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Hydrodynamics, Mass and Heat Transfer in Reactive Distillation

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Abstract

The ethyl acetate synthesis via heterogeneous reactive distillation is studied experimentally using ethanol and acetic acid. Three types of cation exchanging resins were used as catalysts: Zerolit 225, Zerolit 226 and Ambylite 400. Experiments were carried out in two units of the same dimensions. Each unit consisted of three sections: rectifying, reactive and stripping sections of heights (60+25+20) cm respectively and 2.5cm column diameter. The first unit (column-A-) was a fractionation type and the second unit (column-B-) was packed column. The packing type was hollow glass cylinders with 10 mm height, and 4, 5 mm inner and outer diameter respectively.

The experiments were carried out by using two operation modes. The semi-batch and continuous operation mode. In the first part of present investigation, the semi-batch mode was used to evaluate the catalyst type and to evaluate the performance of reactive distillation unit configuration (Fractionation and packed column). Results show that, the column-B- gave higher conversion rates than column-A-. This is attributed to the high surface area available for liquid vapour contact in packed type column, which leads to increasing mass transfer rates. On the other hand, Ambylite 400 catalyst showed higher activity for esterification reaction than other two types of catalysts.

The second part of work continued with column -B- only. It is well known that, the esterification process is regarded one of exothermic reactions. Therefore, the monitoring of the temperature distribution along column axial for all three types of catalysts showed that the temperature distribution was essentially the same due to steady state operation in continuous operation mode. On the other hand, the effect of reflux ratio on temperature distribution was clearly noted, that is as the reflux ratio increased the temperature distribution along the column was reduced for each type of catalysts.

On the other hand, the experimental results point that, as a reflux ratio increases the conversion rates of acetic acid is increased too because such increasing is related to high mass transfer rates between vapour and liquid along reactive distillation column.

Keywords: Reactive Distillation; Esterification; Ethyl acetate; Heterogeneous Catalysts.

Introduction

The combination of chemical reaction with distillation in only one unit is called reactive distillation [1]. The performance of reaction with separation in one piece of equipment offers distinct advantages over the conventional, sequential approach. Especially for equilibrium limited reactions such as etherification, esterification and ester hydrolysis reactions, conversion can be increased far beyond chemical equilibrium conversion due to the continuous removal of reaction products from the reactive zone. This may lead to an enormous reduction of capital and investment costs and may be important for sustainable development due to a lower consumption of resources. Therefore, the main advantages of reactive distillation equipment can be summarized as follows [2, 3]:

- higher conversion, selectivity and yield
- avoid equilibrium restrictions
- removal of side reactions
- removal of recycling streams
- avoidance of non-reactive azeotropes
- reduction of number of units (investment cost)
- reduction of energy demands (heat integration).

Figure (1) shows the general construction of reactive distillation unit, which includes three main sections named rectifying, reactive and stripping sections [2].

Esters are an important class of chemicals, having applications in a variety of areas such as solvents, plasticizers, pharmaceuticals and intermediates. Among them, ethyl acetate (EtAc) is an important organic solvent widely used in the production of varnishes, ink, synthetic resins, and adhesive agents. This ester is typically produced from the reaction of acetic acid (HAc) and ethanol (EtOH) [4,5].

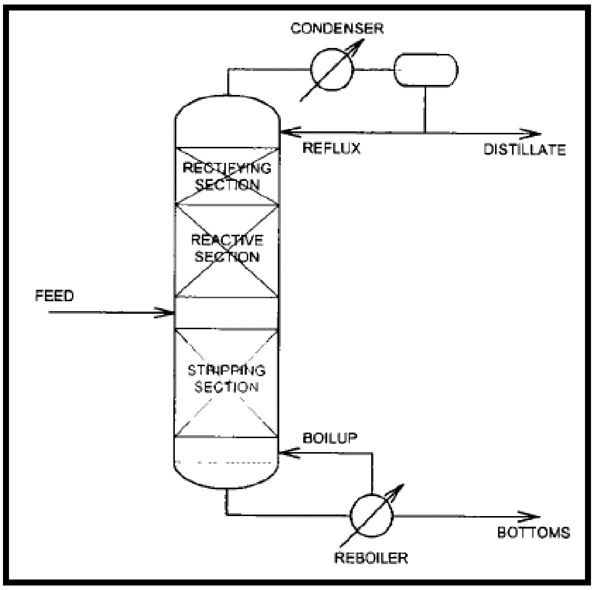

Fig. 1. General Construction of Reactive Distillation.

Both homogenous and heterogeneous catalysts could be used in reactive distillation column to produce EtAc. Sulfuric acid is generally used in homogenous catalysis. Heterogeneously catalyzed reactions involve the use of acidic polymeric catalysts such as ion exchange resins. However, the use of heterogeneous catalysts has become more common in recent times because of its significant advantages over homogenous catalyst. The use of heterogeneous catalyst allows for easy and inexpensive product removal from reaction mixture by filtration or centrifugation. Moreover, heterogeneous catalyst can withstand a wider range of temperatures and pressures [1, 5].

The overall reaction between acetic acid and ethyl alcohol over a catalytically active resin is as follows:

$$CH_3COOH + C_2H_5OH \xrightleftharpoons{\text{catalyst}} CH_3COOC_2H_5 + H_2O$$

This reaction is reversible, and the equilibrium composition is a weak function of temperature. The reaction is acid catalyzed by using the cation exchange resins catalysts [2, 3, 5].

Tang et al. [6] studied the process which contains sulfuric acid as catalyst (homogeneous reaction) using an reactive distillation column with an overhead decanter and a stripping column. Highly pure EtAc product was obtained and all the outlet streams met product and environmental specifications. Tang et al. [7] provide generalization for the study of design of reactive distillation with acetic acid as one feed. Chang and Seider [8] concluded that a continuous reactive distillation column cannot produce pure ethyl acetate at the top due to the ternary minimum boiling azeotrope of ethyl acetate, ethanol and water, which prevents a desired overall reaction conversion. Bock et al. [9] propose a different configuration of a reactive distillation column followed by a non-reactive recovery column to produce pure ethyl acetate under excess reactants.

Research in catalysis by ion exchange resins is undoubtedly interesting, not only from a purely physicochemical point of view but also in terms of the advantages of these types of catalyst over the conventional ones. Ion exchange resins increase the product yield, keep their activity a long time, and do not pollute. Ion exchange resins separate from reaction media easily and they regenerate easily for reuse in chemical processes [10,11, 12, 13].

However, there is a limited work in literature about the performance of reactive distillation column that uses heterogeneous catalysts. On the other hand, the design, operation and optimization of reactive distillation require the knowledge of the hydrodynamics, mass as well as heat transfer characteristics and their interactions. Therefore, due to the complex interactions between chemical reaction, heat, and mass transfer, the present work aims to study the performance of reactive distillation column in esterification reaction to produce ethyl acetate by using heterogeneous catalysts.

Experimenral Work

Figure (2) shows a view of the experimental apparatus, while, Figure (3) shows the schematic diagram of two reactive distillation experimental set-up. The first system is (column-A-) which is a fractionation type distillation column made of Perspex Glass. The height of the column was 105 cm (three sections: rectifying 60 cm, reactive 25 cm, and stripping 20 cm) and 2.5cm column diameter. On the other hand, the second column (column-B-) was packed column made of QVF glass of the same dimensions of the first column. The rectifying and stripping sections were filled with hollow cylinder glass packing (non-reactive packing of 10 mm height, and 4, 5 mm inner and outer diameter respectively) with voidage fraction of 0.66. The middle sections of the both columns were filled with 30 gm of the catalyst.

The top of each column was connected with a condenser where a coolant (T= 20°C) was circulated to condense vapor from the reactive distillation column. The condensate was passed into a solenoid valve. A multi-timer was used as a reflux ratio controller. The bottom of each column was connected to a reboiler (2000cm^3 three neck flask). Heat supply required for the reboiler was regulated by a variable transformer via adjustable voltage.

The temperature along the columns axial were determined by manufacturing an interface system (Computerized Temperature Measurement System) which have sixteen copper-constantan thermocouples (T type) (eight thermocouples for each column). This interface is programmed and run by a computer (P_4), which converts the measured voltages to the corresponding temperatures with the help of appropriate software in Excel Program. The temperature in each section of the column was noted after starting the reaction, and steady state was achieved when the temperatures in various sections of the column were stabilized.

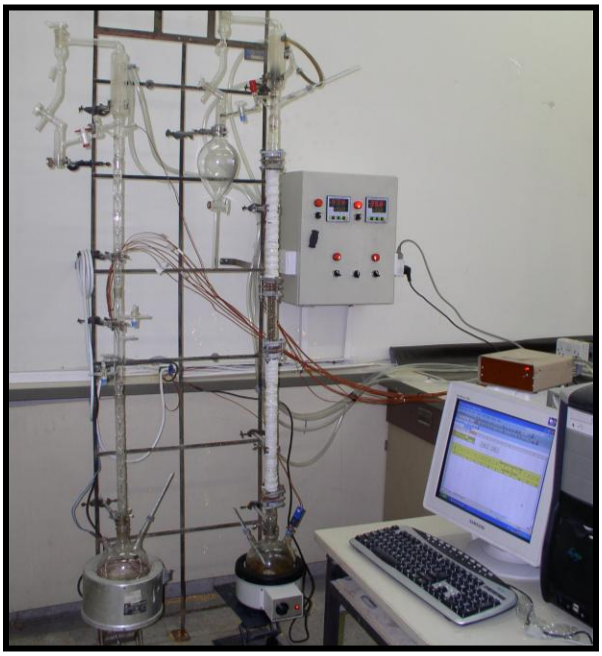

Fig. 2. General View of Experimental Apparatus.

Materials and Catalysts

Three types of catalysts (cation exchange resins) were used in the present investigation, Zerolit 225, Zerolit 226, and Ambylite 400 purchased from BDH. The particle sizes and the total surface area of the resins used are given in Table (1). The wet catalyst was first washed with methanol to remove any water that might be sorbed in the resin catalyst. This step aided in avoiding the collapse of the resin pore structure in the subsequent drying process. Then, dried under vacuum by gentle heating for 6 hours at 100°C. The prepared catalyst was stored in a desiccator in the presence of silica gel.

Acetic acid (99.8%) and ethanol (99.5%) were purchased from Scharlau Company. Table (2) shows the boiling points of feed and products compounds.

Table 1
Properties of Cation Exchange Resins Used in Present Investigation.

Catalyst	Average Particle Size d_p (mm)	Surface Area (m^2/g)
Zerolit 225	0.65	26.2
Zerolit 226	0.54	21.5
Ambylite 400	1.11	34.8

Table 2
Boiling Points of Feed and Products Compounds.

No.	Compound	Boiling point, °C
1	EtOH	78.31
2	HAc	118.01
3	H_2O	100.0
4	EtAc	77.20

Experimental Procedure

The experiments were carried out in order to achieve an optimum column configuration for the production of ethyl acetate in a reactive distillation column. Therefore, two modes of reactive distillation operation were used in the present investigation: semi-batch and continuous operation mode.

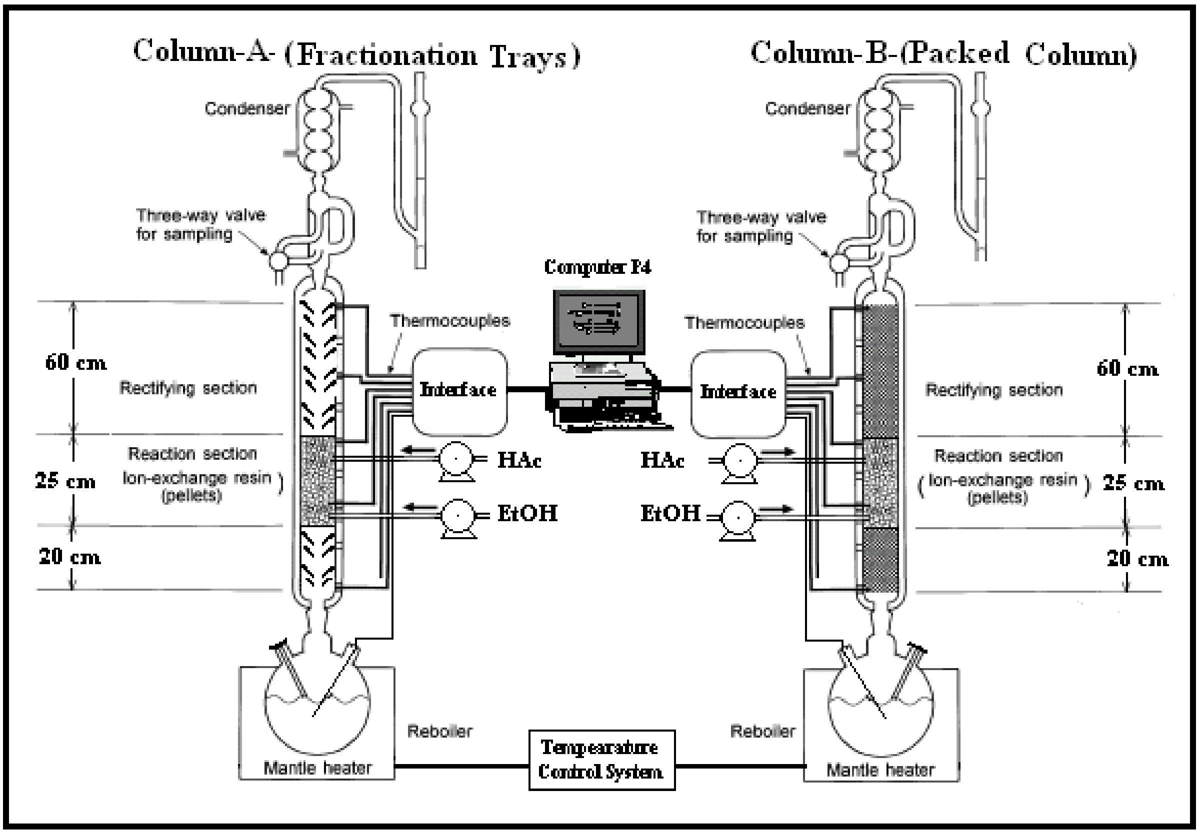

Fig. 3. Experimental Units: A- Fractionation RD, and B- Packed RD System.

Semi-Batch Operation Mode

The semi-batch mode was used to evaluate the catalyst type and to evaluate the performance and design of reactive distillation unit configuration (Fractionation column-A- and Packed column -B). Therefore, a batch of 1000 cm^3 of EtOH was used in the settle (reboiler), while the acetic acid was fed at the top of the reactive section by using dosing pump with flow rate of 5 cm^3/min. The operation conducted under total reflux condition and atmospheric pressure.

Continuous Operation Mode

The continuous operation mode was used to investigate the flowing parameters:
1- the performance of catalyst type, 2- reflux ratio, and 3- temperature distribution along RD column. On the other hand, in continuous operation, two dosing pumps were used to feed the reactants to RD. The acetic acid was fed at the top of the reactive section, while the EtOH fed at the lower part of the reactive section. Therefore, for each test (17.12) mole of HAc was fed to (17.12) mole of EtOH (i.e the mole ratio of HAc/EtOH =1). The reactants were introduced into the reactive distillation column at room temperature and atmospheric pressure. The reaction was carried out until reaching steady state. Top and bottom products were sampled and their concentrations were measured every 1 hr. The products were analyzed in a gas chromatograph (Shimadzu GC-2014) by TCD with a capillary column (S.G.E., length = 25 mm, I.D.= 0.22 mm, film= 0.2μm).

Results and Discussion

Semi-Batch Operation Mode

The design and operation of reactive distillation systems are considerably more complex than those involved in either conventional reactors or conventional distillation columns. The introduction of separation process within the reaction zone leads to complex interactions between vapour-liquid equilibrium, vapour-liquid mass transfer, intra-catalyst diffusion and chemical kinetics.

From the acetic acid recovery point of view, the optimal configuration should give the highest conversion of acetic acid with a minimum concentration of acetic acid at the top, as well as a minimum concentration of ethyl acetate at the bottom. Therefore, in order to evaluate the type of catalysts used in present investigation, the effect of the catalyst on the extent of conversion is presented in Figures (4) and (5) for column-A-and column-B- respectively under semi-batch operation mode.

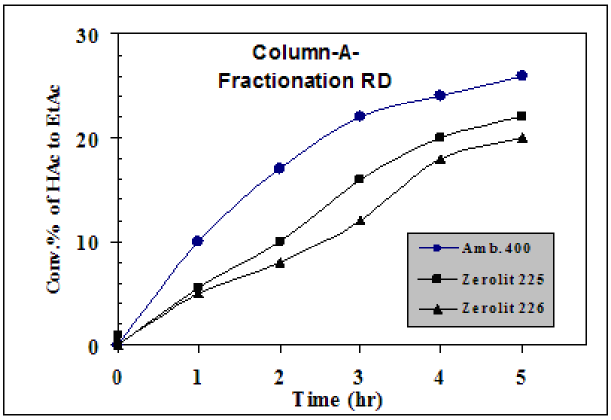

Fig. 4. Influence of Catalyst Type on Esterification of HAc with EtOH to EtAc in Fractionation RD Under Semi-Batch Operation Mode.

The comparison between the catalyst performance of Figures (5) and (6) shows that, the packed column RD (column-B-) gives higher rates of conversion of HAc to EtAc with reaction time than that of fractionation RD (column-A-). This indicates that, the column-B provides an excellent heat and mass transfer between the liquid and vapour phases which arise from its structure of ordered flow channels. Furthermore, the packings helps to promote mixing and distribution of ascending vapour and descending liquid phases in RD due to high total surface area of packing. On the other hand, the packing column leads to a better separation of products from reactants for such equilibrium limited reactions. These results are in agreement with the work of Saha et al. [2] and Tang et al. [6].

Therefore, the second part of the present investigation will continue by using just packed column (column-B-) only with continuous operation mode, because the high surface area that was provided in such column.

Temperature Distribution in RD

Esterification process is regarded one of highly exothermic reactions, therefore, benefits of heat integration are obtained because the heat generated in the chemical reactions is used for vaporization. On the other hand, the reactants and products must have suitable volatility to maintain high concentrations of reactants and low concentrations of products in the reaction zone. Therefore, in esterification process the temperature distribution and liquid-vapour interaction must be known.

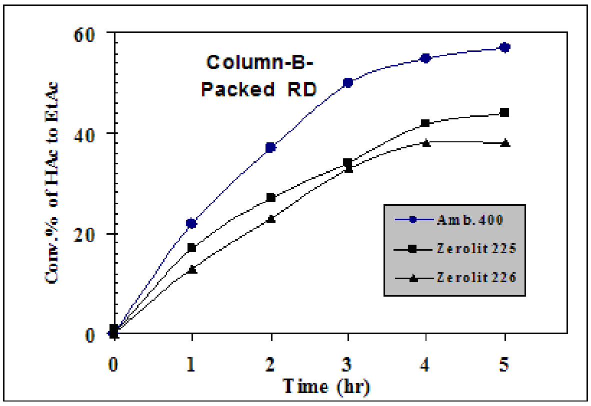

Fig. 5. Influence of Catalyst Type on Esterification of HAc with EtOH to EtAc in Packed RD Under Semi-Batch Operation Mode.

Figure (6) shows the comparison between the temperature distribution of the three types of catalysts used for esterification reaction under constant conditions of: (catalyst weight = 30g, R= 2, and HAc/EtOH=1). The temperature in the bottom was about 84°C. It rapidly changes around the interface of reaction and separation zones. The temperature in rectifying zone is about 77.5°C, which is the azeotropic temperature. From the same figure, it is clear that, the temperature distribution along column axial for all three types of catalysts show an increase in the region of reaction zone because the generated heat from exothermic reaction. On the other hand, the temperature distribution up to condenser is essentially the same due to steady state operation. According to Table (2), the boiling points of HAc and H_2O are higher enough, therefore, such compounds exist in the stripping zone and reboiler.

In order to study the effect of reflux ratio on the temperature distribution along the RD column, Figures (7), (8), and (9) show the effect of the four levels of reflux ratio R (1, 2, 3, and 5) on the temperature distribution under constant operation conditions. For all three types of catalysts, these figures show that, there an inverse relationship between R and temperature distribution for all types of catalysts. Therefore, as the reflux ratio increases the temperature distribution level along the column axial decreases. The explanation of such behavior is based on phenomenon of interaction between liquid-vapour equilibrium in reactive distillation.

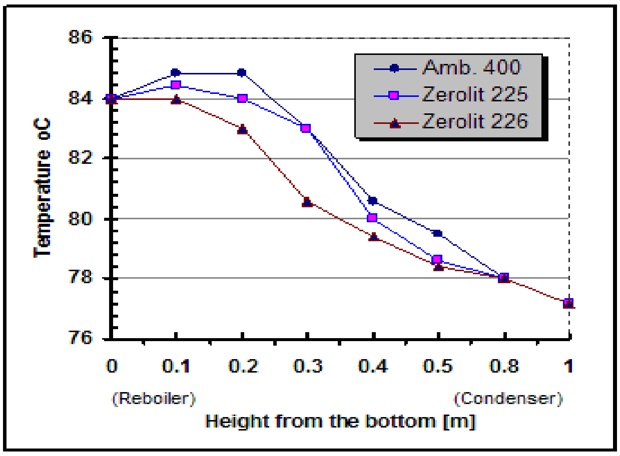

Fig. 6. Comparison of Temperature Distribution Levels Between Catalyst Types Along RD Column.

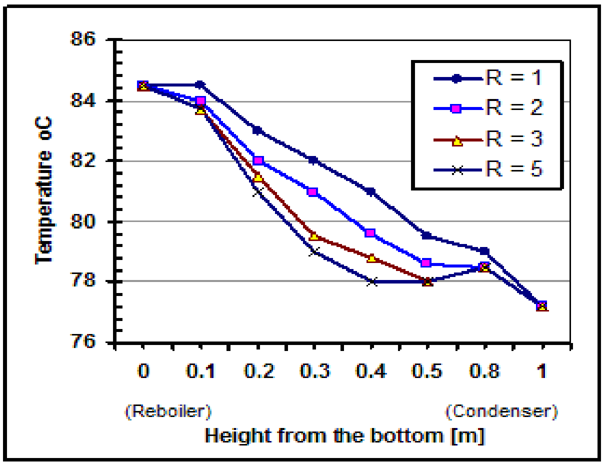

Fig. 7. Temperature Distribution Along RD Column Using Amb. 400 Catalyst at Different Reflux Ratios.

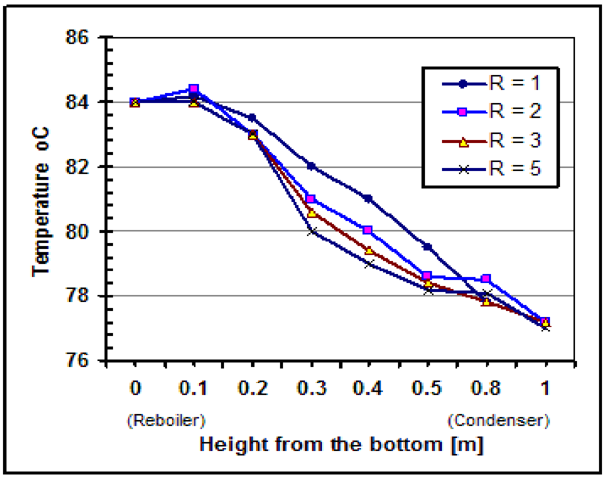

Fig. 8. Temperature Distribution Along RD Column Using Zerolit 225 Catalyst at Different Reflux Ratios.

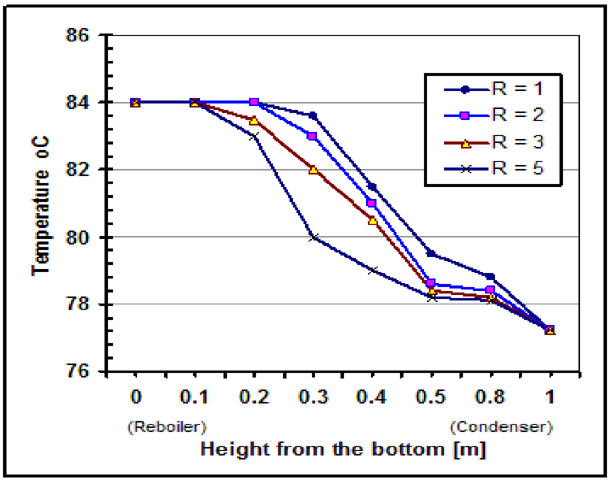

Fig. 9. Temperature Distribution Along RD Column Using Zerolit 226 Catalyst at Different Reflux Ratios.

Effect of Reflux Ratio

The effect of the reflux ratio of the organic phase (of the top product) was investigated to determine the conversion of acetic acid from its aqueous solution. The ranges of reflux ratio values reported by various investigations [1,2, 10] vary between 1 and 6. The present experiments were conducted at values of reflux ratio 0.5, 1, 2, 3, and 5. In all experimental runs, the feed mole ratio of HAc to EtOH was kept at the optimum ratio of 1:1. All other operating conditions were kept constant. There was an increase in acetic acid conversion from 32% to about 53-65% when the reflux ratio of the organic phase was raised from 0.5 to 5 for all types of catalysts as shown in Figure (10). In other words, as the reflux ratio increased from 0.5 to 3 the weight percentage of ethyl acetate production of distillate increased clearly due to high conversion rates of HAc to EtOH.

On the other hand, Figure (10) shows that the Ambylite 400 catalyst gives the highest conversion rates of HAc than other two types of catalysts for all reflux ratios studied. This is due to the high surface area of Ambylite 400 catalyst 34.8 m^2 that is available for chemical reaction than that of 26.2 and 21.5 m^2 for Zerolit 225 and Zerolit 226 respectively.

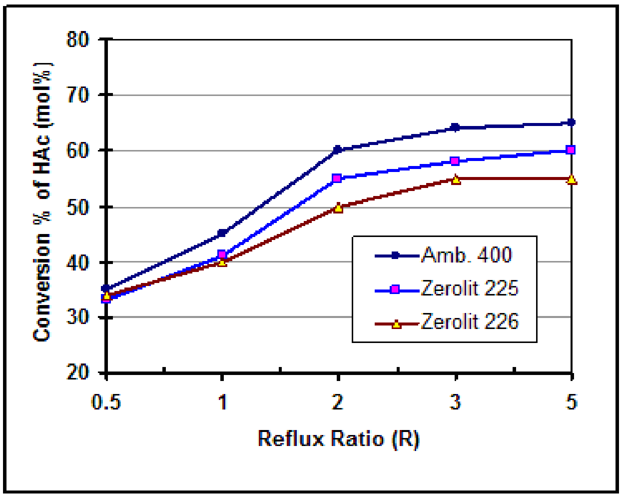

Fig. 10. Effect of Reflux Ratio on % Conversion of HAc to EtOH.

Conclusions

Combining catalytic reaction and separation in the same reactor can improve the conversion and selectivity for much equilibrium limited reactions reduce capital cost and also enhance catalyst lifetime.

In semi-batch operation mode, results pointed out that, the column-B- (packed) shows higher conversion rates than that of column-A- (fractionation). This is attributed to the high surface area available for liquid vapour contact in packed type column, which leads to increase in the rates of mass transfer. On the other hand, Ambylite 400 catalyst shows higher activity for esterification reaction than other two types (Zerolit 225 and Zerolit 226).

Esterification process is regarded one of highly exothermic reactions, therefore, the temperature distribution along column axial for all three types of catalysts is essentially the same due to steady state operation in continuous operation mode. On the other hand, the effect of reflux ratio on temperature distribution is clearly noted, that as the reflux ratio increases the temperature distribution along the column is reduced for all types of catalysts.

The experimental results point out that, as a reflux ratio increases the conversion rates of acetic acid increases. This is due to high mass transfer rates between vapour and liquid. Therefore, increasing reflux rates enhances separation and recycles unreacted reactants to the reaction zone and, thereby, increases conversion.

Nomenclature

Column-A	A Fractionation type reactive distillation column with rods trays.
Column-B	Packed reactive distillation column.
Conv.%	Percentage conversion
d_p	Particle diameter of the catalyst [mm]
EtAc	Ethyl acetate
EtOH	Ethyl alcohol (Ethanol)
HAc	Acetic acid
H_2O	Water
R	Reflux ratio
RD	Reactive distillation

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دراسة سلوكية وانتقال الكتلة والحرارة في أعمدة التقطير ذات المفاعل

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الخلاصة

في هذا البحث تم دراسة عملية تحضير خلات الاثيل Ethyl Acetate باستخدام تقنية المفاعل ذو التقطير Reactive Distillation باستخدام الايثانول وحامض ألخليك كمواد أولية للتفاعل واستخدام العوامل المساعدة الصلبة. حيث تم استخدام ثلاثة أنواع من العوامل المساعدة Cation Exchanging Resins والتي هي: Zerolit 225, Zerolit 226 , and Ambylite 400 . خلال البحث تم بناء منظومتين رياديتين بأبعاد موحدة لإجراء التجارب. كل منظومة تتكون من ثلاث مناطق هي Rectifying, Reactive and Stripping section بأرتفاعات (60+25+20) سم على التوالي و2,5 سم قطر للعمود. اعتمدت المنظومة الأولى (Column-A-) في تصميمها كونها تحتوي على صواني نوع (Fractionation Trays)، أما المنظومة الثانية (Column-B-) فصممت على أنها عمود تقطير محشو (Packed Distillation Column) تحتوي على حشوات زجاجية اسطوانية الشكل بطول 10ملم وقطر داخلي 4 ملم وقطر خارجي 5 ملم.

أجريت التجارب باستخدام نمطين من التشغيل على أساس مرور المواد الأولية: النمط الأول هو عمل نصف الوجبة Semi-batch والنمط الثاني هو الأسلوب المستمر Continuous. حيث استخدم النمط الأول لغرض تقييم كفاءة العوامل المساعدة المستخدمة وتحليل وتقييم أداء التصميمين للمنظومتين (Fractionation and packed column) الأتي استخدمن في البحث. حيث أظهرت النتائج أن المنظومة الثانية Column-B- أعطت معدلات كفاءة وتحول عالية نحو النواتج المرغوب بها أكثر من المنظومة الأولى Column-A-. وهذا في حقيقة الأمر يعود إلى المساحة السطحية العالية للحشوات والتي توفر مساحة تلامس جيدة بين البخار الصاعد والسائل الذي ينزل من أعلى البرج، والذي يؤدي بطبيعة إلى زيادة معدلات انتقال الكتلة. من ناحية أخرى أظهرت النتائج أن العامل المساعد نوع Ambylite 400 أعطى فعالية أعلى في تفاعل الاسترة من النوعين الآخرين.

من ناحية أخرى تم اعتماد العمل باستخدام المنظومة Column-B- فقط وبالأسلوب التشغيلي المستمر. حيث تعد تفاعلات الاسترة من التفاعلات الباعثة للحرارة، ولهذا متابعة توزيع درجات الحرارة على طول البرج وللأنواع الثلاثة من العوامل المساعدة أظهرت النتائج بان التوزيع الحراري تقريباً متساوي لجميع العوامل المساعدة، وهذا يعزى إلى حالة الاستقرار التشغيلي في أسلوب التشغيل المستمر. ومن خلال دراسة تأثير نسبة الراجع Reflux Ratio على توزيع درجات الحرارة في البرج، أظهرت النتائج انه كلما زادت معدلات الراجع كلما انخفضت معدلات توزيع الحرارة داخل البرج ولجميع الأنواع من العوامل المساعدة.

أشارت النتائج العملية إلى لا انه بزيادة قيم الراجع فان معدلات تحول حمض ألخليك سوف تزداد ، حيث يمكن تفسير مثل هذه الزيادة على أساس التحسن الحاصل بمعدلات انتقال الكتلة بين البخار الصاعد والسائل النازل في برج التقطير ذو المفاعل.