

# Equilibrium and Rate Based Simulation of MTBE Reactive Distillation Column

Debashish Panda, Kannan A.

**Abstract**—Equilibrium and rate based models have been applied in the simulation of methyl tertiary-butyl ether (MTBE) synthesis through reactive distillation. Temperature and composition profiles were compared for both the models and found that both the profiles trends, though qualitatively similar are significantly different quantitatively. In the rate based method (RBM), multicomponent mass transfer coefficients have been incorporated to describe interphase mass transfer. MTBE mole fraction in the bottom stream is found to be 0.9914 in the Equilibrium Model (EQM) and only 0.9904 for RBM when the same column configuration was preserved. The individual tray efficiencies were incorporated in the EQM and simulations were carried out. Dynamic simulation have been also carried out for the two column configurations and compared.

**Keywords**—Aspen Plus, equilibrium stage model, methyl tertiary-butyl ether, rate based model.

## I. INTRODUCTION

**I**N reactive distillation reaction and separation takes place in a single column. Taylor and Krishna [1] described the following advantages for reactive distillation: (i) savings on cost (capital and operation) in separation column. (ii) Conversion of reactants may be enhanced to nearly 100% thereby minimizing recycle costs. Hence excess amounts of a reactant may be avoided to push the equilibrium towards the product formation side. (iii) Since stoichiometric quantities of the reactants are used and removal of products from the reactive zone, there by chances of having side reactions are less. Hence, by products formation is minimized and selectivity is achieved. Similar examples are found in the synthesis of propylene oxide from propylene chlorohydrin [2] and alkylation of benzene to cumene [3]. (iv) Catalyst requirements are considerably lower for the same degree of conversion. (v) Heat integration benefits may be accrued. Reboiler heat duty can be reduced by using heat of reaction as heat of vaporization.

Methyl tertiary butyl ether is a compound used as anti-knocking agent in petroleum industry. The production of MTBE is carried out in reactive distillation [4]. There are two mathematical models available to simulate a reactive distillation column: equilibrium stage model (EQM) and rate based model (RBM). In EQM, vapor and liquid assumes to be in thermodynamic equilibrium in a stage. In RBM, mass transfer takes place across the interphase of vapor and liquid. Hence the bulk fluid phases are not in equilibrium. Rate based

reactive distillation has been described and compared with equilibrium model [5]-[7]. Correlations for pressure drop, mass transfer, liquid and vapor hold up are needed to simulate a reactive distillation column in RBM. Physical properties like diffusivity, viscosity, interfacial area, thermal conductivity, surface tension, mass and heat transfer coefficient are the extra parameters are required in the RBM approach. EQM and RBM have been compared for ethyl acetate synthesis [8]. It has been found that in both models, temperature and composition profiles were quite different. Ethyl acetate reactive distillation has been studied with different types of model in PROFILER simulator [9]. Three types of modeling were carried out such as (i) the rate-based model with Maxwell- Stefan equations; (ii) the rate-based model with effective diffusivities; and (iii) an extended equilibrium approach taking account of the reaction kinetics were studied. The packing section was divided into a number of stages. As the number of these stages increased, simulation results were more accurate at the cost of longer computational times. The final conversions and product purities were almost similar for both equilibrium and rate based models but the temperature and composition profiles were different. Both models were compared with experimental data and it was concluded that the rate based model with Maxwell-Stefan equation with fine discretization strategy matched the column profile better than the equilibrium model.

Dynamic simulation provides information about the transient behavior of process variables with time. Since reaction and separation combine in a single column, there is a reduction of manipulated as well as controlled variable in the process. Considerable literature is available for the dynamic simulation of equilibrium model [10]-[13]. Composition or temperature can be controlled in a reactive distillation to maintain the product purity. Dynamic simulation of methyl acetate reactive distillation has been studied. Two temperature control configurations were used and it was concluded that this configuration was effective for feed flow and composition disturbance rejection [10]. In some cases two temperature control configuration did not work properly [11]. Therefore three temperature controllers were used to maintain the product purity. Composition controller has the disadvantage over temperature controller due to large dead time. Dynamic equilibrium stage model simulation of ETBE reactive distillation has been studied [12]. Effect of input variables on product purity and conversion of reactant has been discussed. The interaction between phase and chemical equilibria showed unusual problems in dynamic mode. The location of tray for controlling temperature also has an effect on product purity.

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Dynamic simulation of MTBE and TAME reactive distillation has been carried out [13]. If the reactive part is controlled properly, then rest of the plant can be handled easily.

Dynamic simulation of reactive distillation has been studied reasonably extensively in the literature using equilibrium based model as well as rate based model [14]-[16]. Dynamic simulation of MTBE has been studied by Lin and Douglas [17]. Step tests on methanol flow and reboiler heat duty were performed and the MTBE purity in bottom stream was analyzed. MTBE reactive distillation through EQ and NEQ models has been compared in the dynamic mode [18]. Disturbances in feed and bottom flow rate were given to column and it was found that NEQ model is more sensitive compared to EQ model.

Literature is scarce on the steady state and dynamic aspects of actual reactive distillation columns which are more frequently encountered in industries. Equilibrium is not attained in the trays and hence the dynamic and control studies have to recognize this fact in addition to the more widely studied steady state approach. The column settings and controller parameters for EQM model may not apply for the RBM approach. The objective of this paper is to compare the equilibrium stage and rate based model for MTBE reactive distillation column. Temperature and liquid composition profiles are studied for both the models. Dynamic simulation of equilibrium stage model and equivalent rate based model has been also carried out.

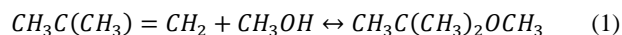
## II. COLUMN CONFIGURATION

The column configuration chosen for the current work has been studied previously by Jacobs and Krishna [19]. Methanol and isobutene reacts to form MTBE. N-butene acts as inert. UNIQUAC and Redlich-Kwong thermodynamic properties are selected for the liquid and vapor phases respectively.

TABLE I  
BINARY INTERACTION PARAMETER [20]

Components	Binary Parameters	
	$b_{ij}$	$b_{ji}$
MEOH-IB	35.38	-706.34
MEOH-MTBE	88.04	-468.76
IB-MTBE	-52.2	24.63
MEOH-NB	35.38	-706.34
NB-MTBE	-52.2	24.63

Binary interaction parameter is also specified and given in Table I [20]. The reaction is given below:



Reaction kinetics has been taken from and Rehfiinger and Hoffmann [21] and is given below:

$$r_{forward} = 3.67 \times 10^{12} \times \exp\left(\frac{-92440}{RT}\right) \frac{X_{IB}}{X_{MEOH}} \quad (2)$$

$$r_{backward} = 2.67 \times 10^{17} \times \exp\left(\frac{-134454}{RT}\right) \frac{X_{IB}}{X_{MEOH}^2} \quad (3)$$

TABLE II  
COLUMN AND FEED SPECIFICATION

Column Configuration		Feed Configuration		
Bottom flow rate kmol/hr	709.2	Parameter	Methanol	Butene
Reflux ratio	7	Feed stage	10	11
Condenser pressure (atm)	11	Feed temperature	320	350
Pressure Drop (atm)	1.5	Feed pressure (atm)	13	13
Catalyst hold up (Kg)	8000	Mole flow kmol/hr	775.8	1976.4
Number of trays	24	Composition		
Number of reactive trays	8	methanol	1	
Reboiler heat duty cal/sec	8694344	isobutene		0.36
Condenser heat duty cal/sec	11609849	n-butene		0.64
Boil up ratio	10	Distillate composition		
Tray type	Sieve	Methanol		0.05367
Column diameter (meter)	6.54	C4H8-5		0.00013
Flooding correlation	Fair	C4H8-1		0.946
Tray spacing (meter)	0.6096	MTBE		0
No. of passes	1	Bottom composition		
Deck thickness (mm)	3.25	Methanol		0.0008
Hole diameter (meter)	0.0127	C4H8-5		0.0001
Sieve area to active area ratio	0.012	C4H8-1		0.007

A reactive distillation for MTBE process is shown in Fig. 1. Column and feed specifications are shown in Table II. The column consists of 17 stages including a total condenser and a partial reboiler. The column consists of three zones: rectification section from stage 2-3, in which separation of inert (n-butene) takes place, reactive zone (4-11) in which methanol and isobutene react to form MTBE, stripping section (12-16) in which separation of products from reactant takes place. In the production of MTBE, the mole fraction of MTBE should be high in the bottom stream.

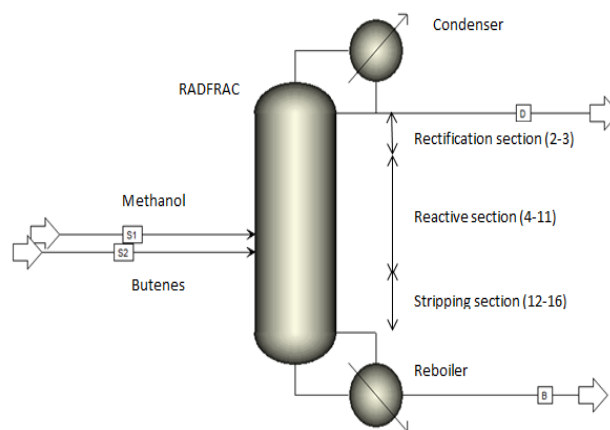


Fig. 1 Column configuration for MTBE reactive distillation process

In EQM model, with proper initial guesses, the simulation converges to a high mole fraction of MTBE in the bottom product. Next step is to simulate MTBE process using the RBM approach. In this model some extra parameters like

column hardware and tray specifications are required. Column diameter is measured from maximum vapor velocity inside the column. Glitsch flooding correlation is used for calculation of column diameter. Column diameter of 6.5 meter is used. Tray spacing of 0.6096 meter is found appropriate.

### III. RESULTS AND DISCUSSIONS

Steady state simulation in RBM and EQ model is carried out and column profiles are compared. Total number of stages, feed stages and column and feed specifications are kept constant for both the models. Temperature profiles for EQ and rate based models is shown in Fig. 2.

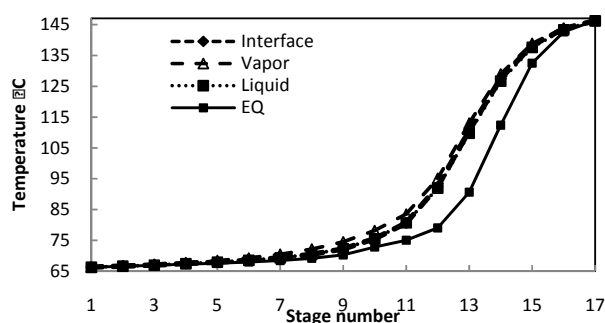


Fig. 2 Temperature profiles for rate based and EQ model

The temperature at the condenser and reboiler is 66.3 and 146.3°C. Temperature differences between the two models for condenser and reboiler are not significant. Temperature difference between the two models is more in the stripping section when compared to the reactive and rectification zones. Temperature rises more rapidly in stripping zone due to the presence of heavy component. RBM approach shows a higher temperature in the stripping section when compared to the EQM approach. Reaction of MTBE is exothermic in nature. Low temperature in the reactive section favors the forward reaction and high conversion of isobutene is attained at this condition. In the reactive section, EQ model show fewer temperatures when compared to the RBM approach. Therefore MTBE mole fraction in the bottom stream is lesser in the RBM approach. If the temperature is more in the reactive zone, decomposition of MTBE starts which lead to low value of MTBE mole fraction in the bottom stream.

Total Number of Stages	$X_{MTBE}$
17	0.990459
18	0.991108
19	0.991291
20	0.99136
21	0.99139
22	0.991406
23	0.991417
24	0.9914385

In rate based model MTBE product purity is less when compared to equilibrium model.

TABLE IV  
COMPARISON OF EQ AND NEQ MODEL

	17EQ		24NEQ	
	Distillate	Bottom	Distillate	Bottom
Methanol	0.053	0.0012	0.053	0.001
C4H8-5	8.09E-05	0.0005	0.0002	0.0001
C4H8-1	0.946	0.0069	0.946	0.0074
MTBE	5.70E-06	0.9914	8.99E-05	0.9914
Total flow kmol/hr	1339.863	709.2	1339.751	709.2
Reboiler heat duty (kW)	36351		36405.5	
Condenser duty (kW)	48612.8		48613	

Fig. 3 shows the liquid composition profile for both EQ and rate based models for 17 stages column. The composition trends for both the models are similar but the values are different in stripping zone. In the distillate n-butene is the major product. MTBE mole fraction increases due to the separation of reactants in the bottom stream.

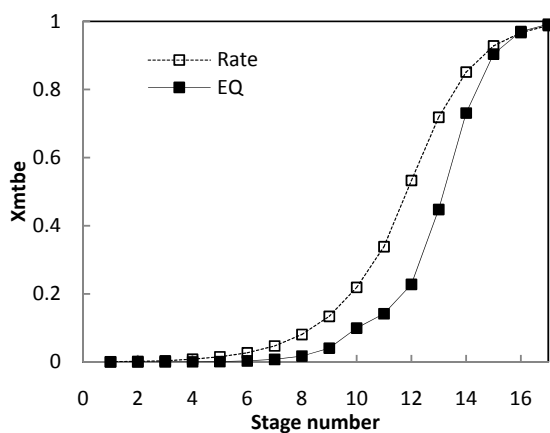
Therefore in order to enhance the MTBE mole fraction in the bottom stream in rate based model, the number of trays in stripping section is increased. The results are given in Table III. Separation of MTBE from the reactants and inert takes place effectively by enhancing the number of stages in stripping section. The MTBE purity is 0.9914 at total number of stages 24 in rate based model. The MTBE purity in 17 stages EQ model is also 0.9914. Heat duty for condenser is also same for both the models at 48913 kW. Due to the extra trays in the 24 stages column, reboiler heat duty is 0.15% more compared to 17 stages column (36351 kW and 36405.5 kW for 17 stages EQ and 24 stages rate based model). Bottom and distillate compositions for the 17 stage EQ and 24 stages RBM is presented in Table IV. In the distillate n-butene and methanol composition are 0.946 and 0.0536 for both the models. The molar flow rate in distillate and bottom streams are also same (1339.8 and 709.2 kmol/hr). Therefore it can be assumed that 17 stages EQ model is comparable with 24 stages rate based model.

### IV. DYNAMIC SIMULATION

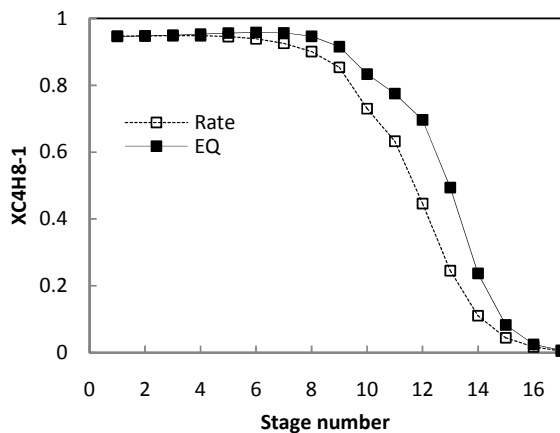
Rate based simulations are not compatible in Aspen Dynamics. In order to compare the dynamics of equilibrium and rate based model, either tray or Murphree component efficiency may be incorporated in the simulation. In that case rate based approach is replaced by an equivalent equilibrium based model. The model incorporated with individual stage efficiencies may be termed as the 24 staged non-equilibrium model (24NEQ). Here individual tray efficiencies from the rate based model are incorporated in the equilibrium model and exported to Aspen Dynamics. Control configuration is shown in Fig. 4. Two PI controllers are used to control the feed flow rate of methanol and butene. The manipulated variables for feed flow controllers are the valve openings in those streams. A pressure controller is installed in the condenser in order to keep the column pressure constant by manipulating heat duty on it. Two Proportional level controllers are installed at the condenser and reboiler. The manipulated variables are flow rate of distillate and bottom

stream respectively. To maintain reflux ratio constant a multiplier is used. Temperature controller is used in the stripping zone to maintain the temperature profile in the

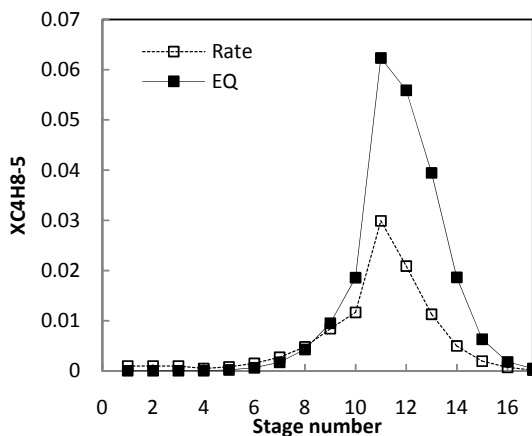
column. Dead time of 1min. is installed for temperature controller. Temperature controller is used at 14<sup>th</sup> and 21<sup>st</sup> tray for 17stages EQM and 24 stages NEQ model respectively.



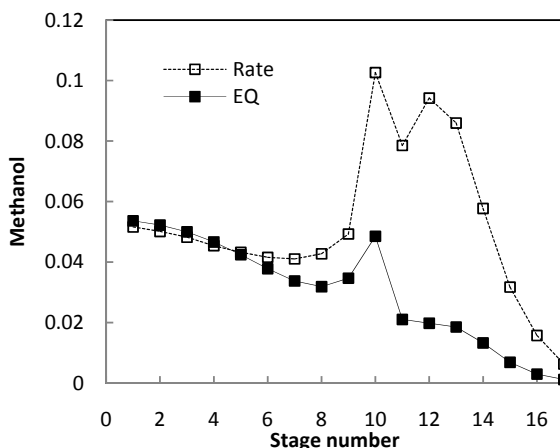
(a) MTBE component in liquid phase



(b) C<sub>4</sub>H<sub>8</sub>-1 component in liquid phase



(c) C<sub>4</sub>H<sub>8</sub>-5 in liquid phase



(d) Methanol component in liquid phase

Fig. 3 Liquid composition in column for EQ and RBM

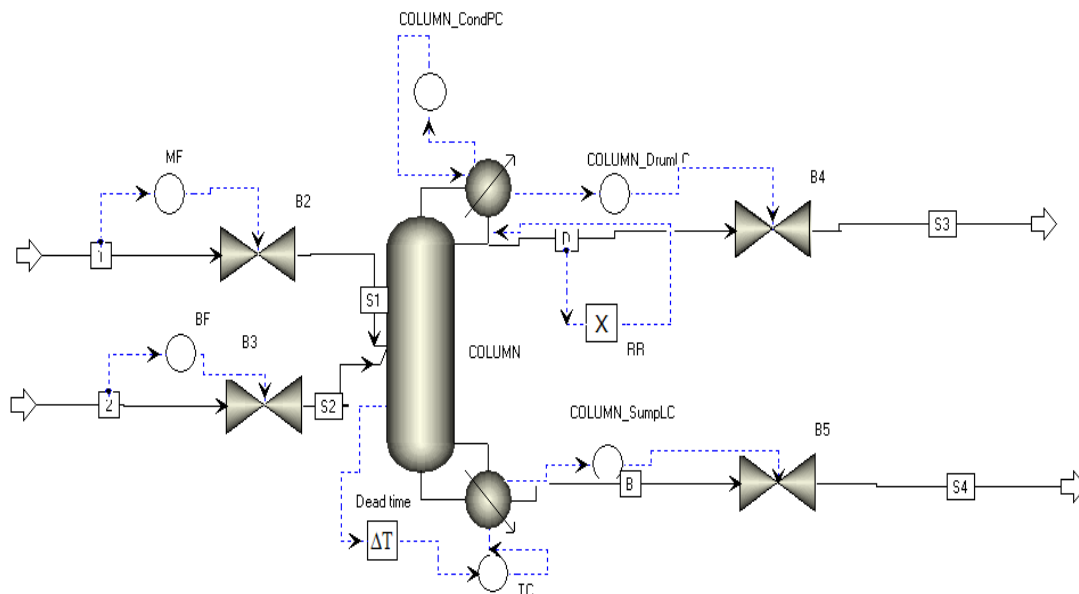


Fig. 4 Temperature control configuration for dynamic simulation

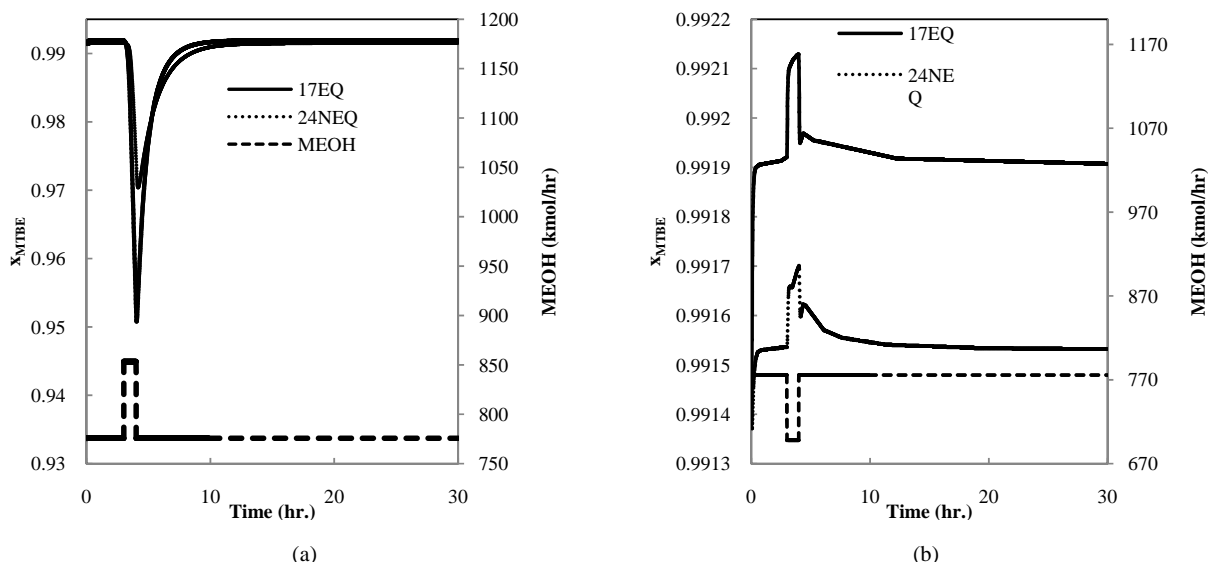


Fig. 5 Effect on MTBE purity: Methanol flow rate step test t=3-4hr (a) +10% (b) -10%

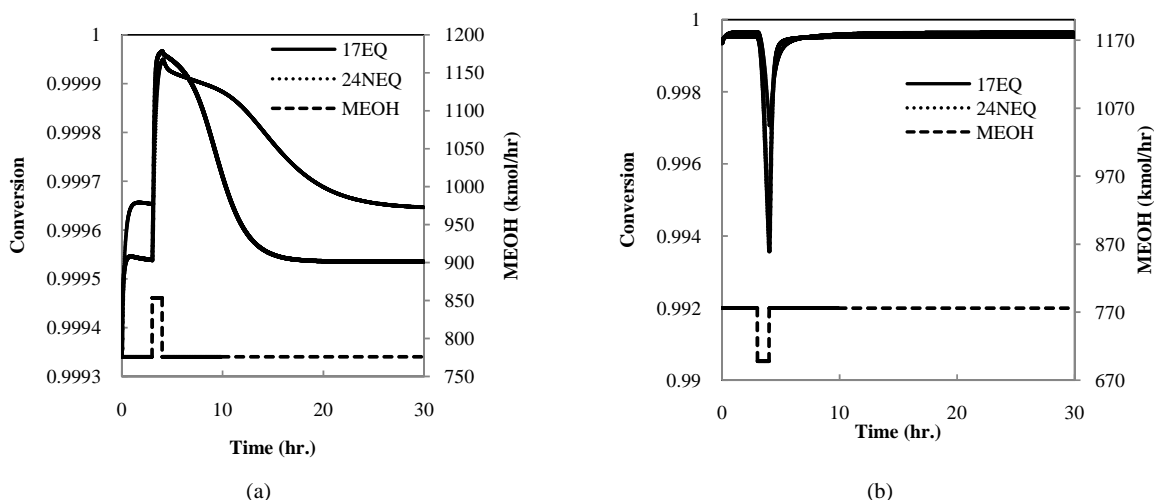


Fig. 6 Effect on isobutene conversion: Methanol flow rate step test  $t=3-4$ hr. (a)+10% (b) -10%

For two level controllers, proportional controllers are used. Controller gain 2 and integral time of 9999 min is used. For pressure controller gain of 20 and integral time of 12 min is used. For feed flow controller gain of 20 and integral time 0.2 works well. However, temperature controller is tuned separately for both 17EQM and 24NEQ configuration and given in Table V. The controllers are tuned with Tyreus-Luyben tuning method. A relay feedback test is run to find out ultimate gain ( $K_u$ ) and ultimate period ( $P_u$ ). From these values controller gain and integral time is calculated as follows:

TABLE V  
CONTROLLER SETTING

	17EQM	24NEQ
Ultimate gain	169.11	412
Ultimate period	1.8	12.6
Controller gain	52.8	130
Integral time	3.96	27.72

The simulation is run until steady state is reached. The column reached steady state in 3 h. At that point methanol flow rate is increased from 775.8 to 853.4 kmol/hr for 60 min. MTBE mole fraction in the bottom stream is shown in Fig. 5 (a). MTBE mole fraction in the bottom stream starts decreasing as methanol flow rate increases in the column. This is due to the imbalance of stoichiometric ratio of reactant. The temperature of the controlled tray remains constant. EQ model shows a faster response compared to NEQ model. This is due to the lower hold up and smaller column height compared to 24 stages column. Nearly 13 h and 17 h are required to bring back the column to its original steady state. Increase in methanol flow rate, decreases the MTBE purity. Similarly methanol flow rate is changed from 775.8 to 698.2 kmol/hr from  $t=3$  h to  $t=4$  h. MTBE purity in this case has been shown in Fig. 5 (b). MTBE purity degradation is less compared to +10% disturbances. In both of the cases (+10%, -10%) of methanol step test, the column is able to come back to its

original steady state. The NEQ model shows a delay in response compared to EQ model. This is due to the large hold up in the column (1850 and 2249 kmol for 17 stages EQ and 24 stages rate based model respectively).

Fig. 6 shows the effect of methanol flow changes on conversion of isobutene. Increase in methanol flow increases the conversion of isobutene. Methanol flow step test is applied after the column has reached the steady state. At  $t=3-4$  h, methanol flow step test is applied for +10% of its base case value. Conversion of isobutene for +10% methanol step test has been shown in Fig. 6 (a). For EQ model, the column can reach its original conversion value in 15 h. For NEQ model, the column need 25 hour of operation to reach the original conversion value. Effect of methanol step test of -10% on conversion of isobutene is shown in Fig. 6 (b).

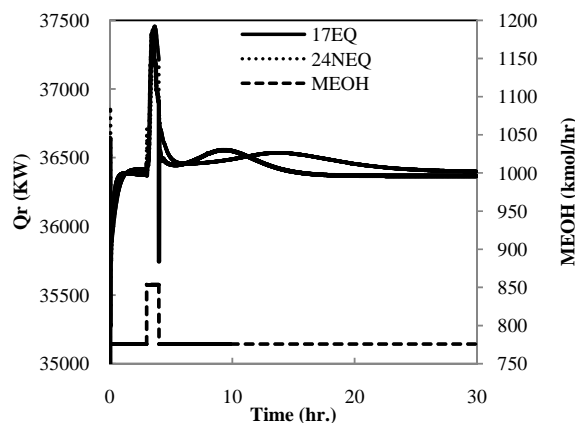


Fig. 7 Effect on reboiler heat duty: Methanol flow rate step test (+10%) at  $t=3-4$ hr

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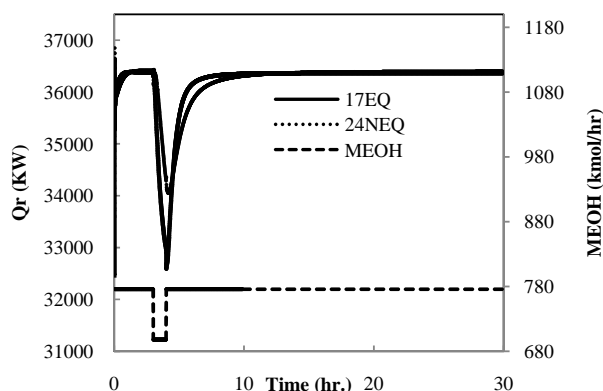


Fig. 8 Effect on reboiler heat duty: Methanol flow rate step test (-10%) at t=3-4hr

As the methanol flow decreases, conversion also decreases. For 17 stages EQ model conversion decreases maximum of 0.55% and for 24 stages 0.25%. The column restores its original conversion value of 99.955 at 8 h and 10 h of operation. Figs. 7, 8 show the effect of methanol flow on reboiler heat duty. Increase in methanol flow shows an increase in reboiler heat duty (Fig. 7). This is due to more amount of liquid comes to the column and hence increases the heat load. After the disturbance is removed, the steady state heat duty is recovered faster in EQ model compared to NEQ model. As the number of stages increases in a column, the height of column also increases. This leads to more delay in response if input disturbances are given. Total holdup also increases for 24 stages NEQ model (2249 kmol) compared to 17stages EQ model (1850 kmol). For +10% increase in methanol flow rate, EQ model reaches the original steady state in 16 h whereas NEQ model reaches in 25 h. For -10% methanol step test, EQ model restores its original reboiler heat duty in 10 h (Fig. 8). For NEQ model column needs 16 hour of operation to restore the same heat duty Therefore it can be concluded that EQ model shows a faster response for reboiler heat duty for disturbance rejection.

## V.CONCLUSION

To reduce operating cost, reactive distillation is a good option when compared to separate distillation and separation columns. Simulation of MTBE reactive distillation has been carried out in rate based model and equilibrium modeling approaches. Temperature profiles is compared for both the models and found that the trend is same but temperature is higher in rate based model. Composition in vapor and liquid phase has been compared and found to be different in the stripping section only. 17 stages EQ model is comparable in terms of MTBE purity in bottom stream with 24 stages rate based model. Two column configurations are studied in dynamic mode and it is found that 17 stages EQ model shows faster response compared to 24 stages NEQ model.

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