



Operation and Control of Reactive Distillation for Synthesis of Methyl Formate

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Esterification of formic acid and methyl alcohol in reactive distillation column is an effective process for synthesis of methyl formate. Operation and control of reactive distillation for synthesis of methyl formate is studied. First, the thermodynamic properties and reaction kinetics are analyzed, then the comparison of the three operation methods of reactive distillation are studied and at last the operation method with formic acid fed at top column is researched. The results show that it works quite well for this synthesis process.

Key Words: Methyl formate, Synthesis, Reactive distillation, Operation.

INTRODUCTION

Methyl formate, HCOOCH_3 , is an important chemical intermediate that has many applications in food, chemical and pharmaceutical industries. Methyl formate can be made of a series of downstream products such as formic acid, acetic acid, ethylene glycol, dimethyl carbonate and formylation agent. In China coal is the main energy and people pay great attention to the research and development of C-1 chemicals in academia and industry. Recently methyl formate has gradually developed into a new starting material and structural unit in C-1 chemicals following methane, synthesis gas and methanol¹. It is one of the important intermediates in the C-1 chemicals.

There are three main methods in production of methyl formate. The first one is the direct esterification of formic acid and methanol. The second one is dehydrogenation of methanol, and the last one is carbonylation of methanol².

Esterification is used very early. However, it is limited to chemical balance and there are several azeotropes in the reacting mixtures. As a result, the traditional process is complex and it needs many reactor and distillation columns^{3,4}.

Reactive distillation offers some advantages over conventional processes where reaction and purification are carried out separately⁵. Combining reaction and separation in a single unit can reduce both operating and capital costs. The direct removal of products or intermediates in reactive distillation columns often results in higher reaction conversion. However, the interaction of equilibrium phase separation and reaction increases the complexity of the operation and control problem⁶. Applications of reactive distillation are limited to systems in which the reaction rates are fairly high and there is no mismatch

of temperatures favourable for reaction and separation. A number of chemical systems have been studied in the literature using reactive distillation columns, most common applications are etherification and esterification⁷⁻¹⁰. Eastman company successfully applies reactive distillation technology to the industrial production of methyl acetate and uses only a reactive distillation column instead of the complex flow sheet. As a result, the reaction conversion rate is over 99.8% and the purity of methyl acetate is higher than 99.5%.

In this work, the operation and control of reactive distillation for the synthesis of methyl formate is presented. First, the thermodynamic properties and reaction kinetics are analyzed; then the comparison of the three modes of reactive distillation operations is studied and at last the optimization and control of operation method with formic acid fed at top column is researched.

EXPERIMENTAL

Thermodynamic properties: Table-1 is Antoine equation parameters of water, reactants and products.

Antoine equation ($\log P = A - B/(t+C)$) is used to calculate the saturation vapour pressure of each component in the reactive distillation mixtures (Table-2). The saturation vapour pressure is used to calculate the relative volatility and the results are listed in Table-3.

Reaction kinetics experiment: The esterification is a reversible reaction, the reaction in this experiment has been taken place to the direction of formation of methyl formate. As a result, the reverse reaction is neglected, only the positive reaction is considered. The reaction equation is shown as below.

TABLE-1
ANTOINE EQUATION PARAMETERS

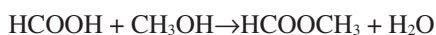
Compounds	A	B	C	Temp. (K)
Methanol	7.4182	1710.2	-22.25	175-279
	7.23029	1595.671	-32.245	275-338
	7.09498	1521.23	-39.18	338-487
	8.18215	2546.019	83.019	453-513
Formic acid	6.5028	1563.28	-26.09	283-384
Methyl formate	6.225963	1088.955	-46.675	279-305
	6.39684	1196.323	-32.629	305-443
Water	7.074056	1657.459	-46.13	280-441

TABLE-2
SATURATION VAPOUR PRESSURE (UNITS: kPa)

Temp. (°C)	Formic acid	Methanol	Methyl formate	Water
20	4.5	13.0	63.7	2.3
40	11.4	35.7	136.9	7.4
60	25.8	84.6	261.7	19.9
80	52.8	181	462.5	47.3
100	99.6	353.6	764	101.3
120	175.3	641.9	1196	198.5

TABLE-3
RELATIVE VOLATILITY

Temperature (°C)	Methyl formate/methanol	Methanol/formic acid	Water/methanol
20	4.91	2.94	5.56
40	3.82	3.12	4.76
60	3.09	3.23	4.17
80	2.55	3.45	3.85
100	2.16	3.57	3.45
120	1.86	3.70	3.23
Average α	3.07	3.33	4.00



Reaction rate is expressed in eqn. 1.

$$r = -dc_A/dt = kc^\alpha c_B^\beta \quad (1)$$

where c_A -the concentration of formic acid; c_B -the concentration of methanol; α -the reaction order of formic acid; β -the reaction order of methanol.

We assume the reaction order of formic acid and methanol is 1, *i.e.*, $\alpha = 1$, $\beta = 1$.

Arrhenius equation is shown in eqn. 2.

$$K = Ae^{-E_a/RT} \quad (2)$$

$$\log k = \log A - E_a/2.303RT \quad (3)$$

According to the experiment and data analysis, we can get that activation energy $E_a = 27.1$ kJ/mol, pre-exponential factor $A = 4.51E-04$ m³/(s*mol).

Operation methods: The esterification reaction of methanol and formic acid is an autocatalytic reaction without the need of using an additional catalyst and considering neither the problems with catalyst separation and recovery nor the special requirements for equipment. In this reaction, acid usually is the heaviest component. Once falls into the still, it always stays here. However, there will be a lot of water at the still in the later period of the reaction. This will reduce the conversion rate of the esterification reaction. Consequently, study on the operation methods of reactive distillation is of practical significance. In this work, there are three ways to operate the reactive distillation process.

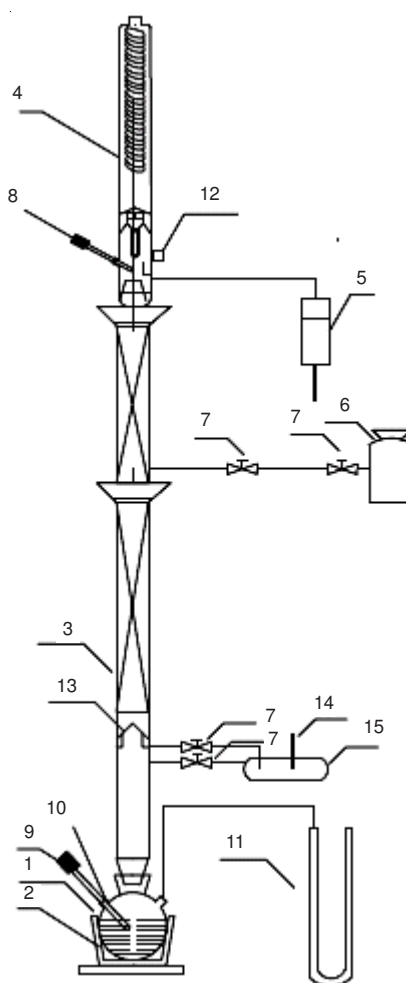
Operation with pH control: In this operation method, a shunt device is installed on the tower up of the still and the

reflux in the distillation process is exported in a tank and then returns to the still. The amount of formic acid flowing into the tank is controlled with the pH meter in the tank.

The experimental reagents is shown in Table-4 and the experimental set up are shown in Fig. 1.

TABLE-4
REAGENT SPECIFICATION AND PARAMETERS

Reagent	Formic acid	Methanol
Formula	HCOOH	CH ₃ CH ₂ OH
Purity (mass fraction)	88.0 %	99.5 %
Specification	AR	AR
Source	Chemical reagent company of Tianjin Jiangtian	Chemical reagent company of Tianjin Jiangtian
Molecular	46.06	32.04
Boiling point (°C)	101.4	64.5
Density/(g/cm ³)	1.214	0.978



1-distillation kettle; 2-heating package; 3-glass packed tower; 4-condenser; 5-product collection tank; 6-formic acid storage tank; 7-valve; 8,9-thermometer; 10-sampling port; 11-u-tube manometer; 12-electromagnet; 13-shunt device; 14-pH meter; 15-tank

Fig. 1. Experimental set up of esterification distillation with acidity control

The specific parameters of the experimental equipment are shown in Table-5.

Experiment processes: 400 mL methanol is added into the still (1) and 350 mL formic acid is added into the storage tank (6). After the liquid in the bottle (1) is heated to boiling,

total reflux operation is carried out for 10 min. And then methanol is full-mined. 40 mL methanol condensate is formed in 30 min and the average velocity of methanol rising steam is 1.33 mL/min. The molar ration of methanol and formic acid is 1:1, so the flow rate of formic acid is 1.5 mL/min. After 20 min of esterification reaction, reflux ratio is setted as 10 and the reaction product methyl formate is carried out to break the reaction equilibrium. When the top temperature rises suddenly and methyl formate is almost all recovered, the experiment ends.

TABLE-5
EXPERIMENTAL EQUIPMENT AND TYPE

Equipment	Description	Number
Three-necked flask	Volume: 500 mL	1
Glass distillation tower	Height: 1.2 + 0.3 m, internal diameter: 29/32 mm	1
Condenser	Having two ports and liquid distributor	1
Thermometer	Range: 0-150 °C	3
Glass packing	3 mm × 3 mm θ net ring	
Sampling needle	Range: 0-5 um	1
Electric heating	Heating power controlled by package	1
Product collection tank	200 mL	1
Formic acid tank	500 mL	1
pH buffer tank	200 mL	1

RESULTS AND DISCUSSION

The results are shown in Fig. 2.

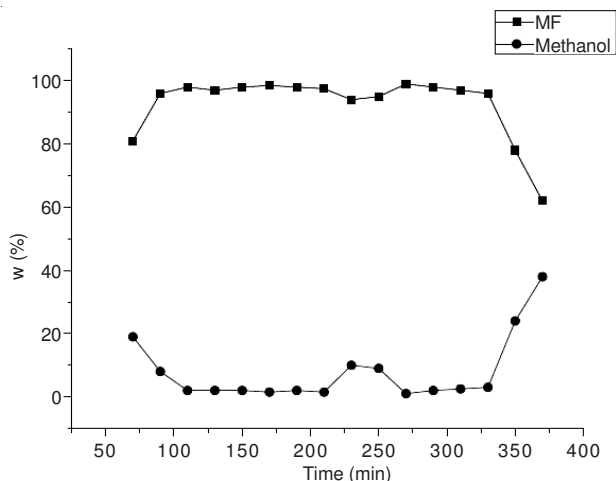


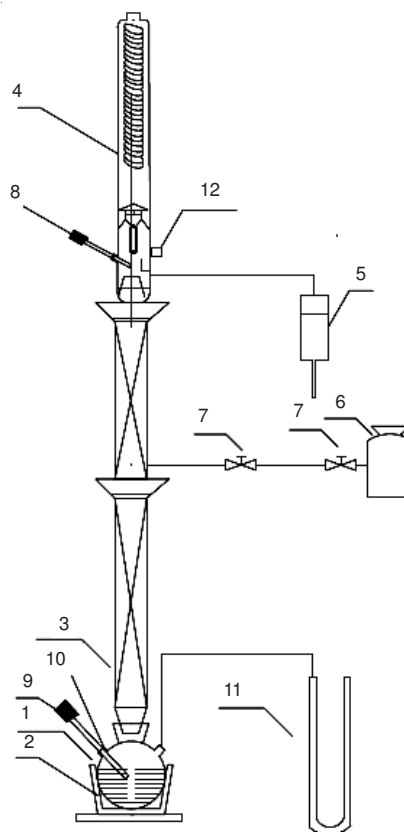
Fig. 2. Component content at top vs. time

The concentration of methyl formate in top product is more than 90 % after the reaction starts and stays at above 95 % soon later. In this reaction process, content of formic acid in tank (15) is controlled by pH meter (14). When the pH value is lower than a given value, formic acid is stopped feeding. Then the content of methyl formate at the top decreases and the content of methanol increases, shown as 200 min-300 min in the figure. This is because that as content of formic acid decreasing, part of methanol rises to the top of the tower. When the reaction finishes, the formic acid conversion rate is 94.3 %.

Operation with formic acid fed in tower: This operation is that formic acid is stored in the feed tank and added in to

the tower to make the esterification reaction shift the reaction equilibrium toward the product side in reaction zone.

Experimental equipments: The experimental setup is shown in Fig. 3.



1- distillation kettle; 2- heating package; 3- glass packed tower; 4- condenser; 5- product collection tank; 6- formic acid storage tank; 7- valve; 8,9- thermometer; 10- sampling port; 11- u-tube manometer; 12-electromagnet;

Fig. 3. Experimental set up of esterification distillation with formic acid fed at top column

The experimental equipment is very similar with that described earlier (Fig. 1) which includes a distillation kettle, two-sectioned packed column (the reactive zone and the rectifying zone), formic acid storage tank, product tank, condensate and reflux system and measuring instruments. And the specific parameters is shown as below.

TABLE-6
EXPERIMENTAL EQUIPMENT AND TYP

Equipment	Description	Number
Three-necked flask	Volume: 500 mL	1
Glass distillation tower	Height: 1.2 + 0.3 m, internal diameter: 29/32 mm	1
Condenser	Having two ports and liquid distributor	1
Thermometer	Range: 0-150 °C	3
Glass packing	3 mm × 6 mm glass spring packing	
Sampling needle	Range: 0-5 um	1
Electric heating	Heating power controlled by package	1

Experiment processes: The processes and conditions are the same as described earlier and the results are as below.

From Fig. 4, we can see that the content of methyl formate in the top product is over 90 % soon after the feeding and stabilizes above 95 % later. With the reaction being carried out, methanol in the distillation kettle is consumed and reaction product water gradually accumulates at the bottom by gravity. When the reaction ends, the content of water at the bottom is up to 80 % while the content of formic acid is less than 10 % and methyl formate has the lowest content, less than 1 %. The formic acid conversion rate is 91.5 %.

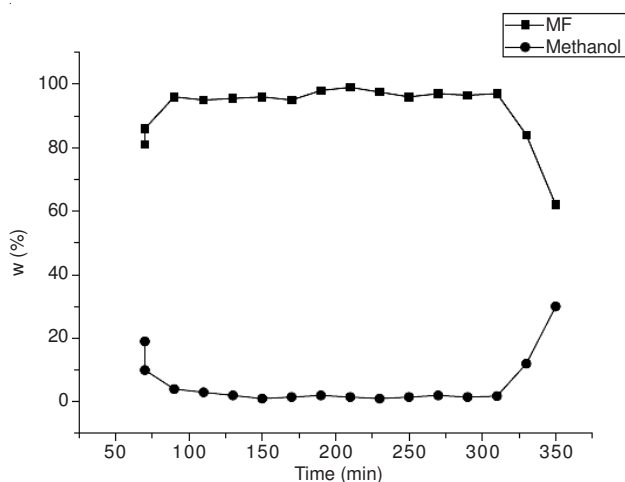
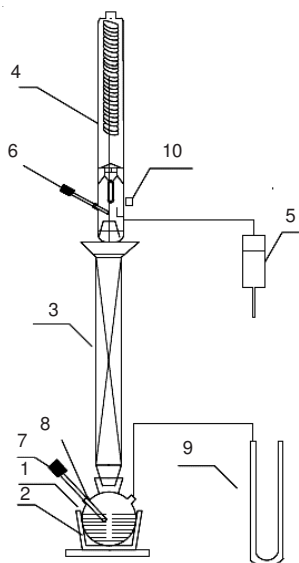


Fig. 4. Component content at top vs. time

Operation with directly adding of reactants: The reactants of formic acid and methanol are directly adding into the distillation kettle in this operation. Methyl formate which has the smallest relative volatility is steamed out by distillation so as to shift the reaction equilibrium toward ester generation side and is collected at the top with high purity.

Experimental equipments: The experimental set-up is shown as below (Fig. 5).



1-distillation kettle; 2-heating package; 3-glass packed tower; 4-condenser; 5-product collection tank; 6-formic acid storage tank; 6,7-thermometer; 8-sampling port; 9-u-tube manometer; 10-electromagnet;

Fig. 5. Experimental facility of esterification distillation with directly adding of reactants

The experimental equipment is very the same as that in experiment 3.2 which includes a distillation kettle, two-sectioned packed column (the reactive zone and the rectifying zone), product tank and condenser.

Experiment processes: 400 mL methanol solution and 350 mL formic acid solution are added into the distillation kettle. After total reflux operation for 30 min, the reflux ratio is adjusted to 10. Three hours later, the reaction almost finishes. Samples are taken from the product storage tank every 20 min to be measured the content of each component. And the experiment results is described in Fig. 6.

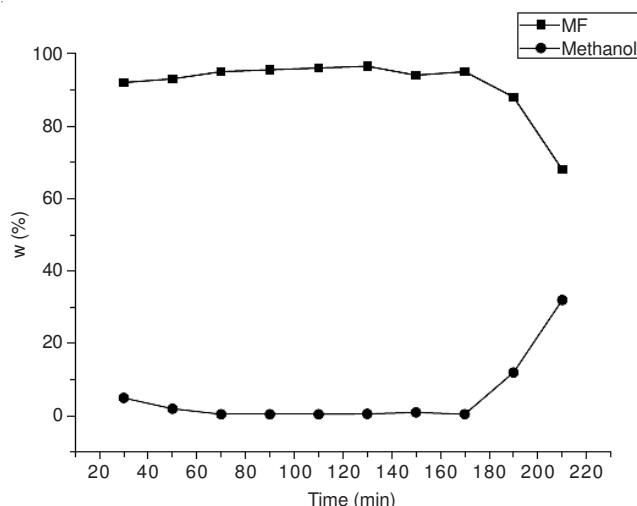


Fig. 6 Component content at top vs. time

After total reflux operation, methyl formate whose purity is over 90 % is collected quickly at the top. And the content of methyl formate is up to 95 % soon later. At the beginning of the reaction, a part of methanol of about 6 % concentration can be gotten at the top. The content of methanol is very low as the reaction proceeded.

The residual liquid at the bottom is collected. And we calculate the conversion of formic acid is 78.7 % by chromatography and sodium hydroxide titration.

TABLE-7
CALCULATION OF ACID QUALITY WITH RAW
MATERIAL FED AT BOTTOM

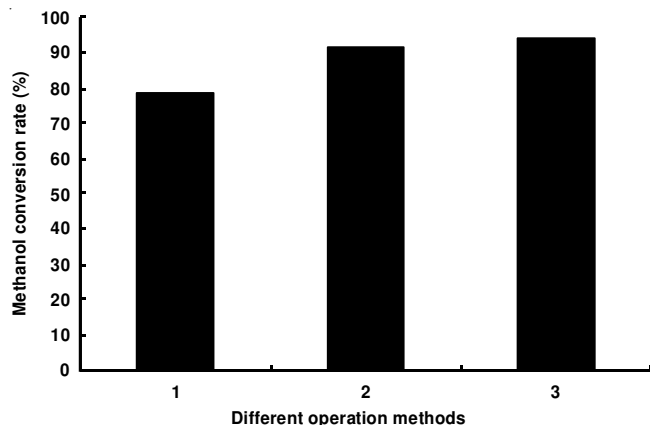
Produced fluid quality (g)	Methanol content in produced fluid (%)	Methanol quality in produced fluid (g)	Reactor liquid quality (g)	Methanol content in reactor liquid (%)	Methanol quality in reactor liquid (g)
245.7	3.6	8.8	347.6	15.6	54.2

Comparison of the three operation method

Conversion rate: The conversion rate of formic acid is listed in Fig. 7. Because all in the three operation methods, methanol content is 400 mL and formic acid content is 350 mL, the difference of the conversion rate is caused by the different operation methods.

From the figure, we can see that the formic acid conversion rate in operation with raw material fed is lower than that in the other two operations. That's because operation with raw material fed accumulates a lot of water at the bottom and it

prevents the reaction shifting toward the positive side. The formic acid conversion rate in the third operation is a little higher than that in the second operation. In the third operation, the content of formic acid is controlled by pH meter and the formic acid falls into the distillation kettle is less than that in the second operation, so the conversion rate is correspondingly higher.



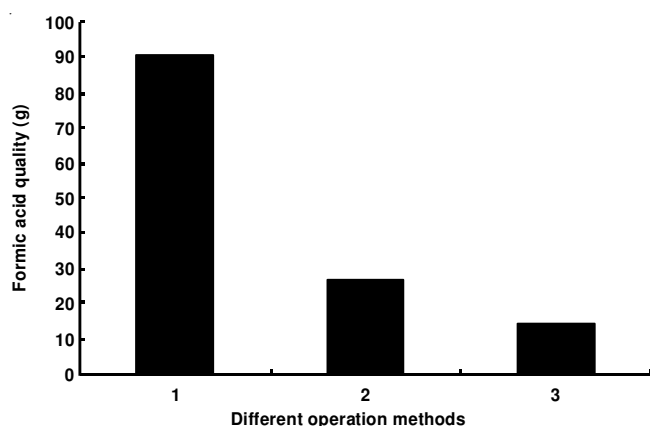
1-operation with raw material fed; 2-operation with formic acid fed at top column; 3-operation with acidity control

Fig. 7. Comparison of formic acid conversion rate under different operation

Top product: High purity product is obtained in the three operation methods and the content of methyl formate is over 95 %. It indicates that the esterification reaction is a self-catalytic reaction which can get high purity product without catalyst.

In the operation with raw material fed, the content of formic acid is over 90 % at the beginning of the reaction. And in the other operations the content is not very high, which is less than 90 %. That's because at the beginning, methanol is heated only and when methanol is full of the tower, formic acid is added to be reacted. In the end of the reaction, the content of methyl formate suddenly decreases and it indicates that most of methyl formate is steamed out.

Reactor liquid: In the end of the reaction, there are a lot of water and a little of methanol in the distillation kettle. And the quality of acid at bottom is shown in Fig. 8.



1-operation with raw material fed; 2-operation with formic acid fed at top column; 3-operation with acidity control

Fig. 8. Quality of acid at bottom under different operation

The figure shows that the quality of acid at bottom under operation with raw material fed at bottom is 90.6 g which is much larger than that under the other two operations. That's because the raw material is directly added into the bottom and positive reaction is inhibited gradually with the reaction proceeding. The quality of acid under the third operation is less than that under the second operation due to the control of formic acid reflux by pH meter.

Reaction time: The operation time with raw material fed at bottom is relatively short and it is about 4 h. The other two operation times negatively correlates to the adding speed of formic acid. In the operation with acidity control, when the pH value reaches a certain value, the acid is stopped adding, so the operation time is even longer.

Optimal control of operation with formic acid fed at top: Also many papers discussed about methyl acetate mixtures, study on methyl formate mixtures is significant and helpful for the production and application. The optimal control of operation with formic acid fed at top is researched.

Reflux ratio influence with the separation: Experimental equipment and processes is the same previously described. The reflux ratio is 1:1, 3:1, 5:1 and the other conditions unchanged. The influence of reflux ratio are shown in Figs. 9 and 10.

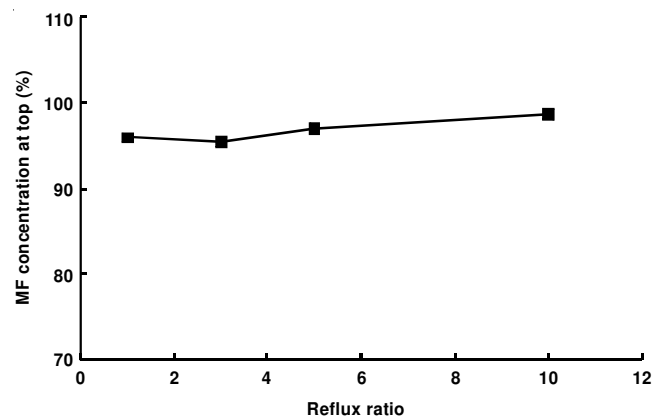


Fig. 9. Reflux ratio vs. methyl formate concentration at top

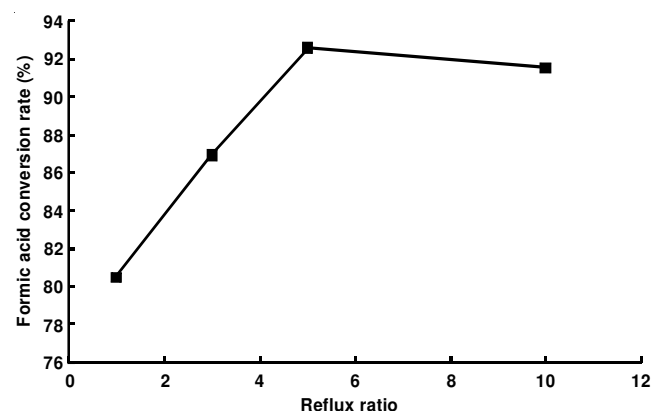


Fig. 10. Reflux ratio vs. conversion rate of formic acid

Fig. 9 showed that methyl formate concentration at top hardly changes. That may be because a lot of internal reflux exists in the tower and it counteracts the influence of the reflux ratio.

Fig. 10 shows that the conversion rate of formic acid rapid increases and then falls slowly with the reflux ratio increasing. When reflux ratio increases, the driving force of the vapour-liquid transfer changes larger and the tower separation performance improves, more and more methyl formate enrichments at the top. And this make the reaction equilibrium shifts to the right, more product is getted. However, if reflux ratio reaches a certain value, the formic acid conversion rate decreases gradually. That's because the increasing of methyl formate reflux make the hydrolysis of methyl formate easily. Meanwhile, a large reflux ratio leads to large energy consumption and long operation time. So when chose reflux ratio, after meet the requirement of top product purity and conversion rate, a small value is considered to reduce operating costs.

Fluence of formic acid feeding speed: Experimental equipment and processes is the same as the experiment 3-2. The feeding speed of formic acid changes and the molar ratio of formic acid and methanol is 0.5:1, 1.5:1, 2:1 and 2.5:1. The other conditions unchange. The results are shown as below.

Fig. 11 indicates that methyl formate content at top changes a little with different reaction molar ratio. However, when the reaction molar ratio is relatively small, the methyl formate content is also low. It may be because a lot of methanol remains in reactive distillation section and it goes up to the top, collected with the methyl formate product together. So the methyl formate content decreases.

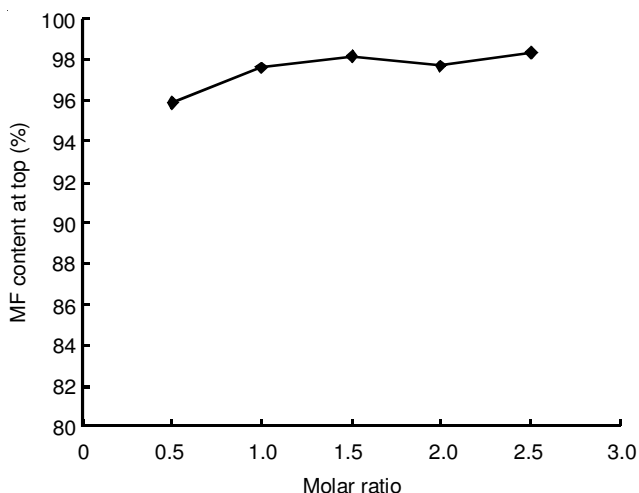


Fig. 11. Different reaction molar ratio vs. methyl formate content at top

It is shown in Fig. 12 that the conversion rate of formic acid decreases gradually with the increasing of the reaction molar ratio. The main reason is that when the reaction molar ratio is relatively large, formic acid remains in reactive distillation section due to the increasing of formic acid fed. And the acid, the heaviest component, transfer to the bottom to lower the conversion rate of formic acid. On the contrary, the formic acid is almost reacted out in reactive distillation section when the reaction molar ratio is small. And the conversion rate of formic acid changes little.

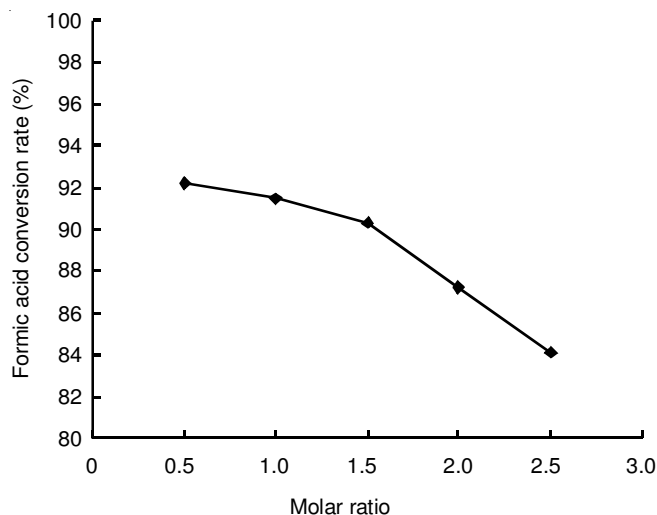


Fig. 12. Different reaction molar ratio vs. conversion rate of formic acid

Conclusion

In the three operation of reactive distillation for synthesis of methyl formate, the operation with raw materials fed has low conversion rate that is 78.7 %. However the operation time is shortest. The conversion rate under operation with formic acid fed at top column is higher than that under the former and it is 91.5 %. The operation time is almost 4 h. Under the operation with acidity control, the conversion rate is even larger, which is up to 94.3 %. And the operation time is even longer than that of the other two operations. The different reflux ratio and reaction molar ratio have influences on the esterification reactive distillation process. In the operation with formic acid fed at top column, a small reflux ratio is considered to reduce operating costs when the top product purity and conversion rate meet the requirement. And a small reaction molar ratio is chosen when the concentration of methyl formate at the top meets the product requirements.

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