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MODELING OF CONTINUOUS STIRRED TANK REACTOR FOR ESTERIFICATION PROCESS

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Abstract. *This paper presents a comprehensive study on the synthesis of ethyl acetate through the esterification of acetic acid with ethanol using a continuous stirred tank reactor (CSTR). Ethyl acetate is a significant solvent in various industries due to its eco-friendly characteristics and economic efficiency. The study develops a detailed mathematical model focusing on the operating of the CSTR to enhance the understanding of the reaction kinetics and thermodynamics in a continuous processing environment. The reactor model was validated with experimental data to optimize process parameters, aiming to improve yield and selectivity. Key variables such as reactant ratios, and operational temperatures were methodically varied to study their effects on the esterification process. Results indicated that optimal conditions achieved a significant yield improvement while maintaining process sustainability. This research not only advances the operational efficiency of ethyl acetate synthesis but also supports the broader application of CSTR in similar chemical processes.*

Keywords. *reaction kinetics, simulation, ethyl acetate, esterification, continuous stirred tank reactor, reaction rate*

Annotatsiya. *Ushbu maqola uzluksiz aralashtirgichli reaktor (CSTR) yordamida sirka kislotasini etanol bilan eterifikatsiya qilish orqali etil asetat sintezi bo‘yicha keng qamrovli tadqiqotni taqdim etadi. Etil asetat ekologik toza xususiyatlari va iqtisodiy samaradorligi tufayli turli sohalarda muhim ertituvchi sifatida foydalaniladi. Tadqiqot uzluksiz ishlab chiqarish muhitida reaktsiya kinetikasi va termodinamikasini batafsil tushunish uchun CSTR ishlashini tavsiflovchi matematik model asosida imitatsion modellashtirish amalga oshirildi. Reaktor modeli jarayon parametrlarini optimallashtirish uchun eksperimental ma'lumotlar bilan muvofiqlikka tekshirilgan bo‘lib, samaradorlik va selektivlikni yaxshilashga qaratilgan. Reaktivlar nisbati va ish harorati kabi asosiy o‘zgaruvchilar ularning eterifikatsiya jarayoniga ta'sirini o‘rganish uchun uslubiy jihatdan g‘zgartirildi. Natijalar shuni kg‘rsatdiki, optimal sharoitlar asosida jarayonning barqarorligini saqlab, unumdorlikni sezilarli darajada oshirishga erishildi. Ushbu tadqiqot nafaqat etil asetat sintezida reaksiya unumdorligini oshiribgina qolmay, balki shu kabi kimyoviy jarayonlarda CSTR ning kengroq qg‘llanilishi bg‘yicha ham tadqiqotlar g‘tkazilishi maqsadga muvofiqligini kg‘rsatadi.*

Kalit sg‘zlar. *reaksiya kinetikasi,imitatsion modellashtirish, etil asetat, eterifikatsiya, doimiy aralashtirish reaktori, reaksiya tezligi*

Аннотация. *В данной статье представлено комплексное исследование синтеза этилацетата путем этерификации уксусной кислоты этанолом с использованием реактора непрерывного действия с перемешиванием (CSTR). Этилацетат является важным растворителем в различных отраслях промышленности благодаря своим экологическим характеристикам и экономической эффективности. В исследовании разрабатывается подробная математическая модель, ориентированная на работу CSTR, чтобы улучшить понимание кинетики реакции и термодинамики в среде непрерывной обработки. Модель реактора была подтверждена экспериментальными данными для оптимизации параметров процесса с целью повышения выхода и селективности. Ключевые переменные, такие как соотношения реагентов и рабочие температуры, методически варьировались для изучения их влияния на процесс этерификации. Результаты показали, что оптимальные условия позволили значительно повысить производительность при сохранении устойчивости процесса. Это исследование не только повышает эффективность синтеза этилацетата, но и поддерживает более широкое применение CSTR в аналогичных химических процессах.*

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Ключевые слова. *кинетика реакций, моделирование, этилацетат, этерификация, реактор непрерывного действия с перемешиванием, скорость реакции*

Introduction

Ethyl acetate is a solvent widely used in industrial applications, including coatings, adhesives, printing inks, and in the pharmaceutical industry. It is most commonly produced via the esterification of acetic acid with ethanol, a reaction that combines environmental friendliness with economic viability[1]. The growing demand for ethyl acetate due to its favorable solvent properties, including low toxicity and relatively fast evaporation rate, necessitates efficient production methods[2].

The continuous stirred tank reactor (CSTR) is among the most extensively utilized types of reactors in chemical process industries due to its simplicity and continuous operation mode[3]. However, the design and optimization of a CSTR for the production of ethyl acetate pose unique challenges due to the reversible nature of the esterification reaction and the need to manage byproduct formation and energy consumption[4]. An accurate reactor model is essential for optimizing these processes, reducing costs, and enhancing yield and selectivity.

Previous studies have focused on the batch processing of ethyl acetate and the kinetics of esterification under varying conditions of temperature and catalyst concentration[5]. Although valuable, these studies often do not translate directly into continuous process applications, which are operationally distinct and economically more viable for large-scale production. Some research has explored continuous processes but has often neglected aspects such as dynamic behavior under different operational settings and comprehensive energy balance considerations [6].

This study aims to bridge these gaps by developing a detailed mathematical model of a CSTR for the esterification process to produce ethyl acetate. By focusing on both the kinetics and thermodynamics within a continuous operational context, this model will provide insights into optimizing process parameters, enhancing reactor design, and improving the overall efficiency and sustainability of the production process. Moreover, this research will contribute to the broader field of chemical process modeling by introducing a validated model that incorporates a nuanced approach to the interaction between reaction kinetics and process dynamics. According to the results of the last research, various catalysts were used in the synthesis of ethyl acetate, including Ni-based [7], ZrC-based nano powder catalyst [8], CuO/CeO2-based catalysts [9], and ion-exchange resin catalysts[10].

Despite the development of heterogeneous catalysts, homogeneous acidic catalysts are still used in many studies. Usually, when ethyl acetate (EtAc) is synthesized based on etherification of acetic acid (HAc) and ethanol (EtOH) in the presence of acidic catalysts (sulfuric acid, methanesulfonic acid, phosphoric acid), water is also formed as an additional substance[11], [12], [13].

$$\mathrm{HAc} + \mathrm{EtOH} \xleftrightarrow{\text{kislota}(\mathrm{H}^+)} \mathrm{EtAc} + \mathrm{H_2O} \quad (1)$$

The acid esterification process has several practical difficulties related to the type of process (batch or continuous). The main problem is that the formation of water slows down the reaction, resulting in less ethyl acetate[14].

In this work, we discussed in detail on the modeling results of ethyl acetate synthesis based on esterification in a CSTR. The effect of key process parameters on the reaction performance is studied and discussed. These parameters include the amount of catalyst, the ratio of reactant ethanol to acetic acid, the initial concentration of ethanol, the reaction temperature, and other such factors. In this study, optimal conditions were selected based on known reaction kinetics and compared with experimental results.

Research Methods

The esterification of acetic acid with ethanol to form ethyl acetate (C) and water (D) can be represented by the following reversible reaction:

$$A + B \overset{cat}{\leftrightarrow} C + D \quad (2)$$

The kinetics of the reaction were assumed to follow first-order kinetics with respect to each reactant and product. The rate of the forward reaction and the reverse reaction are described by the rate constants k_f and k_r, respectively. The net rate of reaction r can be expressed as[15]:

$$r = k_f[A][B] - k_r[C][D] \quad (3)$$

$$k_f = 2.145exp\left(\frac{-13494}{RT}\right) \quad (4)$$

$$k_r = 0.0545exp\left(\frac{-9314}{RT}\right) \quad (5)$$

where, k_f, k_r– values representing the forward and reverse reaction rates, respectively.

The reactor modeled in this study is a continuous stirred tank reactor (CSTR) with a constant volume V. The reactor is equipped with a mechanical agitator to ensure uniform mixing of the reactants and products. The inflow and outflow rates of the reactants and products are controlled to maintain steady state conditions, with inflow concentrations corresponding to typical industrial feed ratios. Esterification of acetic acid with ethanol

was carried out in a two-liter stirred tank reactor. The optimal temperature for the reactor was selected by modelling. The inner diameter of the reactor is 60 mm and the height is 710 mm. It is provided with a water shell (jacket). As the main elements of the continuous system, a magnetic stirrer and a water bath are used to maintain the temperature of the reactor at a certain temperature. The calculated amount of reagents is mixed and the process is carried out at the specified temperature. There is a cooler to prevent substances from evaporating out of the reactor. After the reactants reach the desired temperature, the H_2SO_4 catalyst and the reactants are introduced into the reactor. During the 150-minute experiment, 2 ml of product samples were taken every 10 minutes. Four samples were randomly selected and centrifuged at 2500 rpm for 20 minutes to enhance the separation of the organic phase (ethyl acetate and unreacted acetic acid) and the aqueous phase (ethanol and water). A total of 5 different experiments were performed for different ratios of incoming reagents. During the two-hour experiment, samples were taken from the reactor for analysis every 10 minutes. Four 1 mL samples of the upper organic layer were analyzed by 0.1 M KOH titration method using phenolphthalein indicator to determine acid value (AV). Then, the conversion of acetic acid and the quantitative value of the formed ethyl acetate were calculated using the following equations (Eqs. 6-7):

$$AV = \frac{KOH\ content\ (mL) \times N \times 56.1}{sample\ weight} \quad (6)$$

$$x_{HAc}, \% = \frac{AV_{t0} - AV_t}{AV_{t0}} \quad (7)$$

For each component i (i.e., A, B, C, D), a steady-state mass balance was performed:

$$F_{in,i} - F_{out,i} + r_i V = 0 \quad (8)$$

where $F_{in,i}$ and $F_{out,i}$ are the molar flow rates of component i entering and leaving the reactor, and r_i is the rate of generation (or consumption) of component i per unit volume, V.

The energy balance for the reactor was calculated to account for the thermal effects of the reaction and external heat transfer:

$$Q + F_{in}C_pT_{in} - F_{out}C_pT_{out} - \Delta H_r rV = 0 \quad (9)$$

where C_p is the heat capacity of the mixture, T_{in} and T_{out} are the inlet and outlet temperatures, Q is the heat added or removed, and ΔH_r is the heat of reaction.

According to the obtained experimental results, a simulation model of the process was built in the Aspen Plus program and checked for validity (Fig. 1). In this case, the UNIFAC method based on activation energy was used to take into account the thermodynamic properties of the process. In statistical thermodynamics, the UNIFAC method is a semi-empirical system used to predict non-electrolyte activity in non-ideal mixtures. UNIFAC uses the functional groups present in the molecules that make up the liquid mixture to calculate activity coefficients [16].

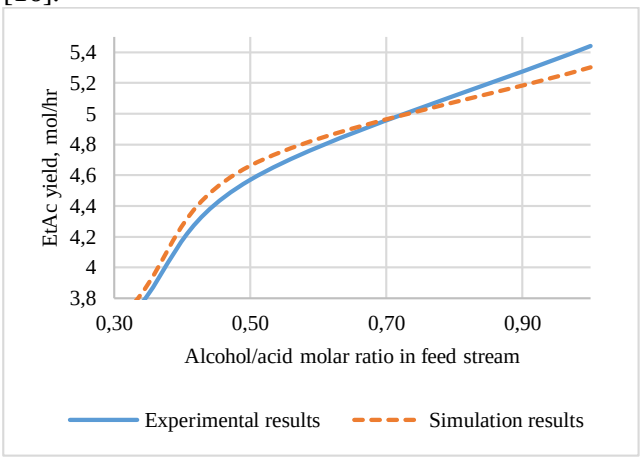

Fig.1. Model validation results

After checking the consistency of the modeling results with the experimental results, the industrial scale ethyl acetate synthesis process was analyzed according to these kinetic parameters. As the initial consumption of raw materials, 100 kmol per hour was chosen for alcohol and acid.

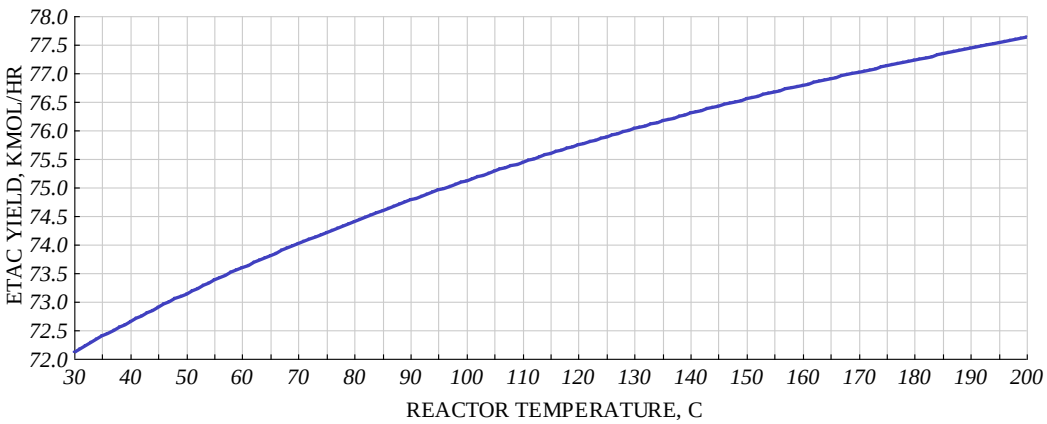

Fig.2. Effect of temperature on reaction yield

Results and discussions

Effect of temperature and residence time on reaction efficiency

The temperature at which the process is carried out is important in reaction kinetics, and according to the Arrhenius equation, the reaction rate constant changes depending on the reaction temperature. When analysing the effect of temperature on the reaction conditions using 99% pure ethyl alcohol according to the given reaction kinetics, it was shown that at a temperature of 95-100 ºC, a yield of at least 75 percent was achieved with respect to the raw materials of acetic acid (Fig. 2), which is consistent with the experimental results. It was observed that the reaction yield increases as the temperature in the reactor increases, but the required reaction yield was assumed to be 75% to ensure consistency with the experimental results and reduce excess energy consumption. In this case, alcohol/acid molar ratio was taken as 1:1.

Figure 3 shows the influence of the reactor residence time on the productivity. The maximum productivity was achieved when the time of the presence of reactants in the reactor was 1.5 hours. Further time change did not significantly affect the yield of this reaction.

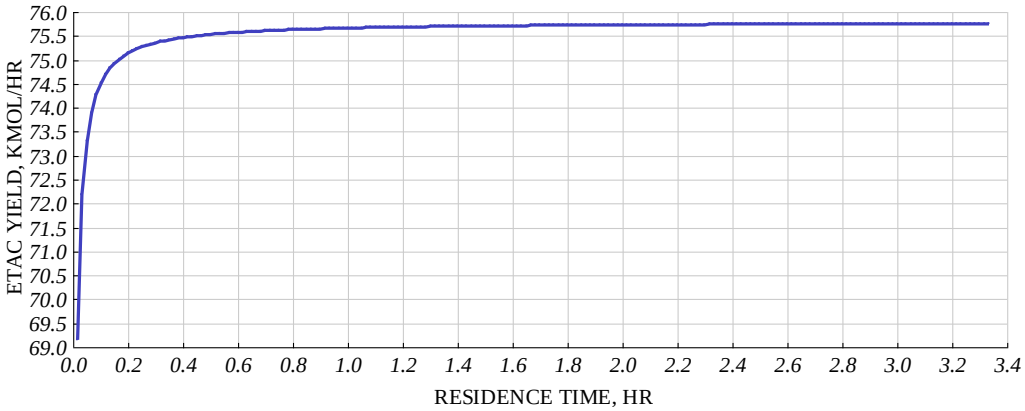

Fig.3. Effect of residence time on reaction yield

Effect of ethanol flow rate and concentration on reaction efficiency

Esterification of acetic acid with ethanol is a stoichiometric reverse reaction at a 1:1 alcohol/acid molar ratio. Usually, an excess amount of ethanol is used to achieve a good yield of ethyl acetate. Table 1 shows the yield of ethyl acetate formation at 95 ºC, τ=90 minutes and in the presence of 4% catalyst, using different concentrations of ethanol at different initial ethanol/acetic acid molar ratios. According to the modeling results, it was observed that the higher the concentration of ethanol, the higher the production efficiency of ethyl acetate. It was found that when the alcohol/acid molar ratio increased from 1:1 to 3:1, the reaction efficiency reached up to 95 molar fractions compared to acetic acid. When this ratio was higher than 3:1, the growth rate did not increase significantly (Fig. 4). In this case, the consumption of acetic acid in the raw material stream was taken in the amount of 100 kmol/h. It should be remembered that the higher the ratio of incoming impurities, the higher the percentage of additional products in the mixture of products leaving the reactor, and this causes to the higher the cost of separating this mixture.

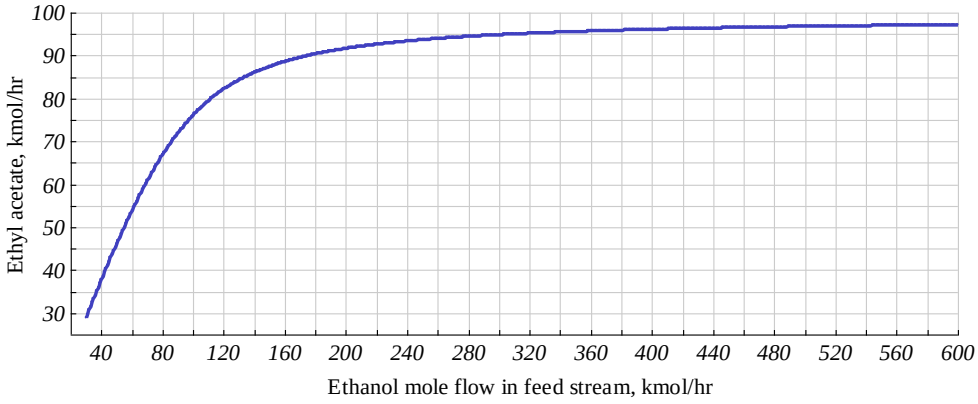

Fig.4. Effect of ethanol flow rate on reaction yield

From Table 2 and for each ethanol concentration, the yield of ethyl acetate increased proportionally with the increase of the alcohol/acid ratio, and it can be understood that when this ratio

increases from 1/1 to 3/1, the yield of ethyl acetate increases significantly, and then this ratio increasing from 3/1 to 6/1 did not significantly increase the ethyl acetate yield. Similarly, increasing ethanol concentration slightly increases the yield of ethyl acetate (Table 1) and produces less water per mole of acetic acid feed.

Table 1

Change in reaction productivity at 95 ºC temperature and in the presence of 4% catalyst at different concentrations of ethanol raw materials

Alcohol/acid molar ratio	Ethyl acetate production efficiency with respect to 100 kmol/hr acetic acid raw-material, kmol/hr		
	90 mol% ethanol	95 mol% ethanol	99 mol% ethanol
1/1	70.1	73.7	75.7
2/1	89.1	90.5	91.5
3/1	93.0	94.1	94.7

Conclusion

This study developed and validated a mathematical model for synthesizing ethyl acetate via esterification in a continuous stirred tank reactor (CSTR), demonstrating its predictive accuracy against experimental data under various conditions. Key findings highlight the significant impact of catalyst selection, reactant ratios, and temperature on reaction efficiency and yield. Optimal conditions were identified that enhance ethyl acetate yield while reducing byproducts and energy use. Notably, using a sulfuric acid catalyst and maintaining a stoichiometric balance between acetic acid and ethanol, along with operating at 95-100°C, optimized the reaction rate and product yield. This research provides valuable insights for applying CSTR dynamics to industrial esterification, offering guidelines that improve efficiency and sustainability. Future work should integrate this model with real-time systems to optimize production further and broaden its application to other esterification processes. This study significantly advances chemical engineering by refining process design and operations for producing ethyl acetate in a CSTR, underscoring the benefits of detailed modeling and experimental validation for sustainable industrial processes.

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