

# Analysis of Pervaporation Membrane Batch Reactor for Esterification Reactions

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**Abstract--** In the present study a pervaporation membrane unit made of composite poly vinyl alcohol membrane was integrated with a batch reactor for studying and improving the overall process efficiency. An esterification reaction of salicylic acid with Ethanol in the presence of homogeneous catalyst was performed in the setup. The influence of parameters like reaction time, characteristics of membrane, excess of reactant, water concentration, forward reaction constant and the equilibrium constant on the reactor performance were studied. The reaction was carried out at temperatures between 338 and 345 K. for various initial molar ratios of Ethanol and salicylic acid, ranging from the 1.0 to 8.0. The by-product was removed selectively from reaction mixture by pervaporation. At 345 K almost complete conversion was attained for an initial molar ratio of 8.0 within 10 h. A mathematical model of the system written in terms of operating variables and design parameters was successful in describing the performance of integrated pervaporation system which can now be used in simulation studies.

**Keywords:** Pervaporation, Esterification, Catalysis, Modelling, Membrane

## I. INTRODUCTION

In general there exists equilibrium limitation when dealing with reversible reactions. Because of this thermodynamic limitations we get only up to an equilibrium conversion. To get an extended conversion the reaction should be shifted to product side. This can be achieved by employing operations like reactive distillation, reactive adsorption, reactive extraction, reactive crystallization and membrane separation operations. Now a days, a lot of work is being carried to combine the reaction and separation in one unit so as to improve the yield and in reversible reactions which ultimately reduce the cost of production.

A three step approach has been adopted in this research:

- Selection of reaction system and membrane
- Modeling of membrane-integrated reactors
- Model validation by comparing with experimental results of membrane-integrated reactor.

Although, esterification reactions represent a significant group of reactions commonly found in the pharmaceutical industry, kinetics data on homogeneous esterification of aromatic carboxylic acids are relatively scarce in the literature. The acid-catalyzed esterification of salicylic acid with ethanol was selected to be the model reaction system for this study because the desired ester product, methyl salicylate, is one of the most important esters in the pharmaceutical industry. Commercially, it is widely used as the pain relieving ingredient in liniments. Salicylic acid, one of the reactants in this esterification reaction, is an aromatic carboxylic acid which is less reactive than aliphatic carboxylic acids because of the fact that most aromatic carboxylic acids require longer reaction times and thus have low yield. Latest techniques that can improve process performance can be essentially important. Pervaporation is one of the membrane processes that can be employed for the separation of liquid mixtures that are difficult or unable to separate by conventional methods. The pervaporation process can be considered as a unit operation with significant potential for various types of solutions. In this process, the volatile species in the reaction zone are selectively vaporized through a membrane which acts as a solid extracting phase. One of the potential applications of pervaporation process is to use it for driving an equilibrium-limited reaction. The separation membrane is a permselective barrier that allows selective permeation of the designated component from a liquid mixture. Thus, an idealized membrane reactor or its equivalent that integrates a membrane unit with a batch reactor is expected to improve the conversion of kinetically or thermodynamically limited reactions. The reaction enhancement occurs through controlled removal of one or more product species from reaction zone. Like reactive distillation, the membrane reactor is another technique for achieving conversions above the equilibrium value.

## II. EXPERIMENTAL PROCEDURE:

A batch reactor, the simplest of all membrane reactor configurations, integrated with pervaporation, was selected as the model reactor system.

A mathematical model was also developed for the system and the influence of process parameters like time of reaction, membrane characteristics,  $\omega(S/V_0)$ , excess of reactant, water concentration,  $k_1$ , the forward reaction constant and  $K_e$ , the equilibrium constant on the reactor performance were studied. The model yielded a successful interpretation of the data obtained with membrane integrated reactor. The model has led to a better understanding of the overall process and can be used in predicting desired regimes for the operating parameters.

### III. RESULTS AND DISCUSSION

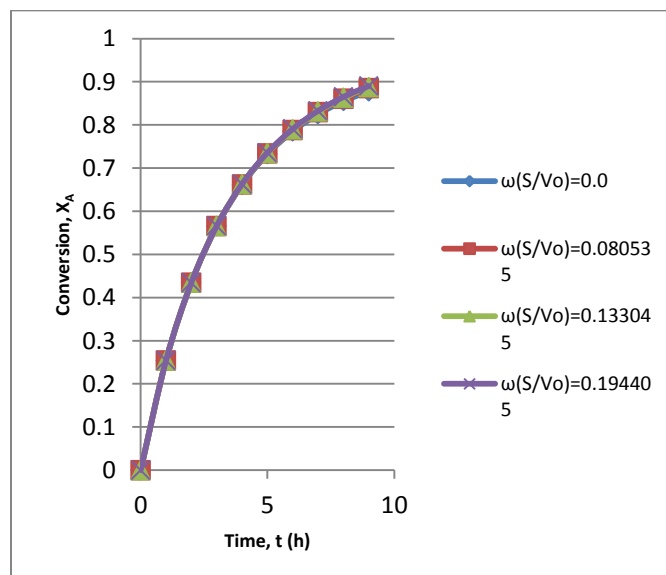
In order to describe, from a theoretical view point, the behavior of the coupling between batch reactor and pervaporation unit, independent kinetics information from the batch reactor of the studied reaction is essential. To validate the model for the pervaporation-coupled batch reactor, the kinetic parameters from the batch studies were incorporated into the model.

#### 1. Conversion as a function of reaction time for different $\omega(S/V_0)$ Values:

Figure 1 is a plot of variation of conversion with time as a function of  $(S/V_0)$  at  $Q_b=5.0$ . As expected with increase of time, the conversion is increasing. Further, one can observe that conversion of membrane reactor can go beyond the equilibrium conversion, which is the maximum conversion that could be obtained. At a given reaction time the higher the value of  $(S/V_0)$ , the higher the conversion. As  $(S/V_0)$  value increased from 0.0 to 0.194405, the conversion increased from 0.87 to 0.89. This is obvious because concentration of water in reactor will be reduced more rapidly when the membrane is more permeable and/or when membrane area per unit reaction volume is larger. For the given case of illustration, the reactor performance approaches the upper limit when  $\omega(S/V_0)=0.194405$ h

**Table 1:**  
Calculated conversion ( $X_a$ ) values for batch esterification when  $Q_b=5.0, K_1=20662 \times 10, v_1=1, y=0, K_c=4.37, C_{a0}=2191$  mol/m,  $T=336$ K and by varying  $(S/V_0)$

TIME t (hr)	$X_a$ for $\omega(S/V_0)$ =0.0	$X_a$ for $\omega(S/V_0)=$ 0.080535	$X_a$ for $\omega(S/V_0)=$ 0.133045	$X_a$ for $\omega(S/V_0)$ =0.1944 05
0	0	0	0	0
1	0.25389	0.25389	0.25389	0.25389
2	0.43443	0.4345	0.43454	0.43459
3	0.56518	0.56553	0.56572	0.56591
4	0.66114	0.66203	0.6625	0.66296
5	0.73223	0.73396	0.73482	0.73564
6	0.78528	0.7881	0.78942	0.79064
7	0.82508	0.82918	0.83102	0.83266
8	0.85505	0.86058	0.86294	0.865
9	0.87769	0.88473	0.88761	0.89006



**Fig. 1:** Calculated conversion ( $X_a$ ) values for batch esterification when  $Q_b=5.0, K_1=20662 \times 10, v_1=1, y=0, K_c=4.37, C_{a0}=2191$  mol/m,  $T=336$ K and by varying  $(S/V_0)$

2. Variation of water concentration in the membrane reactor versus reaction time:

Figure 2 illustrates how water concentration in the reactor changes with reaction time as a function of (S/Vo). For convenience relative concentration  $C_w/C_{ao}$  versus time is plotted. During early period of reaction, the rate of chemical reaction is high, whereas water concentration gradually increases until it reaches maximum when its formation rate and removal rate becomes equal. There after the water removal is faster than formation, resulting in depletion of water in reactor. Naturally, for a given system, the large the value of (S/Vo), the shorter the time required for water to reach maximum concentration and smaller the magnitude of maximum water concentration.

Table 2:

Calculated water concentration (y) values for batch esterification when  $Q_b = 5.0$ ,  $k_1 = 2.662 \times 10$ ,  $v_1 = 1$ ,  $y = 0$ ,  $K_c = 4.37$ ,  $C_{ao} = 2191 \text{ mol/m}^3$ ,  $T = 336 \text{ K}$  and by varying  $\omega(S/V_o)$

TIME t(hr)	Y for $\omega(S/V_o) = 0.0$	Y for $\omega(S/V_o) = 0.080535$	Y for $\omega(S/V_o) = 0.133045$	Y for $\omega(S/V_o) = 0.194405$
0	0	0	0	0
1	0.25389	0.24813	0.24447	0.2403
2	0.43443	0.41076	0.39616	0.3799
3	0.56518	0.51592	0.48649	0.45458
4	0.66114	0.58154	0.53553	0.48702
5	0.73223	0.6195	0.5565	0.492
6	0.78528	0.63794	0.55842	0.47942
7	0.82508	0.64256	0.54751	0.45598
8	0.85505	0.63739	0.52815	0.42624
9	0.87769	0.62537	0.50342	0.39334

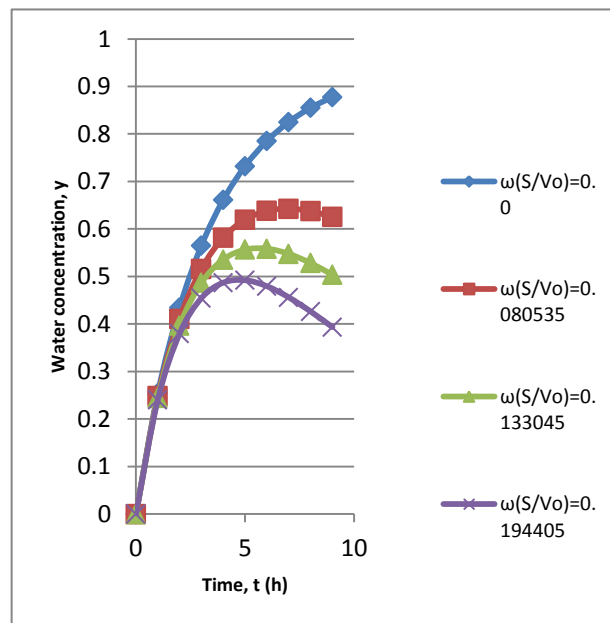


Fig. 2: Calculated water concentration (y) values for batch esterification when  $Q_b = 5.0$ ,  $k_1 = 2.662 \times 10$ ,  $v_1 = 1$ ,  $y = 0$ ,  $K_c = 4.37$ ,  $C_{ao} = 2191 \text{ mol/m}^3$ ,  $T = 336 \text{ K}$  and by varying  $\omega(S/V_o)$

3. Effect of excess of one reactant on conversion of the limiting reactant:

When one of the reactant species is used in excess, a complete conversion of the other is achievable, as shown in figure 3 plotted at  $(S/V_o) = 0.194405$ . This is come from by the results of experiment that the final reaction mixtures may not contain water after 60hrs of reaction mixtures of salicylic acid and methanol (in excess) at  $95^\circ\text{C}$ . Apparently the larger the excess the faster the reaction to reach completion. This is superior to simply batch reaction where no matter where the excess of one reactant; the limiting reactant is never completely reacted.

**Table. 3:**  
Calculated conversion values for batch esterification when  $\omega(S/V_0)=T=336K$  and by varying  $Q_b$  values.

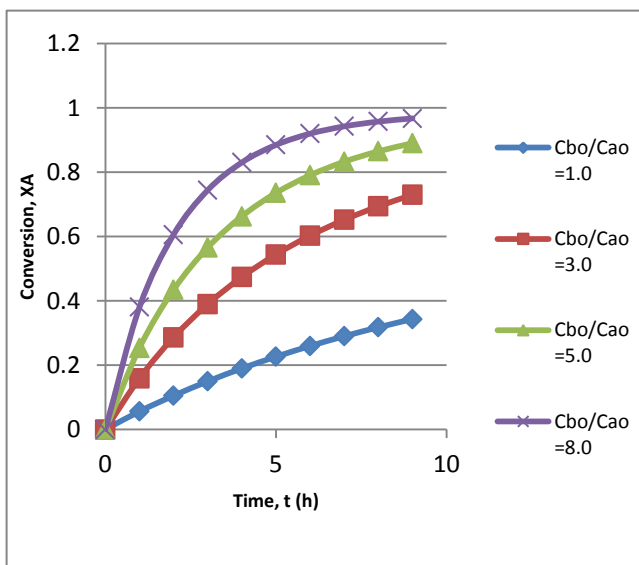
Time (t) hr	Xa for Cbo/Cao =1.0	Xa for Cbo/Cao =3.0	Xa for Cbo/Cao =5.0	Xa for Cbo/Cao =8.0
0	0	0	0	0
1	0.05662	0.15934	0.25389	0.3805
2	0.10529	0.28663	0.43459	0.60621
3	0.14988	0.38973	0.56591	0.74429
4	0.1901	0.47425	0.66296	0.83037
5	0.22656	0.54428	0.73563	0.8849
6	0.25975	0.60282	0.79064	0.91987
7	0.29007	0.65213	0.83266	0.94255
8	0.31789	0.69396	0.865	0.95743
9	0.3435	0.72966	0.89006	0.96731

4. *Effect of excess of one reactant on conversion of limiting reactant: Conversion versus reaction time for different  $Q_w$  values:*

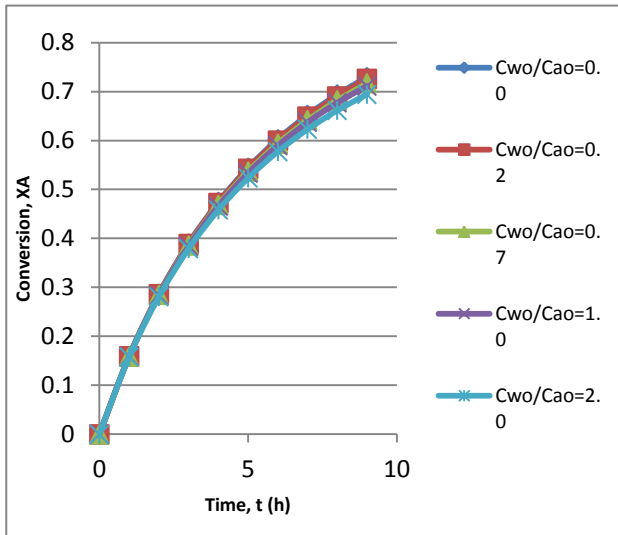
Figure 4 illustrates how conversion changes with reaction time for varying conditions i.e for various values  $C_{wo}/C_{ao}$ . As expected, with increase of water concentration the conversion is decreasing for a given value of  $(S/V_0)$ . With increase of  $(S/V_0)$  for a given  $C_{wo}/C_{ao}$ , the conversion Increasing. Further the study reveals that even in presence of water there is significant conversion at higher concentration. When water is present in the reactor the thermodynamic equilibrium will be decreases. Surprisingly tolerate the presence of water.

**Table.4:**  
Calculated conversion ( $X_a$ ) values for batch esterification when  $Q_b=3.0$ ,  $\omega(S/V_0)=0.194405$ ,  $k_1=2.66 \times 10^{-5}$ ,  $v_1=1$ ,  $y=0$ ,  $K_c=4.37$ ,  $C_{ao}=2191 \text{ mol/m}^3$ ,  $T=336K$  and by varying water concentration values.

TIM E t(hr)	Xa for Cwo/Cao=0.0	Xa for Cwo/Cao=0.2	Xa for Cwo/Cao=0.7	Xa for Cwo/Cao=1.0	Xa for Cwo/Cao=2.0
0	0	0	0	0	0
1	0.15934	0.15917	0.15874	0.1585	0.15766
2	0.28663	0.28603	0.28454	0.28366	0.28073
3	0.38973	0.3886	0.38582	0.38416	0.37873
4	0.47425	0.47259	0.46848	0.46604	0.45809
5	0.54428	0.54213	0.53673	0.53356	0.52326
6	0.60282	0.60017	0.59366	0.58982	0.57744
7	0.65213	0.64907	0.64155	0.63714	0.62294
8	0.69396	0.69054	0.68215	0.67724	0.66151
9	0.72966	0.72592	0.7168	0.71147	0.69446



**Fig. 3:** Calculated conversion values for batch esterification when  $\omega(S/V_0)=T=336K$  and by varying  $Q_b$  values.



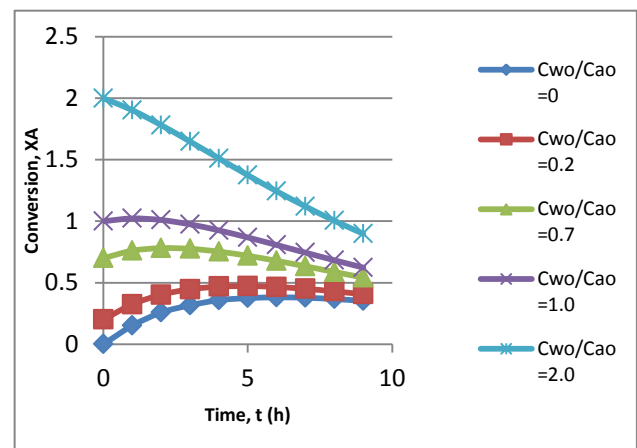
**Fig.4:** Calculated conversion ( $X_a$ ) values for batch esterification when  $Q_b=3.0$ ,  $\omega(S/V_0)=0.194405$ ,  $k_1=2.66 \times 10^{-5}$ ,  $v_1=1$ ,  $y=0$ ,  $K_c=4.37$ ,  $C_{a0}=2191 \text{ mol/m}^3$ ,  $T=336 \text{ K}$  and by varying water concentration values.

**5. Variation of water concentration with reaction time when water is initially present in the reactor:**

Figure 5 illustrates how water concentration in the reactor changes with reaction time for varying conditions i.e. for various  $C_{w0}/C_{a0}$  values. When water is used as reactant medium the water content in the early period of reaction maybe considerably high, but fortunately the forward reaction at the stage is not sensitive to product concentration on reaction rate becomes significant as reaction proceeds, water content has already been reduced to a low level by per evaporation. This is one of the favorable characteristics of the membrane reactor.

**Table.5:**  
Calculated conversion ( $y$ ) values for batch esterification when  $Q_b=3.0$ ,  $\omega(S/V_0)=0.194405$ ,  $k_1=2.66 \times 10^{-5}$ ,  $v_1=1$ ,  $y=0$ ,  $K_c=4.37$ ,  $C_{a0}=2191 \text{ mol/m}^3$ ,  $T=336 \text{ K}$  and by varying water concentration values.

Time t(hr)	Y for Cwo/Cao=0	y for Cwo/Cao=0.2	y for Cwo/Cao=0.7	y for Cwo/Cao=1.0	Y for Cwo/Cao=2.0
0	0	0.2	0.7	1	2
1	0.15089	0.32453	0.76015	1.02257	1.903
2	0.25761	0.40223	0.78105	1.00991	1.7815
3	0.31625	0.44677	0.77559	0.97464	1.64796
4	0.35824	0.4678	0.7527	0.92535	1.51054
5	0.37456	0.47223	0.7186	0.86797	1.37458
6	0.38074	0.46507	0.67773	0.80662	1.24356
7	0.37727	0.44997	0.63318	0.74413	1.11966
8	0.36705	0.42964	0.58719	0.68245	1.0041
9	0.35224	0.40605	0.54128	0.62289	0.89748



**Fig.5:** Calculated conversion ( $y$ ) values for batch esterification when  $Q_b=3.0$ ,  $\omega(S/V_0)=0.194405$ ,  $k_1=2.66 \times 10^{-5}$ ,  $v_1=1$ ,  $y=0$ ,  $K_c=4.37$ ,  $C_{a0}=2191 \text{ mol/m}^3$ ,  $T=336 \text{ K}$  and by varying water concentration values.

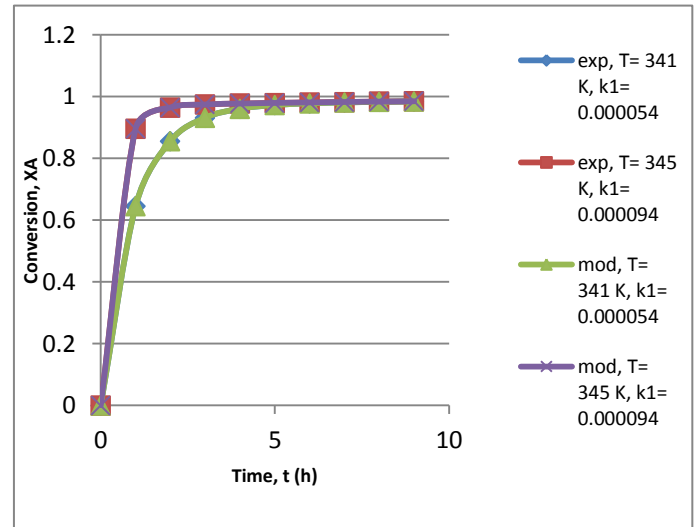
6. Effect of reaction rate constant  $k_1$  on reactor performance:

Figure 6 illustrates the effect of reaction rate constant  $k_1$  on the reactor performance. Fast reaction will severe equilibrium limitations benefit most of the form continuous removal of by product by a membrane. In practice large  $k_1$  and value is always preferred and can be obtained elevating reaction temperature and using suitable catalyst while a little control over  $k_c$  value can be achieved. Only slight variation in  $k_c$  with temperature is expected for reactions in which the difference the enthalpy of product and reactants Is small and methanol-salicylic acid esterification. however increase in temperature often enhances membrane permeability significantly. It is obvious that the reaction temperature, another important operating parameter, influence performance of a membrane reactor primarily through its effect on permeation rate and reaction rate.

**Table.6:**

Calculated conversion ( $X_a$ ) values for batch esterification when  $Q_b=8.0$ ,  $\omega(S/V_0)=0.194405$  and by varying temperature, rate constant and  $k_1$  values.

TIME T (hr)	$X_a$ for $K_1=0.000054$ , $T=341K$	$X_a$ for $K_1=0.000094$ , $T$ $=345K$
0	0	0
1	0.64501	0.89623
2	0.85562	0.96454
3	0.93157	0.97431
4	0.96067	0.97741
5	0.97266	0.97942
6	0.97809	0.98106
7	0.981	0.98245
8	0.98283	0.98366
9	0.98416	0.98471



**Fig.6:** Calculated conversion ( $X_a$ ) values for batch esterification when  $Q_b=8.0$ ,  $\omega(S/V_0)=0.194405$  and by varying temperature, rate constant and  $k_1$  values.

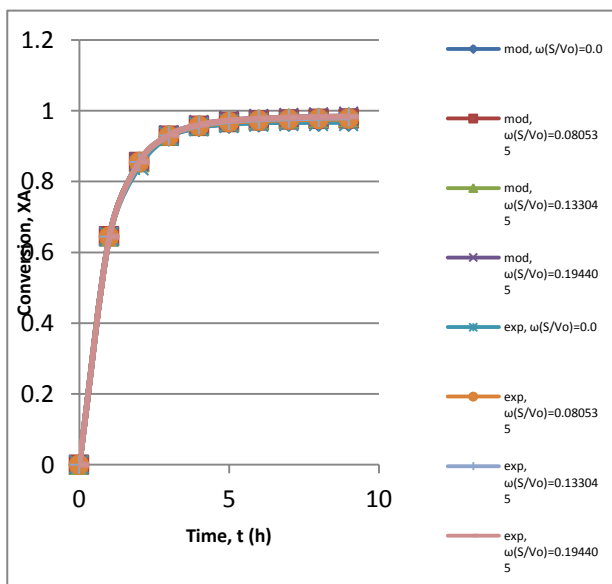
7. Conversion of function of reaction time for different? ( $S/V_0$ ) values:

Figure 7 is a plot of variation of conversion with time as a function is ( $S/V_0$ ).As expected with increase of time the conversion is increasing. Further, one can observe that conversion of membrane reactor can go beyond the equilibrium conversion which is maximum conversion that would be obtained the equilibrium, the higher the conversion. The conversion increased form because the concentration of water in reactor will be reduced more volume is larger. For the given case of illustrations, the reactor performance approaches the upper limit.

**Table.7:**

Calculated conversion (Xa) values for batch esterification when Qb=8.0, T=341K and by varying temperature values.

TIME t(hr)	Xa for $\omega(S/V_0)=0.0$	Xa for $\omega(S/V_0)=0.080535$	Xa for $\omega(S/V_0)=0.133045$	Xa for $\omega(S/V_0)=0.194405$
0	0	0	0	0
1	0.64401	0.64401	0.64401	0.64401
2	0.84432	0.8549	0.85525	0.85559
3	0.9278	0.92957	0.93054	0.93156
4	0.95428	0.95739	0.95903	0.96065
5	0.9639	0.9683	0.97054	0.97261
6	0.9674	0.97304	0.97566	0.97809
7	0.96867	0.97539	0.97836	0.98093
8	0.96913	0.97684	0.98006	0.98282
9	0.96931	0.97784	0.98131	0.98356



**Fig.7:** Calculated conversion (Xa) values for batch esterification when Qb=8.0, T=341K and by varying temperature values.

#### IV. CONCLUSIONS

- By integrating a Pervaporation unit into a conventional batch reactor the production rate of Esterification process can be increased substantially.
- Conversion can be enhanced by using Pervaporation to remove water from the reactor simultaneously.
- Conversion exceeding equilibrium limits can be achieved and a complete conversion of one reactant is obtainable when the other reactant is in excess.
- The mathematical model described successfully the performance of the integrated system
- The validated model can be used in simulation studies for parameter sensitivity and optimization purposes.
- However, cost optimization would be needed if an industrial operation is considered.

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