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Benzenesulfonic Acid - an Green Efficient Esterification Catalysts for Continuous Synthesis of n-propyl Acetate

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Abstract: *The esterification of acetic acid and n-propanol catalyzed by benzenesulfonic acid and its derivatives in the batch and continuous rectification tower was studied, in order to develop a new effective and green catalyst instead of the oxidative and corrosive sulfuric acid. A series of the comparison system with sulfuric acid was build for the targeted and fast evaluation of catalysts. The results showed that the catalytic esterification activity of p-phenolsulfonic acid and p-toluenesulfuric acid is very closed to sulfonic acid in the continuous rectification tower. Furthermore, the stability test for continuous esterification with p-toluenesulfuric acid presented that the high yield of n-propyl acetate could maintain 50 hours and stability. Therefore, p-phenolsulfonic acid and p-toluenesulfuric acid could be prospective substitutes for sulfuric acid for the continuous synthesis of n-propyl acetate in the rectification tower.*

Keywords*: Esterification, n-propyl acetate, benzenesulfonic acid, continuous synthesis*

1. Introduction

As we know, sulfuric acid has been widely used as the catalyst in esterification. However, it is extremely oxidative and corrosive, leading to the formation of side reaction and the corrosion of equipment [1]. Worse still, it requires additional neutralization and separation steps with the catalyst being disposed as salts, which generally increases processing costs and contributes to strong acid contaminative source [2]. To overcome these drawbacks, the use of homogeneous and heterogeneous catalysts, such as p-toluenesulfuric acid [3-5], acidic ionic liquids [6, 7], acid resins [8-10], heteropoly acids [11, 12], solid acids [13, 14] and molecular sieves [15-17] have been reported. Nevertheless, in general, these catalysts have been almost used in the batch reactor, and no comparison with sulfuric acid, especially in continuous synthesis of acetate esters.

In the recent years, the continuous synthesis process of n-propyl acetate have been used to enhance the reaction efficiency and save energy consumption, compared to the traditional batch reaction [18-21].

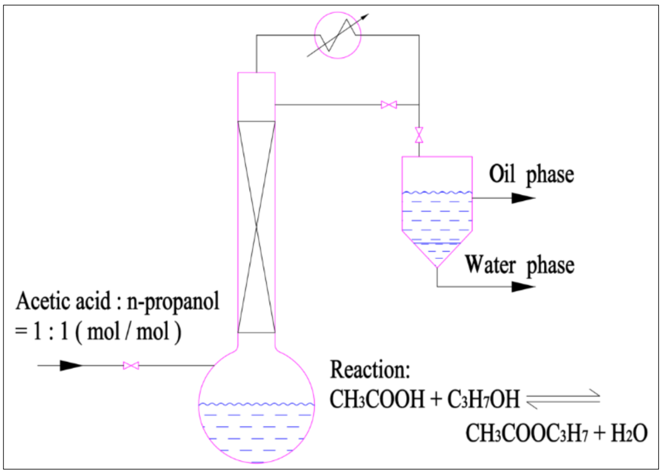

Figure 1. the continuous synthesis process of n-propyl acetate

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As shown in Figure 1, the reaction product is removed along with the reaction in the continuous reactive distillation, due to water and n-propyl acetate can be formed azeotrope with low boiling point. This is benefit to esterification reaction and catalyst consumption [22, 23]. However, the oxidative product and corrosion problems is unavoidable for sulfuric acid [14, 19, 21]. In order to improve those defects, the researchers introduced reactive distillation with solid catalysts, which typically utilizes a acid resin as catalyst. But the resin exhibit relatively poor heat-resistance and regeneration, not suitable for the continuous synthesis process [19]. Thus, it is significantly to develop a new effective catalyst that can replace sulfuric acid.

Benzenesulfonic acid and its derivatives are strong organic acids with sulfuric acid groups (-SO_3H). These catalysts have weaker oxidation and corrosion properties than sulfuric acid. Yao et al. [5] studied esterification with p-toluenesulfuric acid in the microchannel reactor. The yield of n-propyl acetate reached 92.2%, and had no other byproducts. Tran et al. [24] used benzenesulfonic acid and its derivatives as catalysts for transesterification of soybean oil in batch. Moreover, benzenesulfonic acid has present an effective catalytic performance in other acid catalyzed reactions [25, 26]. Nevertheless, in general, these catalysts have been almost no comparison with sulfuric acid during their study.

In fact, the esterification for acetate esters is an autocatalytic reaction [27-29]. However, the reaction rate of autocatalytic esterification reaction is still low, and uneconomical for industrial production. Thus, catalyst is a must for these reaction. This work attempted to provide basic information used for comparison with the catalytic performance of sulfuric acid. Specifically, the aim of this research focused on benzenesulfonic acid and its derivatives as catalysts for the continuous synthesis process of n-propyl acetate.

2. Materials and methods

2.1. Materials and reagents

Esterification of acetic acid (99.5%, Shanghai Aladdin) and n-propanol (99.5%, Shanghai Aladdin) occurred in the reaction kettle or rectification tower. Sulfuric acid (SA，98%) was procured from Sinopharm Chemical Reagent Co., Ltd. P-toluenesulfuric acid (PTSA, 99%), p-phenolsulfonic acid (PPSA, 99%), benzenesulfonic acid (BSA, 98%), 2, 4-dimethylbenzenesulfonic acid (DBSA, 98%), 2-naphthalenesulfonic acid (NSA, 98%), 4-aminobenezesulfonic acid (ABSA, 99.5%) and calcium dobesilate (CD, 98%) were obtained from Shanghai Aladdin, and used without further purification.

2.2. Experimental methods

In a typical batch reaction, a 150 mL round bottomed flask equipped with reflux condenser was used. Acetic acid (0.80 mol) and n-propanol (0.80 mol) were charged into the flask. After achieving the reaction temperature (50℃), the weighed quantity of catalyst (5-20 mmol) was added into the mixture. The reaction mixture collected at regular intervals was analyzed immediately.

In the general continuous esterification process with rectification tower, a 250 mL round bottomed flask equipped with rectifying column (internal diameter 25 mm, height 500 mm, glass spring filler), reflux condenser, micro-infusion pump (Shanghai Lande) and temperature recorder (Hangzhou Meacon) was used. Acetic acid (1.20 mol), n-propanol (0.40 mol) and catalyst (10 mmol) was previously added into the flask. The reaction mixture in the tower bottom was preheated to 105±3℃. Then, the reflux condenser in the tower top was turned on. When the condensed fluid was found and flowed into the tower, the reactants began to feed continuously with a total flow (25 mL h-1) into the tower bottom. The molar ratio of acetic acid and n-propanol is 1:1. After 30 min, the distilled product in the tower top was cut out with a reflux ratio 1:1. The oil phase and water phase were collected separately after standing and layering.

The stability test for esterification with PTSA in the rectification tower was similar with continuous esterification process. The initial feed in the tower bottom was acetic acid 1.2 mol, n-propanol 0.4 mol and catalyst PTSA 20 mmol. The continuous feed in the tower bottom was 50 mL h^{-1}, and composed of acetic acid and n-propanol (mole ratio 1 : 1.02). The reflux ratio is 1:1. At intervals of about 10 h, the product in the tower top and the reaction liquid in the tower bottom was detected.

2.3. Analysis methods

The analysis of the samples was done with a gas chromatograph (Shimadzu, GC-2018) equipped with a FID detector and a capillary column 0V-19 (30 m × 0.32 mm × 0.25 μm) by normalization method. Detection was conducted at column temperature of 50℃ for 5 min, then heated with a rate of 25℃ min-1 to 100℃ and kept 3 min. The temperatures of the inlet and the detector were set to be 200℃.

Ultraviolet-visible spectra (UV-vis) of samples were obtained on a UV-vis spectrometer (UVmini-1280, Shimadzu).

3. Results and discussions

3.1. Esterification with SA in Reaction Kettle

One-pot synthesis is a fast and effective methods for catalyst sifting [30-32], and is also applied for esterification. In addition, due to SA has excellent catalytic efficiency. It would be shown very distinct catalytic activity among different content of SA in reaction mixture. This is a good comparison system for developing a new catalyst on the esterification reaction.

It is observed that the yield of n-propyl acetate increases as reaction time increases in Figure 2. However, there is not much gain in product after 120 min, except for SA-0 that without any catalyst. The highest yield of n-propyl acetate is about 70%. This is attributed to chemical reaction equilibrium at the last of esterification. The difference of ester yields at 60 min is most obviously. Thus, these catalytic activities with the same reaction condition at 60 min would be a uniform comparative standard.

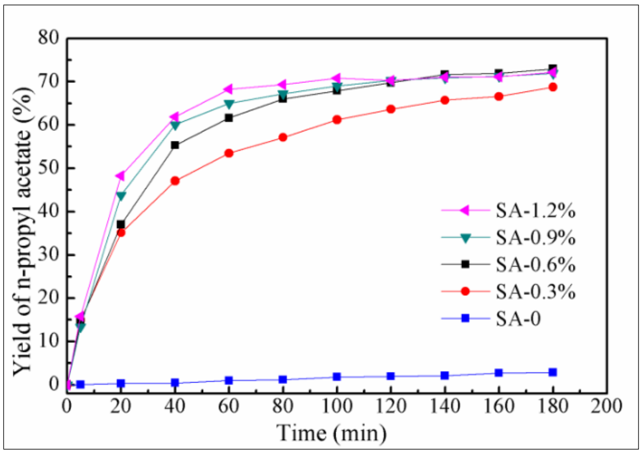

Figure 2. Effect of different dosage of SA on the yield of n-propyl acetate in the reaction kettle.
Catalyst: (acetic acid + n-propanol) = 0 ~ 1.2: (50 + 50) (mol/mol), reaction temperature at 50℃.

3.2. Esterification with SA in Rectification Tower

Table 1. The esterification reaction of acetic acid and n-propanol with different dosage of SA in rectification tower

Sr. No	Catalyst amount (mmol)	Volume distribution (%)			The composition of oil phase (%)			
		Oil phase	Water phase		n-propanol	Acetic acid	n-propyl acetate	Others
SA-20	20	84.97	15.83		1.24	0	98.73	0.03
SA-15	15	83.33	16.67		1.26	0	98.71	0.04
SA-10	10	82.10	17.90		1.39	0	98.57	0.04
SA-5	5	83.19	16.81		1.74	0	98.22	0.04

The effects of SA concentration in rectification tower were also investigated. It is presented that the product at the top of the rectification tower was divided into Oil phase and water phase after standing for layering, in Table 1. The volume fraction of Oil phase was 82~85%, and was not changed regularly with the dosages of SA ranging from 5 mmol to 20 mmol. Moreover, the purity of n-propyl acetate has a little improvement. The others attributed to impurity of the starting materials. However, these variation of product properties was so slight that it is difficult to evaluate the catalytic activity in the continuous esterification process.

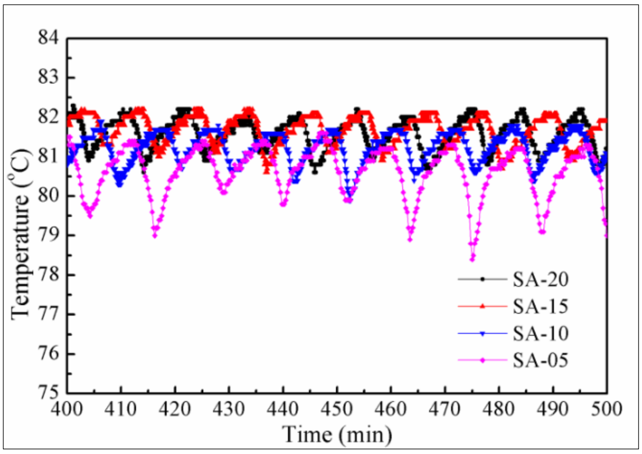

Figure 3. The temperature variation regularity from 400 min to 500 min at the top of the rectification tower after the reaction begins

The temperature at the top of rectification tower is the azeotropic point of distillate [33, 34]. Thus, a real time measurement of the tower top was done to detection the variation of distillate in time. The temperature variation regularity from 400 min to 500 min after the reaction begins is presented in Figure 3. The temperature was shown an obvious periodical change characteristics. The fluctuation range of these temperature profiles is from 78.4 to 82.3℃. Moreover, it decreased with reducing the dosage of SA, as well as the wave peak and trough. These could be attributed to the catalytic rate in the tower decreased as the catalyst content declines.

Furthermore, despite the continuously feed with the molar ratio 1:1 of acetic acid and n-propanol, the concentration of n-propanol in the product was detected, due to the formation of ternary azeotrope of n-propanol/water/n-propyl acetate. The mentioned characteristics result that the acetic acid would be enriched endless in the tower bottom. However, this had no influence for the evaluation of catalysts. Therefore, the continuously variable temperature in the tower top could be the comparison parameter, which is used to evaluate the catalytic activity with that of SA.

3.3. Esterification with BSA and its Derivatives in Reaction Kettle

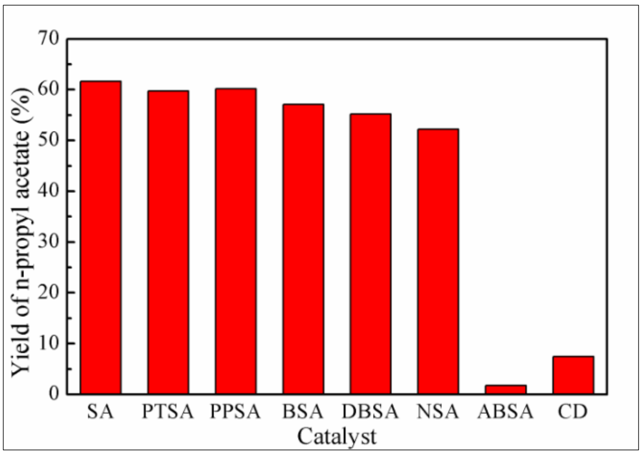

Figure 4. The yield of n-propyl acetate of benzenesulfonic acid and its derivatives in the reaction kettle. Catalyst: (acetic acid + n-propanol) = 1.2: (50 + 50) (mol/mol), reaction temperature at 50℃, reaction time 60 min.

The effectiveness of benzenesulfonic acid and its derivatives with the same reaction condition for the esterification of acetic acid and n-propanol in reaction kettle was investigated. As shown in Figure 4, the order of yield of n-propyl acetate formed was SA > PPSA > PTSA > BSA > DBSA > NSA > CD > ABSA. And the catalytic activity of PPSA and PTSA was about 60%, and very close to that of SA. Whereas, CD and ANSA catalyze the esterification reaction to have yields of only 7.5% and 1.8% respectively. This is primarily ascribed to the worst acidity from their molecular structure among all the catalysts investigated. Therefore, it is demonstrated that the activity order of the catalysts is consistent with the acidity order. The excellent catalytic performance of PPSA and PTSA offers the possibility to develop a eco-friendly and low corrosion catalyst in the continuous synthesis of n-propyl acetate.

3.4. Esterification with BSA and its Derivatives in Rectification Tower

The results in Table 2 and Figure 5 presented the esterification reaction of acetic acid and n-propanol with PPSA and PTSA in rectification tower. The volume fraction of Oil phase was 82~84%, and close to the stoichiometric ratio of n-propyl acetate and water. It was obvious that the catalytic efficiency of PPSA-10 is very close to that of SA-10. While in the case of PTSA-10, its yield of n-propyl acetate fell little to that of PPSA-10. In general, all these data show that the catalytic activity of PPSA and PTSA is closed to that of SA with the same reaction condition, agreed with the results in the reaction kettle. In addition, compared to SA, PPSA and PTSA have less by-product in the continuous esterification reaction.

Table 2. The esterification reaction of acetic acid and n-propanol with PPSA and PTSA in rectification tower

Catalyst	Catalyst amount (mmol)	Volume distribution (%)			The composition of oil phase (%)			
		Oil phase	Water phase		n-propanol	Acestic acid	n-propyl acetate	Others
SA	10	82.10	17.90		1.39	0	98.57	0.04
PPSA	10	83.56	16.44		1.67	0	98.31	0.02
PTSA	10	82.67	17.33		1.98	0	98.00	0.02

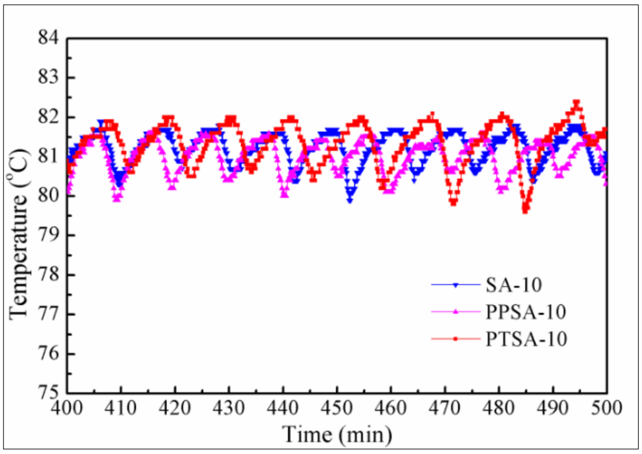

Figure 5. The temperature variation regularity from 400 min to 500 min at the top of the rectification tower after the reaction begins

The temperature variation regularity from 400 min to 500 min after the reaction begins is presented in Figure 5. The temperature was shown an obvious periodical change characteristics caused by the incompatibility between reaction and separation. The fluctuation range of these temperature profiles is from 80°C to 82°C. There is no obvious difference, and also means their similar catalytic activity.

3.5. Stability test for esterification with PTSA

To evaluate the stability of PTSA for the continuous esterification reaction, an intermittent activity test for a total 50 h had been done. The result showed that the yield of n-propyl acetate has little change in the whole reaction process. After five sections, the catalytic performance remain close to 99% and no further deactivation could be observed. In addition, the esterification was reacted, and the product (n-propyl acetate and water) was separated at the same time in the continuous process. Then, the reaction efficiency would be increased. The temperature on tower top was in the range of 82-85℃, and kept stable for a long time as well as the yield of n-propyl acetate in Figure 6. Furthermore, UV-vis analysis clearly shows that the coke and side product content in reaction liquid is higher after reaction in Figure 7. However, this change decreases gradually with the reaction, and has no effect on the conversion efficiency in the short run. These indicates that the continuous esterification reaction for PTSA is stable during the reaction time.

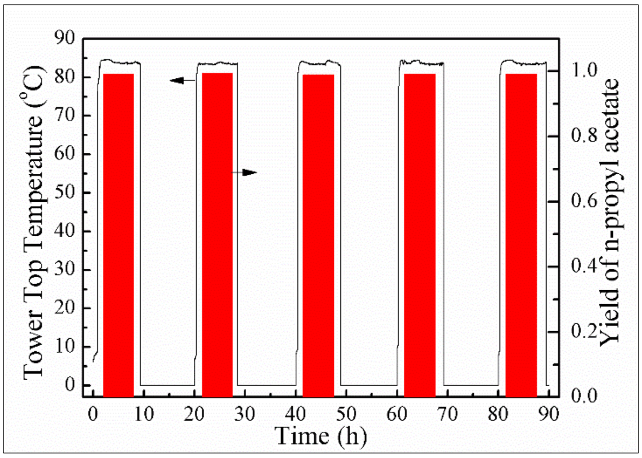

Figure 6. The stably test of the continuous synthesis of n-propyl acetate catalyzed by PTSA

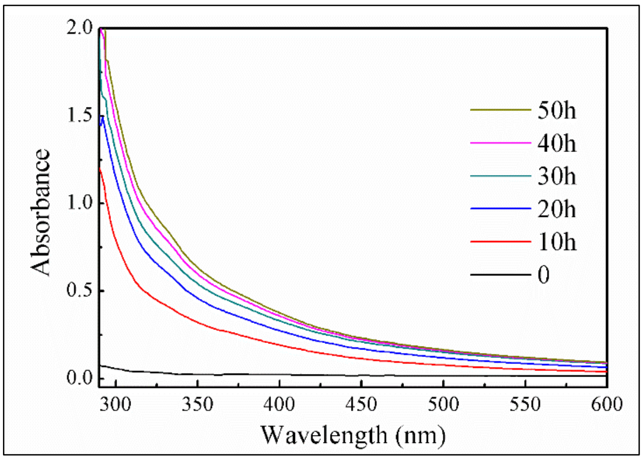

Figure 7. UV-vis spectra of the reaction liquid with different period of time

4. Conclusions

In this work, we developed an green efficient and stable catalyst for continuous synthesis process of n-propyl acetate. In the batch process, the catalytic activity of benzenesulfonic acid and its derivatives has been fast evaluated by the comparison system with sulfuric acid. The results presented that the yield of n-propyl acetate for PPSA and PTSA was about 60%, and slightly worse than that of SA in the same reaction condition. However, in the continuous process, acetic acid was completely converted into n-propyl acetate for PPSA and PTSA, due to reaction and distillation. Moreover, their performance was closed to SA, and had less by-product. The intermittent stability test for 50 h showed that PTSA catalyst had excellent stability. Therefore, benzenesulfonic acid could be a suitable replacement for the oxidative and corrosive sulfuric acid catalyst used in the continuous esterification.

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