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Research Article

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Synthesis and optimization of long-chain fatty acids via the oxidation of long-chain fatty alcohols

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Abstract: The oxidation of long-chain fatty alcohols with Jones reagent to prepare long-chain fatty acids is an efficient and economical method. The by-product of chromium sulfate is electrolyzed and oxidized to hexavalent chromium, which is recycled to avoid the emission of toxic by-products. In this article, the process conditions for the preparation of carboxylic acid by chromium reagent oxidizing alcohol are optimized, and the effects of various reaction conditions on the experiment are explored. Innovatively, the reaction was optimized by reverse addition. The two synthesis methods are compared by orthogonal experiments, and the optimal reaction conditions for oxidation are determined: the organic solvent of alcohol is added to the acidified Jones reagent by reverse addition; the amount of chromium reagent is 1.5 times the required stoichiometry; the chromium concentration in chromium reagent is 2.5 mol·L^{-1}; the reaction temperature was lower than 30°C and the reaction time was 4 h. Under the optimized reaction conditions, the formation of by-products was effectively inhibited, and the conversion rate of alcohol oxidation to carboxylic acid was increased from 80% to more than 90%.

Keywords: Jones reagent, long-chain fatty alcohol, long-chain fatty acid, orthogonal experiment

1 Introduction

Long-chain fatty acids are important and abundant organic compounds [1] that are widely used in food, medicine [2], plastics, surfactants [3], extractants [4], lubricants [5], and other industries. Therefore, the production and preparation of long-chain fatty acids has always been the research hotspot of the chemical industry.

The synthesis methods of carboxylic acids mainly include the catalytic oxidation of alcohols or aldehydes [6–9], the hydrolysis of nitriles or lipids [10], etc. The hydrolysis of nitrile is generally carried out in the water solvent of concentrated sulfuric acid, but in some cases, the hydrolysis of nitrile will stay in the amide step, which is difficult to further hydrolyze, and the production process is complex [11]. The hydrolysis of esters requires reflux in an aqueous solution of KOH or NaOH, and this reaction also produces by-products that are difficult to separate, which makes it difficult to satisfy the needs of industrial production [12]. One-step catalytic oxidation of primary alcohols to carboxylic acids can be completed at room temperature using oxygen in the air as an oxidant using noble metal catalysts. This method has a wide range of applicability and selectivity, and the yield of carboxylic acids is more than 80%. However, the price of the catalyst is extremely expensive and difficult to recover, and some catalysts will also lead to the deactivation of the oxidant in the reaction [13]. Therefore, the preparation of carboxylic acids remains a great challenge, and more efficient and economical methods are needed to synthesize organic carboxylic acids.

Among the methods for preparing carboxylic acids, preparing carboxylic acids by oxidation of alcohols is one of the most basic chemical methods [14]. Long-chain fatty alcohols are difficult to oxidize owing to their stable properties and, like most organic matter, are insoluble in water. Therefore, it needs to be achieved by stoichiometric and efficient oxidants. The preparation of carboxylic acid by alcohol oxidation is generally achieved by stoichiometric high-efficiency oxidants, and common inorganic oxidants include potassium permanganate [15], chromate [16], ruthenium

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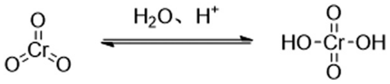
tetroxide [17], and others [18]. One of the reagents mentioned above is chromium(VI)-based reagents that are widely utilized in the oxidation of alcohols to carbonyl compounds, and Jones reagent is the most commonly used reagent in these chromium(VI)-based reagents. During the Jones oxidation of primary alcohols, aldehydes react with water and alcohols under acidic aqueous media to produce hydrates and hemiacetals [19], which are then oxidized to carboxylic acids and by-product dipolyesters, respectively, resulting in a low conversion rate [20]. Therefore, this study innovatively uses the "reverse addition" Jones oxidation method to prepare long-chain fatty acids with long-chain fatty alcohols as raw materials. The orthogonal experiment was designed to compare the two experimental methods of reverse addition and forward addition, and it was confirmed that this method can effectively inhibit the production of polyester by-products. The reaction time, the amount of Jones reagent, the concentration of chromium in Jones reagent, the concentration of sulfuric acid in Jones reagent, and other conditions were optimized, and finally, the optimal process conditions for the preparation of long-chain fatty acids by this method were obtained. For the chromium by-products produced by Jones oxidation, trivalent chromium was oxidized to hexavalent chromium by electrolysis and reused to avoid the harm of toxic by-products to the environment.

2 Principles and methods

2.1 Experimental principles

The reaction of the chromium reagent oxidizing alcohols is performed in an aqueous solution, starting with the reaction of chromium trioxide with water under acidic conditions, resulting in a balanced mixture containing chromic acid and its oligomers [21], as shown in Scheme 1. Chromic acid first reacts with the primary alcohol to form chromate, which gradually evolves into an intermediate aldehyde. This aldehyde is in equilibrium with its hydrate, after which further the reaction of the aldehyde water mixture with chromic acid results in the formation of a new chromate [22,23], which is decomposed into a carboxylic acid as in Scheme 2.



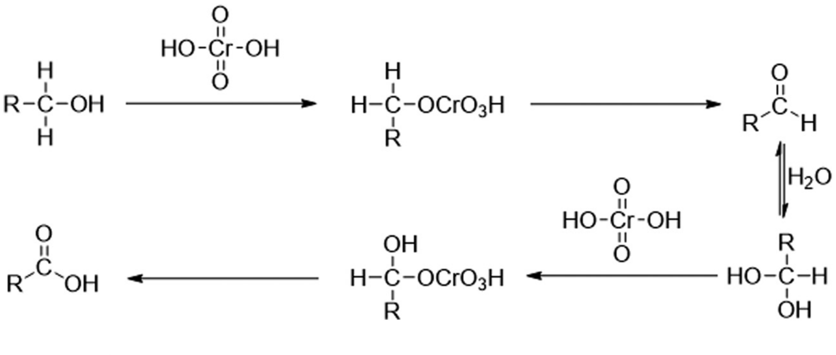
Scheme 1: Synthesis of Jones' reagent.

The by-product reaction is expressed in Scheme 3. In the process of dropping Jones reagent to primary alcohol, a large amount of alcohol is first contacted with a small amount of Jones reagent to form a large amount of intermediate aldehyde. The alcohol in the system reacts with an aldehyde to form a hemiacetal by-product, and then a dipolyester by-product is formed under the reaction of chromic acid [24].

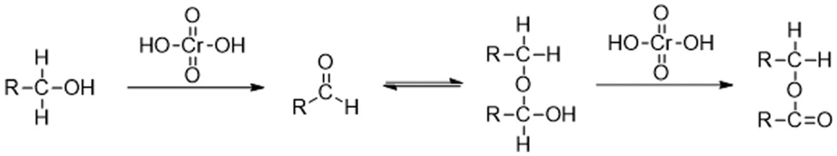
2.2 Experimental method

The normal addition of the Jones oxidation method: An appropriate amount of chromium trioxide was placed in a 500 ml beaker, and an appropriate amount of deionized water was added and stirred to dissolve. A certain concentration of sulfuric acid solution was prepared and slowly added to the chromium oxide solution, stirred to cool to room temperature to obtain the chromium reagent. Then, a certain amount of long-chain fatty alcohol was taken in a 1 L three-necked flask, and three times the quality of dichloromethane was added to it as a solvent. The prepared chromium reagent was slowly added dropwise to the dichloromethane solution of long-chain fatty alcohol below 20°C. After the chromium reagent was added dropwise, it was allowed to stand for a certain time to stop the reaction. The liquid organic matter, which was the crude product, was separated.

The reverse addition of the Jones oxidation method: The configuration method of the Jones reagent and



Scheme 2: Mechanism of oxidation of primary alcohols to carboxylic acids.



Scheme 3: Mechanism of by-product reaction.

dichloromethane solution of long-chain fatty alcohol is the same as that of the previous process. The difference is that the chromium reagent solution was slowly added to the dichloromethane solution of the long-chain fatty alcohol rather than slowly adding the chromium reagent to the dichloromethane solution of the long-chain fatty alcohol. Similarly, after the reaction was complete, the crude product was separated.

2.3 Characterization and measurements

2.3.1 Determination of the conversion rate

The reaction conversion rate is calculated by the acid value of the product. The acid value is a measurement standard for the number of free carboxylic acid groups in the product. The higher the acid value, the more alcohol hydroxyl groups are converted into carboxyl groups, and the higher the conversion rate. The determination of acid value was carried out in a 250 ml conical flask. The sample with a mass of m (g) was added and dissolved in 20 ml deionized water and 10 ml ethanol. After shaking well, four to five drops of phenolphthalein were added dropwise. The titration was carried out with KOH standard solution at a concentration of c_1 (mol·L^{-1}). When the sample solution was slightly red, and there was no significant fading within 15 s, the titration endpoint was determined. The volume of the standard titration solution consumed is recorded as V (ml). Blank experiments were performed according to the above steps, and the volume of the standard titration solution consumed was recorded as V_1 (ml). The iodine value was calculated using Eq. 1, where X_{av} is the acid value (mg·g^{-1}).

$$X_{\mathrm{av}} = \frac{(V - V1) \times c1 \times 56.1}{m} \tag{1}$$

In this study, the product is a mono-saturated carboxylic acid, so the conversion rate of the reaction can be calculated according to Eq. 2 according to the acid value. Among them, X_{av} is the acid value of the product, M_{r} is the relative molecular mass of the carboxylic acid product, and Conv. is the reaction conversion rate (%).

$$\text{Conv.} = \frac{X_{\mathrm{av}} \times M_{\mathrm{r}}}{56.1 \times 1{,}000} \times 100 \tag{2}$$

2.3.2 Determination of the iodine value

The iodine value is an indicator of the degree of unsaturation in fatty acid organic compounds. The iodine value was determined in a 250 ml conical flask. The sample with a mass of m (g) was weighed using an analytical balance, and the sample was dissolved with 40–60 ml alcohol. The pipette was accurately moved into 10 ml Wechsler's reagent (iodine chloride–acetic acid mixed solution). After shaking, the conical flask was sealed in the dark for 0.5 h, and then the excess concentration of 15% potassium iodide solution was added. The sodium thiosulfate standard solution with a calibrated concentration of c_2 (mol·L^{-1}) was titrated. When the yellow color of iodine was close to disappearing, the excess starch solution was added to continue the titration until the blue just disappeared at the titration endpoint. The volume of the standard titration solution consumed is recorded as V_2 (ml). Blank experiments were performed according to the above steps, and the volume of the standard titration solution consumed was recorded as V_3 (ml). The iodine value X_{iv} (g/100 g) was calculated using Eq. 3,

$$X_{\mathrm{iv}} = \frac{(V2 - V1) \times c2 \times 12.69}{m} \tag{3}$$

3 Results and discussion

3.1 Jones oxidation under normal addition

3.1.1 Effect of chromium reagent dosage

Jones reagent is an important oxidant in the reaction of alcohol oxidation to prepare carboxylic acid. The amount of Jones reagent in the reaction directly affects the conversion rate of carboxylic acid. The effect of the amount of

Jones reagent on the conversion rate of carboxylic acid was investigated under the following conditions: temperature was <30°C, the holding time was 4 h, and the chromium concentration in the chromium reagent was 2.5 mol·L^{-1}. The results are presented in Figure 1.

The conversion rate of carboxylic acid increased with the increase of the amount of Jones reagent. When the amount of Jones reagent reached three times, it was stable at about 90%. When the amount of Jones reagent reached four times of stoichiometry, the acid value of long-chain fatty acids was the highest, which was 91.7%, while the iodine value was always at 3 g/100 g, indicating that the content of unsaturated by-products in the product was low. When the amount of Jones reagent increased five times, the conversion rate of carboxylic acid decreased to a certain extent. This may be because when the amount of Jones reagent reaches a certain amount, the strong oxidation of Jones reagent will lead to the cleavage of the carbon–carbon bond of the intermediate chromate, which in turn produces some by-products. The broken carbocation group R+ has strong stability, which further strengthens the side reaction. Therefore, the optimized Jones reagent dosage is selected at 3.5 times of stoichiometry.

3.1.2 Effect of the reaction time

The effect of the reaction time on the conversion rate of carboxylic acid was investigated by controlling the stoichiometric amount of Jones reagent to 3.5 times, the reaction temperature to be lower than 30°C, and the concentration of chromium in Jones reagent to be 2.5 mol·L^{-1}.

As presented in Figure 2, at 0.5 h, the acid value of carboxylic acid is low, while the iodine value is high. This is because, in the initial stage of the reaction, chromic acid reacts with primary alcohol to form intermediate products such as chromic acid ester and aldehyde, and the intermediate product is converted into carboxylic acid as the reaction proceeds. After 1 h of reaction, the acid value of carboxylic acid almost no longer increases, indicating that the Jones oxidation reaction is relatively rapid, and the conversion rate of carboxylic acid is stable at more than 85%. This is because as the reaction proceeds, a large number of carboxylic acids and some intermediate aldehydes and esters are produced in the system. The presence of these by-products inhibits the conversion of alcohols to carboxylic acids, and the reaction system tends to be stable. However, the conversion rate of carboxylic acid decreased after 6 h of reaction time, which may be due to the esterification reaction between the raw material primary alcohol and the product carboxylic acid in the presence of sulfuric acid. The appearance of the ester was confirmed by the mass spectrum of the product carboxylic acid. Under the limitation of sulfuric acid concentration and temperature, the esterification reaction was not complete, so the conversion rate of carboxylic acid did not decrease significantly. Considering comprehensively, the optimal reaction time was determined to be 4.5 h.

3.1.3 Effect of concentration of Jones reagent

Jones reagent is an aqueous solution composed of chromium trioxide, sulfuric acid, and water in a certain proportion, in which the stoichiometric ratio of chromium

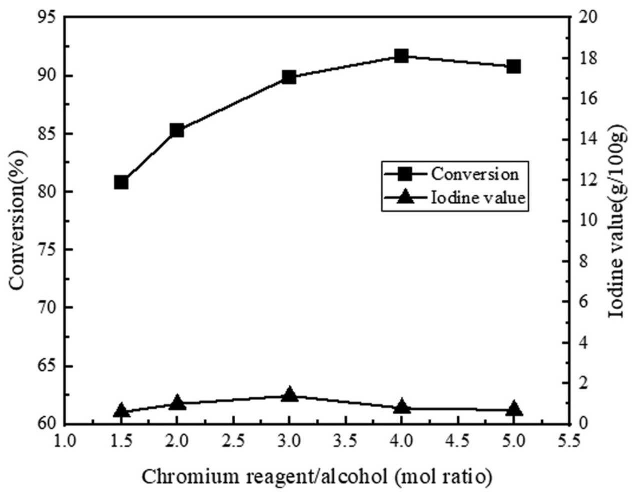


Figure 1: Effect of chromium reagent dosage.

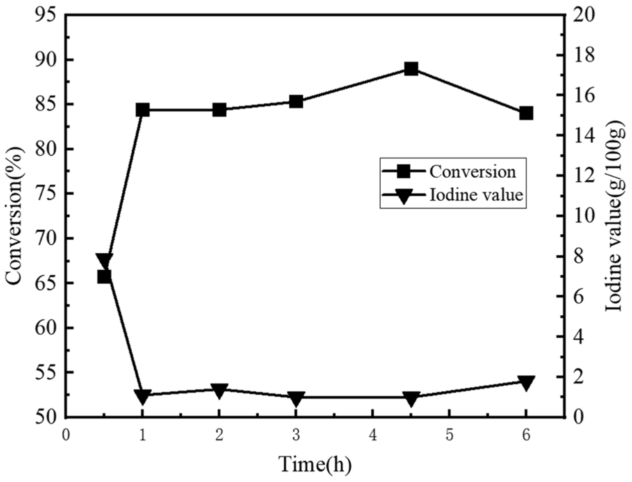


Figure 2: Effect of the reaction time.

trioxide and concentrated sulfuric acid is 2:3. The maximum concentration of chromium in the chromium reagent is not more than 3 mol·L^{-1}. By controlling the reaction temperature below 30°C, the amount of chromium reagent is three times the stoichiometry, and the reaction time is controlled at 4 h. The influence of the concentration of chromium in the chromium reagent on the oxidation reaction is explored, and the results are presented in Figure 3.

When the concentration of chromium in the Jones reagent is lower than 1.5 mol·L^{-1}, the conversion rate of the product carboxylic acid is significantly lower than that when the concentration of chromium in the Jones reagent is higher than 1.5 mol·L^{-1}. This is because the presence of a large amount of water reduces the oxidation of the Jones reagent and limits the oxidation reaction. When the concentration of chromium in the Jones reagent is higher than 1.5 mol·L^{-1}, the oxidation of the Jones reagent is sufficient to meet the requirements of the reaction. This experiment shows that the oxidation of the Jones reagent increases with an increase in chromium concentration. However, the volume proportion of the Jones reagent with higher concentration in the reactor is smaller, and the reaction efficiency is higher when other reaction conditions are consistent. Therefore, the higher chromium concentration in the Jones reagent is beneficial to the oxidation reaction.

3.2 Jones oxidation under reverse addition

In this study, the method of reverse addition is used to carry out the experiment, and the two addition programs are compared. The results are shown in Figure 4.

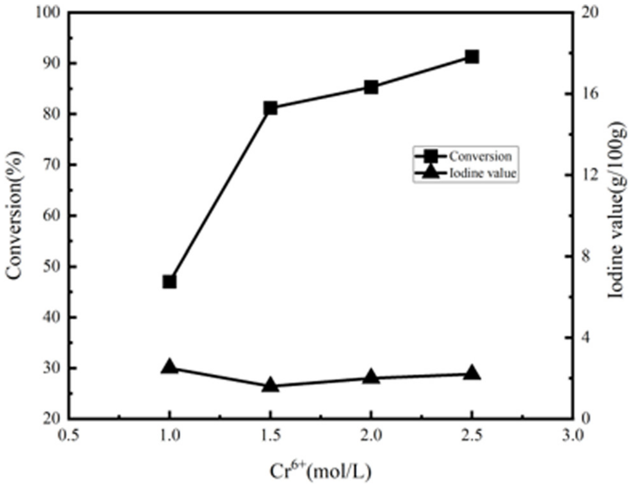


Figure 3: Effect of the concentration of the chromium reagent.

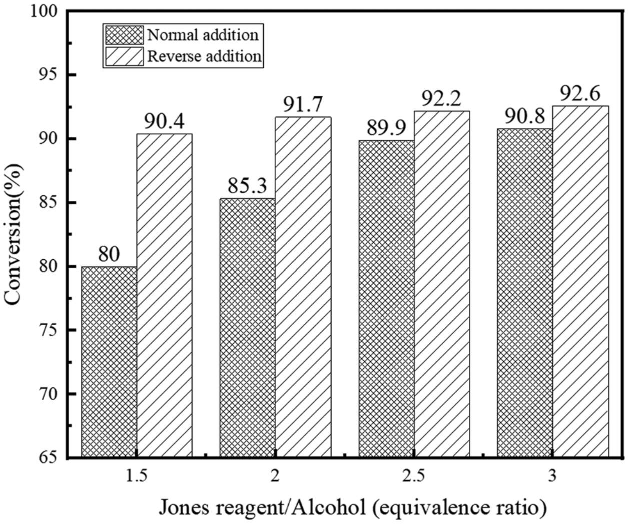


Figure 4: Comparison of two oxidation methods.

Through the comparison of histograms, it was found that under the same oxidation conditions, the reverse addition method effectively improved the conversion rate of the reaction. This is because, in the process of slowly adding alcohol to the Jones reagent, the alcohol first comes in contact with a large amount of excess chromic acid and is quickly converted into carboxylic acid [25]. In this way, the accumulation of high-concentration intermediate aldehydes is effectively prevented, and the contact reaction with the starting alcohol is avoided to form a large number of hemiacetals, which reduces the concentration of hemiacetals formed in the reaction and increases the conversion rate of carboxylic acids [26]. With an increase of the amount of Jones reagent, the conversion rate of primary alcohol to carboxylic acid did not increase significantly, which indicated that the amount of Jones reagent had little effect on the conversion rate of the reaction. Therefore, the effect of feeding time and sulfuric acid concentration on the reaction was investigated under the condition that the amount of Jones reagent was 1.5 times stoichiometric.

3.2.1 Effect of the feeding speed

Feeding speed is an important factor affecting the conversion of the intermediate aldehyde to carboxylic acid. Controlling the feeding speed can avoid contact between the intermediate aldehyde and alcohol. Therefore, we investigated the effect of the feeding rate of alcohol on the reaction results by adding quantitative alcohol to the Jones reagent by fixing the amount of Jones reagent to be 1.5 times of the stoichiometry, the reaction time to be 4 h, and the chromium concentration in the Jones reagent to be 2.5 mol·L^{-1}.

As presented in Figure 5, the feeding rate is reflected by changing the time when the quantitative alcohol is completely added to the Jones reagent. The change in the feeding rate has no significant effect on the conversion rate and iodine value of the product carboxylic acid, which indicates that the intermediate aldehyde is not easy to accumulate in the system. The mixture of aldehyde and water is converted into carboxylic acid at an extremely fast rate in the system. The faster the feeding rate, the higher the temperature of the reaction system, which also has a certain effect on the conversion of aldehydes into carboxylic acids. However, a very fast feeding speed will make it difficult to control the temperature of the system. When the reaction temperature reaches above 40°C, the solvent loss is large. Therefore, 3 h is the optimized reaction condition.

3.2.2 Effect of sulfuric acid concentration

The higher concentration of sulfuric acid will improve the oxidation ability of the Jones reagent, which in turn makes the high concentration of intermediate aldehydes convert into carboxylic acids faster. In order to investigate the effect of sulfuric acid concentration in the Jones reagent on the experiment, the reverse feeding method was used. The amount of Jones reagent was 1.5 times the stoichiometric amount, the reaction holding time was 4 h, and the chromium concentration in the Jones reagent was 2 mol·L^{-1}. The experiment was carried out with the concentration of sulfuric acid in the Jones reagent as a variable. The experimental results are shown in Figure 6.

The results show that the concentration of sulfuric acid in the Jones reagent is smaller than that below 3.92 mol·L^{-1} when the concentration of sulfuric acid is above 3.92 mol·L^{-1}. This is because with the increase of sulfuric acid concentration, the oxidation ability of the Jones reagent increases, which increases the conversion rate of carboxylic acid. When the concentration of sulfuric acid in the Jones reagent reaches 5.31 mol·L^{-1}, the conversion rate of carboxylic acid begins to decrease. This is because when the concentration of sulfuric acid is too high, the oxidation of Jones' reagent is too strong, which may cause the cracking of long-chain fatty alcohols, which in turn produces other by-products. This can be seen from the increase of iodine value. Although the higher concentration of sulfuric acid in the Jones oxidation reaction system has higher oxidizability, this may cause the reaction of acid-sensitive functional groups or protective groups in the reactants. In this case, when the reaction substrate is in contact with a large amount of excessive oxidants, the sensitive functional groups will be destroyed, and the target product will not be obtained, resulting in a decrease in the conversion rate of carboxylic acids. Although the increase of sulfuric acid concentration can increase the oxidizability of Jones reagent, the concentration of chromium in the system is relatively reduced, and the volume of Jones reagent required is relatively increased, thus reducing the production efficiency. Therefore, it is not an ideal method to increase the conversion rate of carboxylic acid by increasing the concentration of sulfuric acid.

3.3 Comparison of orthogonal experiments

Under the condition that the amount of Jones reagent is 1.5 times stoichiometric, the concentration is 2.5 mol·L^{-1}, and the reaction holding time is 4 h, the conversion rate of

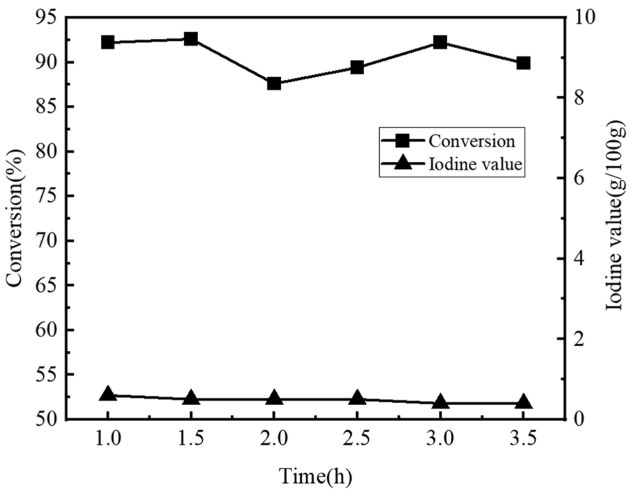


Figure 5: Effect of the feeding speed.

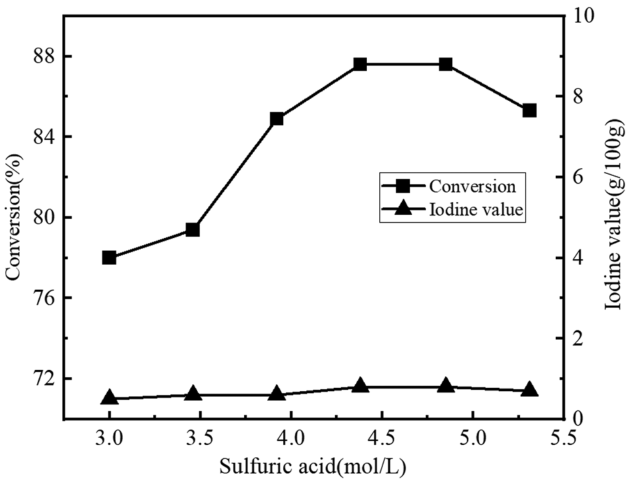


Figure 6: Effect of sulfuric acid concentration.

carboxylic acid obtained by the oxidation method under normal addition is about 80%. The conversion rate of carboxylic acid can reach more than 90% when the oxidation method under reverse addition is used, which indicates that the oxidation method under the reverse procedure can effectively inhibit the formation of by-products, thereby increasing the conversion rate of carboxylic acid.

In order to analyze the influence of the two methods on the oxidation results more comprehensively, reagent concentration, reagent dosage, and holding time were selected as variables to design orthogonal experiments. In this experiment, an L9 (3^3) orthogonal experiment table was selected. Among them, the Jones reagent concentration factor setting level was 2.5, 2, and 1.5 mol·L^{-1}; the level of Jones reagent dosage factor setting was two, three, and four times stoichiometry; the levels of reaction time factors of normal addition were 3, 4.5, and 6 h; and the levels of reaction time factors of reverse addition were 2, 3.5, and 5 h. The orthogonal experimental design schemes of forward addition and reverse addition with three factors and three levels were obtained, respectively. The specific parameter settings are shown in Table 1.

According to the design of the orthogonal experiment table for experimental analysis, the acid value results of the product carboxylic acid in an orthogonal experiment are shown in Table 2 (normal addition) and Table 3 (reverse addition).

The range analysis was carried out according to the acid value of the product carboxylic acid obtained by the orthogonal experiment. The analysis results are listed in Table 4 (normal addition) and Table 5 (reverse addition). The order of the factors affecting the acid value in the forward addition method is chromium reagent concentration > chromium reagent dosage > reaction time, and the order of the factors affecting the acid value in the reverse addition method is chromium reagent dosage > chromium reagent concentration > reaction time.

From the data in the table, it can be found that the optimum acid value of the carboxylic acid obtained by the two experiments is above 200 mg·g^{-1}, and the conversion rate of alcohol oxidation to carboxylic acid is about 91%. It is difficult to further improve the conversion rate of carboxylic acid. It may be because, in most cases, Jones oxidation is carried out by mixing the chromic acid solution with the acetone solution of the alcohol at room temperature, and a solvent other than acetone is rarely used. Because acetone is a polar organic solvent, when acetone is used as an organic solvent, the reaction intermediate, aldehyde–water mixture, can be better produced in the system and then converted into carboxylic acid. As an organic solvent with less polarity than acetone, dichloromethane can

Table 1: Orthogonal experimental design table

Method	Level	Experimental factors		
		Cr^{6+} (mol·L^{-1})	Dosage (stoichiometric multiples)	Time (h)
Normal addition	1	2.5	2	3
	2	2	3	4.5
	3	1.5	4	6
Reverse addition	1	2.5	2	2
	2	2	3	3.5
	3	1.5	4	5

Table 2: Orthogonal experimental results (normal addition)

Number	Cr^{6+} (mol·L^{-1})	Dosage (stoichiometric multiples)	Time (h)	Acid value (mg·g^{-1})
1	2.5	2	3	181
2	2	3	3	181
3	1.5	4	3	159
4	2.5	3	4.5	188
5	2	4	4.5	185
6	1.5	2	4.5	179
7	2.5	4	6	196
8	2	2	6	178
9	1.5	3	6	187

Table 3: Orthogonal experimental results (reverse addition)

Number	Cr^{6+} (mol·L^{-1})	Dosage (stoichiometric multiples)	Time (h)	Acid value (mg·g^{-1})
1	2.5	2	2	167
2	2	3	2	183
3	1.5	4	2	169
4	2.5	3	3.5	195
5	2	4	3.5	193
6	1.5	2	3.5	159
7	2.5	4	5	199
8	2	2	5	171
9	1.5	3	5	174

Table 4: Range analysis of the orthogonal experiment (normal addition)

Level	Concentration	Dosage	Time
K1j	565	540	521
K2j	544	556	552
K3j	524	538	560
Rj	14	6	13

Table 5: Range analysis of the orthogonal experiment (reverse addition)

Level	Concentration	Dosage	Time
K1j	560	497	519
K2j	547	551	547
K3j	502	561	543
Rj	19	21	9

inhibit the formation of a high concentration of aldehyde–water mixture to a certain extent, so the conversion rate of alcohol oxidation to prepare carboxylic acid has a limit. This factor, together with various by-products and other factors, makes it difficult for the conversion rate of alcohol to carboxylic acid in this system to reach more than 95%. However, since dichloromethane is easier to separate and recycle, it can simplify the process and save costs in industrial production. Therefore, dichloromethane was selected as the organic solvent.

The optimized Jones oxidation conditions are as follows: the oxidation method of the reverse process is adopted, the solvent is dichloromethane, the dosage of Jones reagent is 1.5 times of stoichiometry, the concentration of Jones reagent is 2.5 mol·L^{-1}, the feeding time is 3 h, and the reaction time is 4 h. Under these reaction conditions, the conversion rate of long-chain fatty alcohol to long-chain fatty acid was more than 90%.

3.4 Treatment of chromium sulfate by-product

In order to deal with chromium by-products and avoid serious pollution to the environment, the electrolytic method is used to oxidize the chromium sulfate solution to hexavalent chromium for recycling. In this study, the process conditions of electrolysis were explored by using chromium sulfate solution produced after the oxidation reaction as raw material.

The effect of electrolysis time on the concentration of Cr^{6+} was investigated by using 30% sulfuric acid at 20°C and 40°C. As shown in Figure 7, at 20°C, the conversion rate is stable at 24.64% after 6 h of electrolysis time, and the concentration of hexavalent chromium generated by electrolytic oxidation is about 0.62 mol·L^{-1}. At 40°C, the conversion rate can reach 24.3% after 6 h of electrolysis time and keeps increasing. However, with an increase of hexavalent chromium concentration, the damage of its strong oxidation to the equipment also increases. Therefore, the reaction ends after 8 h, and the hexavalent chromium concentration is about 0.86 mol·L^{-1}. By comparing the results at different temperatures, it can be found that increasing the temperature can effectively increase the electrolysis efficiency. It should be noted that the residual organic matter in the solution during the electrolysis of chromium sulfate solution may form a polymer on the electrode surface, which hinders the occurrence of the oxidation reaction on the electrode surface, thus affecting the current efficiency of Cr^{3+} electrolytic oxidation. The organic matter in the chromium sulfate solution can be extracted before the electrolysis operation to avoid the influence of the organic matter content on the electrolytic oxidation efficiency.

On the other hand, the concentration of sulfuric acid has a great influence on the electrolysis efficiency. As shown in Table 6, when the concentration of sulfuric acid increases from 20% to 40%, the concentration of hexavalent chromium increases first and then decreases. When the concentration of sulfuric acid is 30%, the concentration of hexavalent chromium produced by electrolysis is up to 0.855 mol·L^{-1}. This is because the addition of sulfuric acid is beneficial to reduce

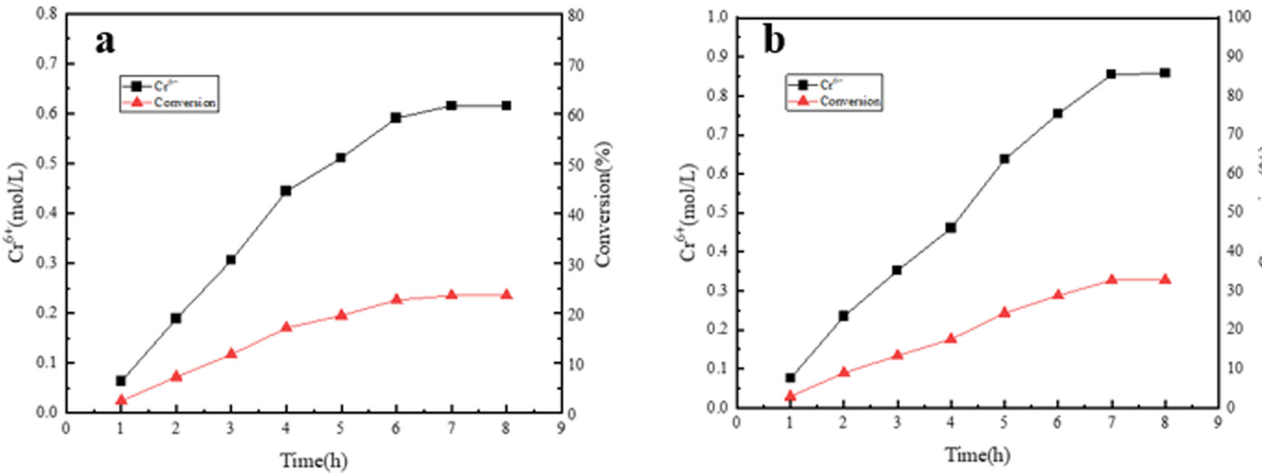


Figure 7: The effect of time on the electrolysis results at 20°C (a) and 40°C (b).

Table 6: Effect of sulfuric acid concentration on electrolysis

Sulfuric acid concentration (%)	Time (h)	Cr^{6+} ($mol \cdot L^{-1}$)	Concentration (%)
20	6	0.807	30.8
30	6	0.855	32.7
40	6	0.821	31.4

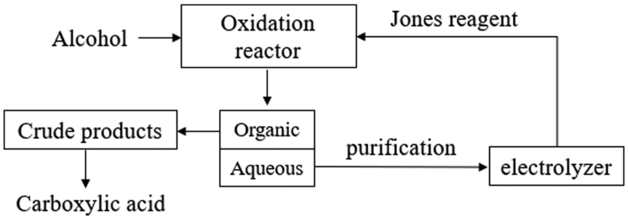


Figure 8: Schematic representation of the experiment.

the resistance, improve the conductivity of the solution, increase the current density, and shorten the reaction time. However, on the other hand, sulfuric acid is one of the products of the electrolysis reaction, and the excessive concentration of sulfuric acid is unfavorable to the oxidation reaction. In this experiment, when the amount of sulfuric acid added exceeds 30%, the hindering effect of sulfuric acid is greater than its promoting effect, so the concentration of sulfuric acid needs to be maintained within a certain range.

The long-chain carboxylic acid was prepared from long-chain primary alcohol using the Jones oxidation method. The whole oxidation process and by-product electrolysis process were designed, as shown in Figure 8. The oxidation process was carried out in an oxidation reactor. The reaction products were carboxylic acid (oil phase) and chromium sulfate (aqueous phase). After separation, the crude product of the oil phase was separated and purified to obtain carboxylic acid, and the by-product chromium sulfate was used as the electrolyte. After preliminary treatment, Cr^{3+} was oxidized to Cr^{6+} by electrolysis, and then the primary alcohol was oxidized as an oxidant.

4 Conclusions

In summary, long-chain fatty carboxylic acids were prepared using two different methods of Jones oxidation, using long-chain fatty alcohols as raw materials. The preparation process of carboxylic acids was optimized by single-factor experiments, and orthogonal experiments were designed to compare the two methods. The results showed that the optimal production conditions for the preparation of long-chain fatty acids by the oxidation of long-chain fatty alcohols by Jones reagent were as follows: the organic solvent of alcohol was added dropwise to the Jones reagent for production, the amount of the Jones reagent required was 1.5 times of stoichiometry, the concentration of the Jones reagent was 2.5 $mol \cdot L^{-1}$, the feeding time was 3 h, and the reaction time was 4 h. Under the optimal conditions, the conversion rate of primary alcohol to carboxylic acid was more than 90%. Chromium sulfate is electrolyzed and oxidized to form hexavalent chromium for recycling, which meets the requirements of a green, clean, and environmentally friendly synthesis process.

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