

Study on Optimization of Product Processing of Pyruvic Acid Its Separation and Purification

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Abstract

The preparation of pyruvic acid from lactic acid with hydrogen peroxide as the oxidant and ferrous sulfate as the catalyst was carried out with the ratio of lactic acid and hydrogen peroxide being 1:1.1 the reaction was processed at 40 °C and the amount of ferrous sulfate was 1.5g. After 4 hours, raw product of pyruvic acid was taken and the separation and purification process started using an ion exchanging resin D315 then vacuum distillation respectively and pyruvic acid content was determined by the UV spectrophotometer.

Keywords: lactic acid; pyruvic acid; catalytic oxidation; UV spectrophotometer

Introduction

Pyruvic acid is an organic acid; it has a carboxylic acid and a ketone functional group, and is the simplest homologue of the α -keto acids finding its uses in almost all the industries such as food, pharmaceutical, cosmetics, pesticides, feed and others. Pyruvic acid is a colorless liquid with a smell similar to that of acetic acid and is miscible with water. It was first characterized and named by Jöns Jacob Berzelius a year after Théophile-Jules Pelouze distilled both tartaric acid (L-tartaric acid) and racemic acid (a mix of D- and L-tartaric acid) and isolated pyro tartaric acid (methyl succinic acid [1]) and another acid [2] in 1834. The demand for pyruvic acid and its derivatives is increasing. Its high value-added market potential is huge making it a very good developing prospects.

The carboxylate anion of pyruvic acid, a Brønsted–Lowry conjugate known as pyruvate, is an important compound in biochemistry and is a key intersection in several metabolic pathways. Pyruvate is the output of the metabolism of glucose known as glycolysis. [3], converted back to carbohydrates (such as glucose) via gluconeogenesis, or to fatty acids through acetyl-CoA. It can also be used to construct the amino acid alanine and be converted into ethanol. Pyruvic acid supplies energy to living cells through the citric acid cycle (also known as the Krebs cycle) when oxygen is present (aerobic respiration), and alternatively ferments to produce lactate when oxygen is lacking (fermentation).

Pyruvic acid is the simplest homologue of the α -keto acids, which were recently reviewed by Cooper et al. [4]. Established procedures for synthesis of pyruvic acid are the dehydrative decarboxylation of tartaric acid in the presence of potassium hydrogen sulfate and the hydrolysis of acetyl cyanide. Vapor-phase contact oxidation of alkyl lactates to corresponding pyruvates has already been attempted in patents using V_2O_5 -based mixed oxide catalysts [5, 6]: $CH_3-CH(OH)-COOR + 0.5O_2 \sim CH_3-CO-COOR + H_2O$ where R is generally a methyl or ethyl group. The selectivity to pyruvate is about 90 mol-% at a lactic acid conversion of above 95%. Hayashi and co-workers [7, 8] have studied the catalytic performances of various MoO_3 -based mixed oxides for the reaction of ethyl lactate to form ethyl pyruvate. They proposed TeO_2-MoO_3 catalysts as the best; the selectivity to ethyl pyruvate reached more than 90 mol-% at an ethyl lactate conversion of about 80%.

There are different ways of synthesis of pyruvic acid such as enzymatic, biotechnological, chemical...; but more and more the chemical method has been used. Here we want to design and synthesize pyruvic acid by simple and reproducible methods in the laboratory level so that this synthesis can be extended to the industry level therefore optimizing the use of pyruvic acid in the different industries. So we prepare our pyruvic acid from lactic acid hydrogen peroxide and ferrous sulfate.

Experiment

* Material

All the materials are listed in the following tables 1 to 2.

Table 1- Experiment reagents

Name	molecular formula	norms	manufacturers
Lactic acid	CH ₃ CHOHCOOH	analytically pure	Chinese medicine group reagent co., LTD
Hydrogen peroxide	H ₂ O ₂	analytically pure	Chinese medicine group chemical reagent co., LTD
Ferrous sulfate	FeSO ₄ •7H ₂ O	analytically pure	Chinese medicine group chemical reagent co., LTD
Potassium iodide-starch paper	-	-	-
Distilled water	H ₂ O	analytically pure	Chinese medicine group chemical reagent co., LTD
Hydrochloric acid	HCl	analytically pure	Chinese medicine group chemical reagent co., LTD
Sodium hydroxide	NaOH	analytically pure	Chinese medicine group chemical reagent co., LTD
Acetic acid	CH ₃ COOH	analytically pure	Chinese medicine group chemical reagent co., LTD
Ethanol	CH ₃ CH ₂ OH	analytically pure	Chinese medicine group chemical reagent co., LTD

Table 2 - Experiments instruments

Instrument name	Manufacturers
UV spectrophotometer	Institute of production of the instruments from Shimadzu
Water bath pot	Guohua electric appliance co., LTD
Power electric blender JB50 - type D	Jiangyin poly research machinery co., LTD
Analytical balance	Shanghai OHAUS Company
Electronic balance YP1200	Shanghai precision scientific instrument co., LTD
Three neck flask	—
Thermometer	—
Condenser	—
Iron stand	—

3- Other materials

D315 anionic exchange resin Nankai university chemical plant
 Glass ion exchange column Φ20mmx1000mm

4- Main solvents

- (1) 5% NaOH solution: Used for washing and recycling the resin;
- (2) 5% HCl solution: Used for washing and recycling the resin;
- (3) 2mol/L HCl solution: Used as eluent, extraction and ion exchange resin on adsorption of pyruvic acid

* Preparation

28.8ml lactic acid (0.4mol) is added into a three-necked flask with a condenser tube and a stir in it. A little ferrous sulfate is added too (1.5g) as a catalyst. Hydrogen peroxide is dropped slowly (6.5ml each 30 minutes till it reach the total amount of 35.5mL) while stirring. At the same time, the flask is put into water bath at 40°C for 4 hours. We check the arrival of the reaction by dipping the tip of the potassium iodide-starch paper; the lack of coloration indicates the absence of ferrous sulfate therefore we know that all our reagents have reacted. The raw product is taken for the thin layer chromatography.

* Separation

The resin used in this case is D315 a weak base type ion exchanging resin. D315 will be pretreated before use for the separation by washing it first with HCl and NaOH solutions respectively at a temperature under 50°C; then washed with tape water in order to neutralize the acidity or basicity of the hydrochloric acid or sodium hydroxide used before (ph=7). The pretreatment is done with the resin already in the column.

Now the separation can start in the column which is an ordinary burette in this case; we put all of these in a particular order: a thin layer of wool or cotton in this case to prevent the stationery phase to be washed out of

the column, then our resin followed by the mixture to separate that is our raw product and finally the solvent on top that we keep adding so that the column never dries out as it keep running through. We collect what comes out of the bottom of the column in a whole series of labelled tubes. The quantity of resin used is 1.1 times the biggest amount of raw product that the resin can adsorb. We identify which of our samples collected at the bottom of the column contain the desired product by the method of the UV spectrophotometer and compared the results with those of the standard of our desired product.

* Purification

Once the sample containing our pure product is identified, we finally proceed to the purification by the method of vacuum distillation to remove the solvent, it was simulated by the software Aspen plus.

Result and Discussion

As shown in fig.1, three different standards were used: pyruvic acid, acetic acid and lactic acid; through the comparison of each standard on the spectra curve we find that when the wavelength is measured at 320 nm, lactic acid and acetic acid absorbance value is almost zero therefore will not affect the determination of pyruvate. The molecules of pyruvic acid here have properties of strong absorption band in 290 -340 nm, hence established a spectrophotometric method of determination of pyruvate concentration.

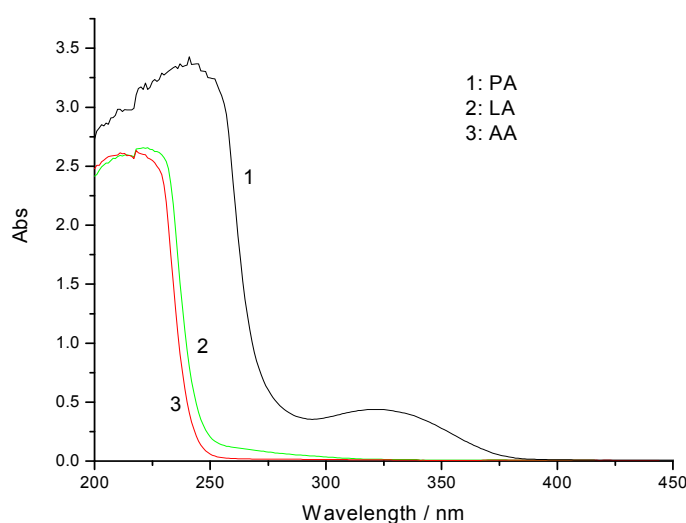


Fig. 1 Ultraviolet absorption spectra of acetic acid, lactic acid and pyruvic acid

Standard curve of pyruvic acid is shown in Fig. 2 x represent the quantity of pyruvic acid; c the concentration of the solution; A the UV absorbance value of pyruvic acid. According to the standard curve shown in the figure above the regression equation drawn is:

$$y = 0.10902x - 0.00727 \text{ with the coefficient of correlation } R = 0.99755; c = 9.1726A + 0.0667$$

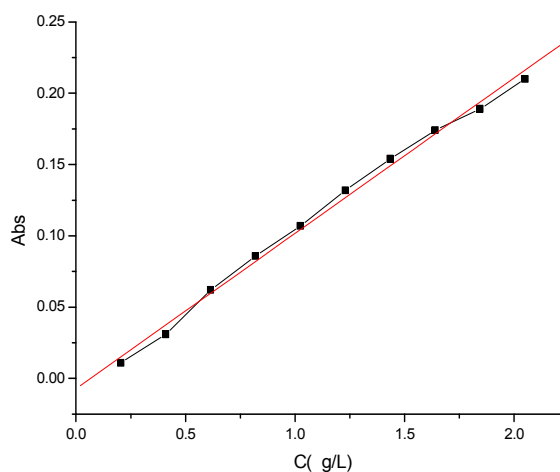


Fig.2 Standard curve of pyruvic acid

So by this equation, the absorbance of pyruvic acid can be obtained same for the product concentration and the yield of the reaction calculated.

$$A = 0.505; c = 9.1726A + 0.0667 = 4.6989 \text{ mg/L}$$

Number of dilution 160, so the actual concentrations: $4.6989 \times 160 \div 1000 = 0.7518 \text{ mg/ml}$

The actual volume of solution is: 120 mL; so the quantity is: $120 \times 0.7518 = 90.216 \text{ g}$

The total quantity of the raw product is 150.34g; the yield of the reaction is $\frac{90.216}{150.34} \times 100\% = 60.01\%$

The quantity of resin used was calculated after establishing the table of the uptake of the quantity of pyruvic acid (standard) adsorb per time in table 3.

Q_t was calculated as follow: we took 10 g after pretreatment of D315 resin, put into a beaker, add 50 ml of 60.028 g/L of pyruvic acid standard solution, and put the beaker into the air bath under 25 °C in a thermostat oscillator with a generator speed of 120 r/min. Each time we take 50uL of supernatant fluid at a certain ratio diluted took it to the UV absorbance measurement.

$$Q_t = \frac{(C_0 - C_t)V}{m}$$

C_0 — the initial concentration;

C_t — concentration at time t;

V — the volume of the solution;

m — the dosage of the resin.

Table 3 . The uptake of the quantity of pyruvic acid (standard) adsorb per time

T (min)	0	5	30	75	105	135	255	315	375	435
Q_t (mg/g)	0	175.71	186.53	209.50	240.59	270.33	267.63	267.90	268.10	268.34

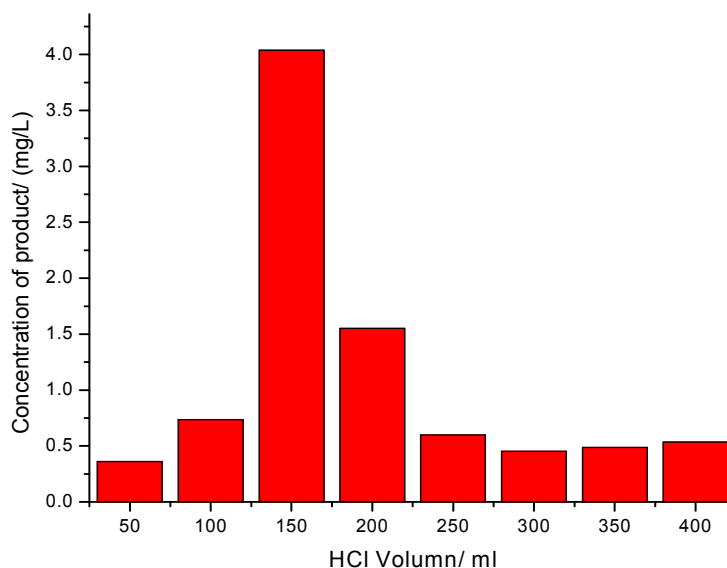


Fig.3 Curve of the resin elution

D315 resin maximum adsorption quantity of the pyruvic acid crude product is 267.63 mg/g. it can be seen from the diagram in fig.3 that for hydrochloric acid solution volume equals to 150 ml we have the maximum concentration of pyruvic acid eluted. The best proportion of hydrochloric acid eluent is 20:300g/ml

The quantity of standard pyruvic acid is 20g the required amount of the resin is: $\frac{20 \times 60.01\% \times 1000}{267.63} \times 1.1 \approx 50 \text{ g}$

These are the graph obtained from both the standard of pyruvic acid and our samples collected. According to the characteristics of pyruvic acid molecules, spectrum in 290 ~ 340 nm zone has strong absorption band, hence established and determined by spectrophotometry at 320 nm, pyruvic acid concentration is 0.2 ~ 2.8 g/L within the scope of Lambert-Beer law.

By using the Aspen plus software we simulate the vacuum distillation process. The data are shown in Table 4 and Fig.4. It can be seen that pyruvic acid can be separated and purified from other byproducts by vacuum distillation. Vacuum distillation conditions were determined as follows:

- Vacuum pressure: 0.08 Mpa, temperature 70 °C we steamed out by-products;
- Improve the vacuum degree to 0.09 Mpa, the temperature to 100 °C, refined products are obtained.

Table 4 Boiling points of PA, AA and W at the different pressures

Case	pressure / Mpa	pyruvic acid (PA)	acetic acid (AA)	distilled water (W)
1	0.010	99.6	56.0	45.8
2	0.015	109.5	65.2	54.5
3	0.20	116.8	72.1	60.1
4	0.025	122.7	77.7	65.0
5	0.030	127.7	82.4	69.1
6	0.035	132.0	86.5	72.7
7	0.040	135.9	90.2	75.9
8	0.045	139.3	93.4	78.7
9	0.050	142.5	96.4	81.3
10	0.055	145.4	99.2	83.7
11	0.060	148.1	101.7	86.0
12	0.065	150.6	104.1	88.0
13	0.070	152.9	106.4	90.0
14	0.075	155.1	108.5	91.8
15	0.080	157.2	110.5	93.5
16	0.085	159.2	112.4	95.2
17	0.090	161.1	114.2	96.7
18	0.095	162.9	115.9	98.2
19	0.100	164.6	117.6	99.6
20	0.105	166.3	119.2	101.0
21	0.110	167.8	120.7	102.3

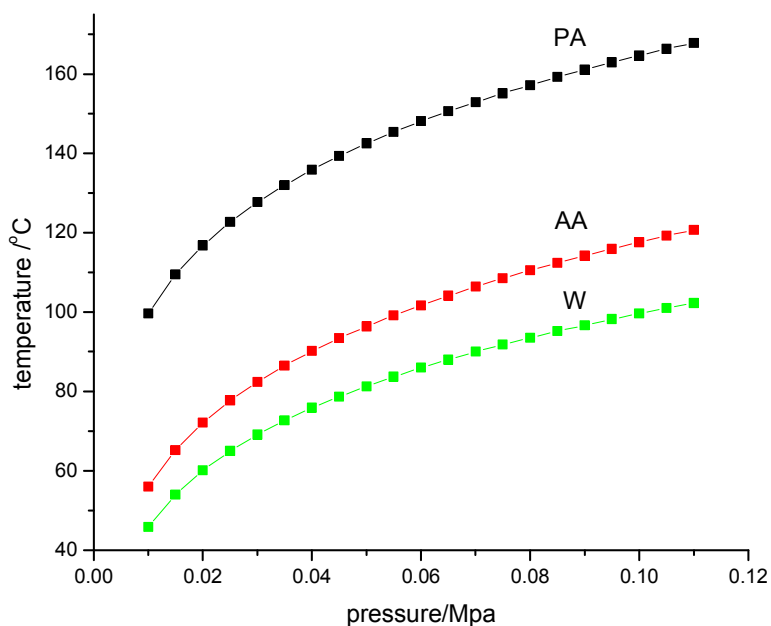


Fig.4 Boiling points of PA, AA and W at the different pressures

Fig.5 is the ultraviolet absorption spectrum of pyruvic acid standard solution (1), pyruvic acid crude products (2), refined pyruvic acid products (3). The three samples have strong absorption peak in 315~330 nm and are described to make appear strong and consistent absorption peak in 290 ~ 340 nm in comparative

literature, explaining the existence of pyruvic acid; However, because of the coarse product the influence of iron ions and some by-products, maximum absorption peak drift and some deviation from the whole curve after separation of refined curves are in good agreement with standard sample showing that the method is effective and feasible.

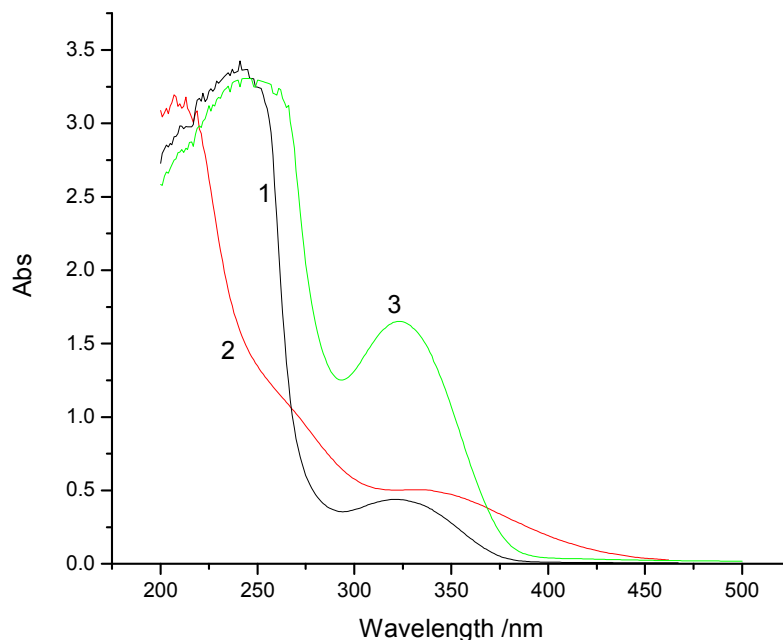


Fig. 5 Ultraviolet spectrogram of standard, raw and purified pyruvic acid

Fig.6 is gas chromatograph chart of pyruvate coarse product (1) and the standard sample (2), it was based on the time as the abscissa, peak height as the ordinate. We can see from the table that on the chromatograph chart 2, in the same retention time the chromatographic peak in the crude products is the same as the standard liquid ingredients. Thus the crude products, contains pyruvic acid and the content is very high.

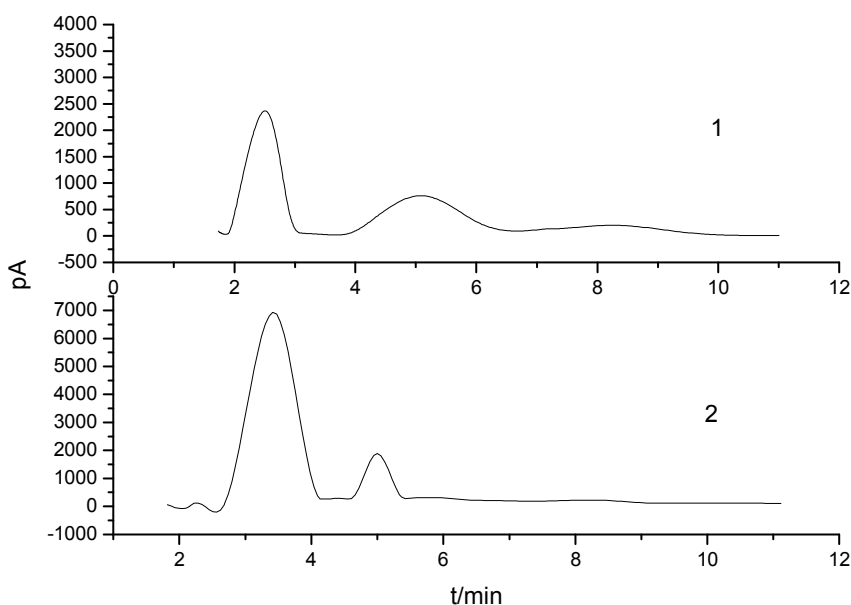


Fig.6 Gas chromatograms of raw (1) and standard (2) pyruvic acid

Conclusion

This paper used hydrogen peroxide as the oxidant, ferrous sulfate as a catalyst to synthesize pyruvic acid from lactic acid by catalytic oxidation. It focused on the synthesis and separation methods of pyruvic acid. The method of determination of pyruvic acid's content was studied by UV spectrophotometer. The processing had been analyzed when pyruvic acid was absorbed by D315 resin. Furthermore, the kinetics and thermodynamics models had been founded. All we did can be used as a reference for industrial production of pyruvic acid.

The method of determination of pyruvic acid's content was studied by UV spectrophotometer. Pyruvic acid could achieved high absorption at the wavelength of 320nm, and other impurities had little effect, the content of pyruvic acid from 0.2 to 2.8g / L obeyed the Lambert-Beer's law. The equation of standard curve is $y = 0.10902x - 0.00727$, and $R = 0.99755$, where x is the content of pyruvic acid and y is absorption value of pyruvic acid.

D315, a kind of weak base type ion exchanging resin used in our study, was selected to separate pyruvic acid and 2mol/L hydrochloric acid as eluent can achieve better extraction. It was better without inorganic ions such as Cl^- and at room temperature. Then pyruvic acid had biggest uptake Q of 267.63mg/g when pH was around 3. During the elution, the better ratio between raw product of pyruvic acid and 2mol/L hydrochloric acid was 20:300 g/ml, it could be finished after 150min.

This method is easy to operate and has high accuracy which is suitable for industrial production.

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