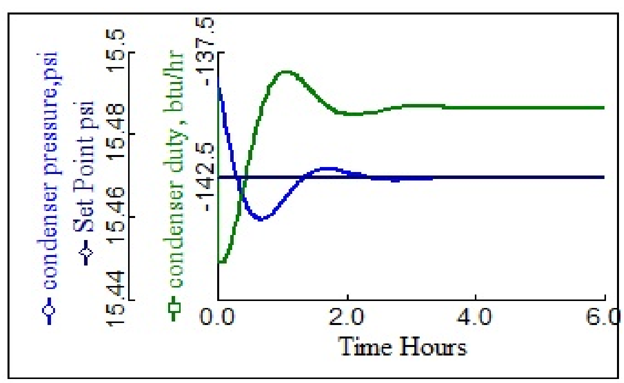

Fig. 6: Condenser pressure control

Further on repeatedly making large changes to overshoot the target purity, the output i.e. Side stream flow rate oscillates around the set point in a constantly decaying sinusoidal manner. Therefore the system is stable.

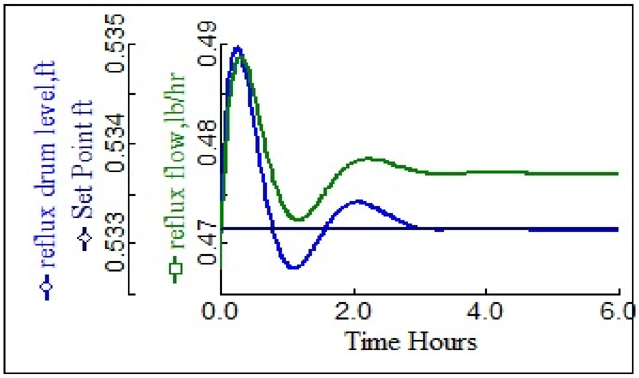

Fig. 7: Reflux drum level control

Controller parameters obtained using Z-N tuning relation is found to be K_U=0.832561, P_U=49.4129. Based on these values the ultimate gain and ultimate period are tabulated in table 3.

Table 3: ZN Tuning Output Results

PID	Kc	ꚍI	ꚍD
	0.4898	24.70645	6.17661

5. COSNCLUSION

Membrane assisted reactive distillation is a novel technique of improving the yield of product in the case of synthesis of tert amyl ethyl ether, an oxygenate of ether family. It was observed that application of this novel technique improves the purity of a side stream up to 60% apart from the top product of 60% purity. Thus we are getting more product of almost same purity thus higher increased conversion efficiency. Further we have studied the time varying behavior of this module and controlled the most critical parameters i.e, condenser pressure, reflux drum level, TAEE purity using PID controllers. Zeigler Nicolas tuning rule is implemented to calculate the ultimate gain and ultimate period of the system. It was observed that time to steady state for this system as per the graphs obtained is around 7 hours, while the integral time and derivative time is 24.7 and 6.17 respectively.

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