Study on the Isomerization of Maleic Acid to Fumaric Acid without Catalyst

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Fumaric acid is an important food additive and industrial intermediate compound. The traditional methods of producing fumaric acid were catalyzed by maleic acid isomerization. In this study, isomerization of maleic acid in water without catalyst was investigated at elevated temperature, which addressed the problem of sewage discharge. HPLC analysis showed maleic acid converted into fumaric acid and small amount of malic acid simultaneously. The effects of concentration of maleic acid, reaction temperature, reaction time, and stirring on the yield of fumaric acid were investigated. The optimum reaction conditions were also explored. The results showed the isomerization of maleic acid reached equilibrium at about 1 h, stirring did not affect the reaction rate, and conversion due to the monomolecular mechanism. In order to achieve "zero emission," the recycle of filter liquor was also studied. The pH of filter liquor changing signifies the lower pH was in favor of the conversion of maleic acid to fumaric acid. The high yield and recyclability suggested that this process had promising application in fumaric acid production.

Keywords: Isomerization, Maleic acid, Fumaric acid

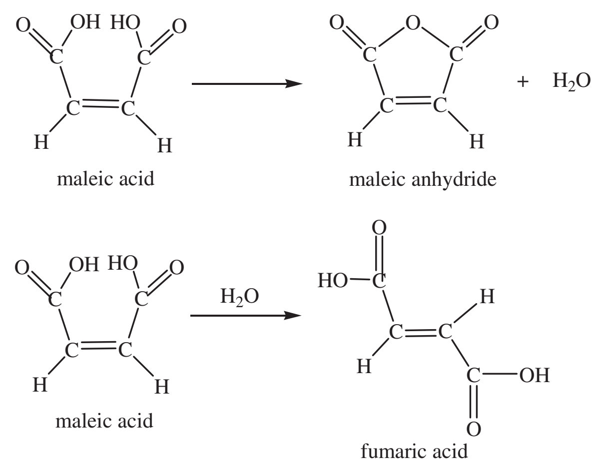
Introduction

Fumaric acid is a food additive that is commonly added in sweet foods such as baked goods and dairy-based desserts. It is also an important industrial intermediate compound for food manufacturing, feed processing, paint and resin producing, even used in pharmaceuticals.[1–8] Recent studies showed that fumaric acid also can be used to treat psoriasis.[4,9–11]

In industry, fumaric acid is mainly derived from the isomerization of the maleic acid in the presence of catalysts. Numerous catalysts were used for maleic acid isomerization.[12] Thiourea is used most commonly because of its low cost.[13–16] Other catalysts, such as inorganic acid, KCN, Br_2, NH_4Br, etc. are also used.[17–19] But these catalysts have some disadvantages, such as difficult to separate and reuse, etching apparatus and polluting environment. Moreover, the fumaric acid produced is of low purity and sometimes further purification is required.[20,21] Besides the traditional homogeneous catalysts, in recent years, some heterogeneous catalysts have been developed, such as silica, zeolites and carbon, etc.[22,23] Comparing to the homogeneous catalysts, solid catalysts can be easily separated from the reaction system, but the lower selection and stability limited their application in the scale of industry.[24–26]

In 1988, Rateal reported the study of kinetics of isomerization of maleic acid in concentrated solutions.[27] In this paper, isomerization of maleic acid to fumaric acid was performed at the temperature of 110–130 °C and the reaction involved was shown as followed.

Though the process of producing fumaric acid without catalysts was not studied deeply, this paper offered a more environmental friendly route of producing fumaric acid from maleic acid. In our study, isomerization of maleic acid to fumaric acid without catalysts under high temperature and pressure in aqueous solution was investigated. The effect of reaction conditions on the yields of fumaric acid were investigated, such as initial reactant concentration, temperature, and solution pH. The yield of 86% was obtained, at the same time, filter liquor can be recycled and no waste water discharge. Obviously, comparing



with catalyzed reaction, this process is more fit in the conception of atomic economy and green chemistry, and much easier to perform industrial production of fumaric acid.

Experimental

Materials. Maleic anhydride was supplied by Tianjin Bohai Chemical industry group (Tianjin, China). Aqueous solutions were prepared using deionized water.

Reaction System. The isomerization of maleic acid to fumaric acid was carried out in 50 mL hydrothermal reactor at high pressure and high temperature without any catalyst. In a typical experiment, 19.6 g maleic anhydride and 9.4 g deionized water were added into 50 mL hydrothermal reactor. The reactor was sealed and heated in oil batch to 200 °C and maintained for 1 h. Then the reactor was cooled to 80 °C. The paste-like product was washed with 40 mL deionized water and filtered. The filter liquor was kept as analyst and reused. The filtrate was dried at 120 °C in vacuum oven for 8 h and the white powders were obtained. The yield of the product was calculated according to the following equation:

The fumaric acid yield (%) = $W/W_0 \times 100$.

Where W was the weight of the isolated product and W_0 was the weight of maleic acid which was from the hydrolysis of maleic anhydride.

The filter liquor was analyzed by HLPC to determine the conversion of maleic acid and other by-products. All experiments were duplicated and the standard deviation of the duplicated experiments was less than ±5.0%. The error of the yield of the fumaric acid production was lower than 3.0%.

Sample Analysis. All filter liquor was analyzed through high-performance liquid chromatography (HPLC, Agilent 1200, Karlsruhe, Germany) with a DAD detector and reverse-phase Cosmosil Packed column(4.6 × 250 mm). The mobile phase was 0.1% phosphoric acid with flow rate of 0.5 mL/min and sample size of 20 μL. The DAD detection wavelength was 210 nm and the temperature was set at 50 °C. All samples were filtered through 0.45 μm membrane filters before detection. The products were analyzed by ^{1}H NMR to confirm its structure and purity.

Results and Discussion

Isomerization of the Maleic Acid under High Temperature and High Pressure without Catalysts. Isomerization of the maleic acid without catalysts was carried under high temperature and high pressure without catalysts, and the separated solid and filter liquor were investigated by ^{1}H NMR and HPLC. The ^{1}H NMR spectrum of solid product was showed in Figure 1. This spectrum was well fitted to the standard spectrum of fumaric acid and there was no impurity's peak, which indicated maleic acid was able to convert into fumaric acid without any catalyst.

The filter liquor was analyzed by HPLC and the result was presented in Figure 2. By comparing with the retention time of standard samples, including fumaric acid, maleic acid, and malic acid, the compounds in filter liquor were determined. In standard samples, the peak time of malic acid was 4.179, the peak time of maleic acid was 6.335, and the peak time of fumaric acid was 10.396. So the filter liquor contained fumaric acid, unreacted maleic acid, and by-product malic acid. So the reaction of isomerization of the maleic acid without catalysts can be expressed as

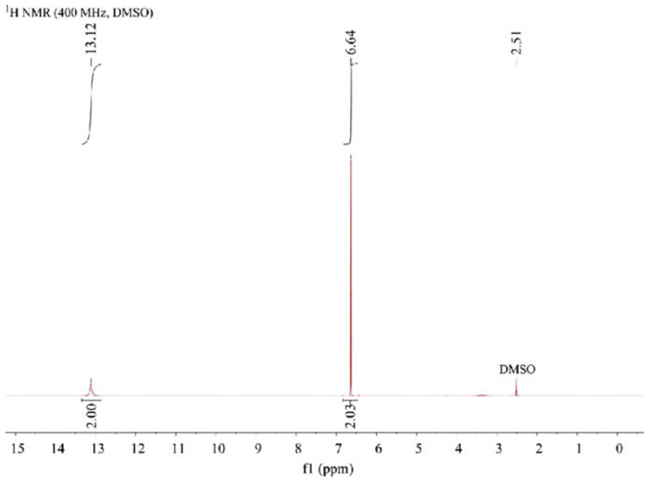


Figure 1. The ^{1}H NMR spectrum of the product.

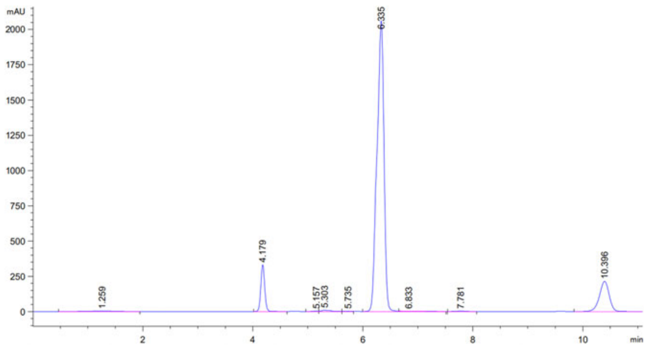


Figure 2. HPLC of filter liquor.

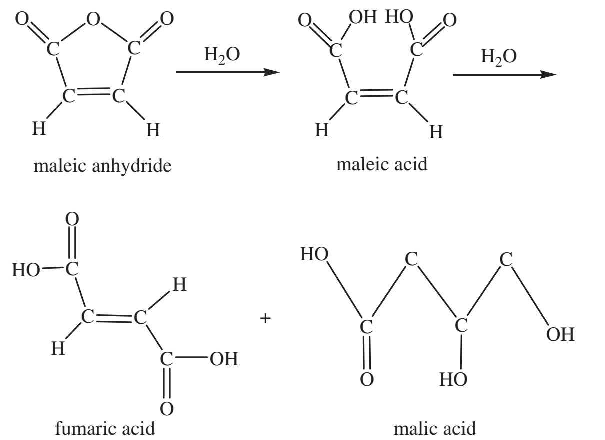


Figure 3. The isomerization of maleic acid under high temperature without catalysts.

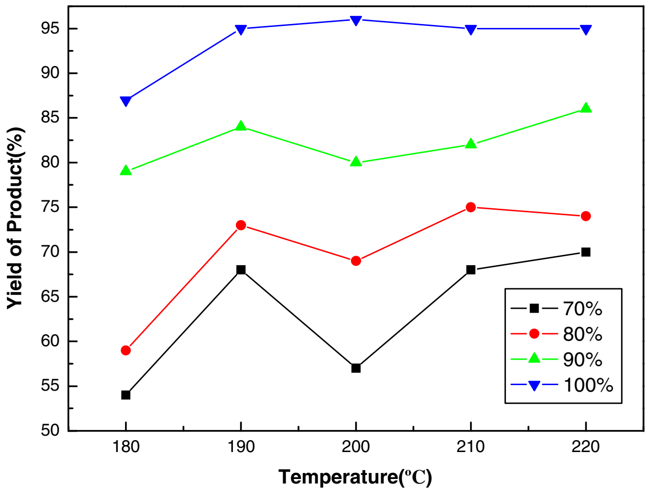


Figure 4. The effect of the concentration of maleic acid and reaction temperature on the yields.

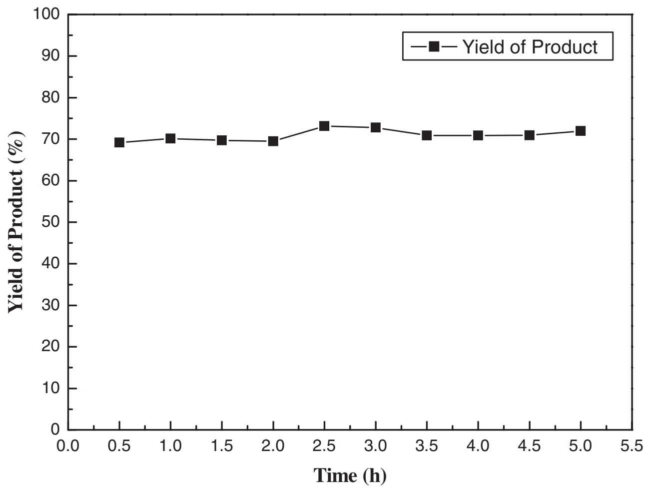


Figure 5. Effect of reaction time on the yield.

Figure 3. The mechanism of the study was fumaric acid and malic acid was produced by maleic anhydride aqueous solution under high temperature and high pressure.

Effect of the Concentration of Maleic Acid and Reaction Temperature. The effects of initial concentration of reactant and reaction temperature on the yield of fumaric acid were investigated. The initial concentrations of maleic acid, which hydrolyzed from maleic anhydride in water, were arranged from 70% to 100%, and the reaction time was kept for 1 h. The experiments were carried at 180, 190, 200, 210, 220 °C, respectively without stirring. The results were showed in Figure 4.

At the certain concentration of maleic acid, with the increase of the temperature from 180 °C to 220 °C, the yields of fumaric acid increased at first, then decreased from 190 °C to 200 °C, finally rose from 200 °C to 220 °C. When the reaction temperature was above 200 °C and the concentration was above 90%, the yields of the fumaric acid can reach above 80%. However, in practice, when the reaction temperature was above 200 °C, the product was pale yellow, which may limit its application in some special fields. At all the experiment temperatures, the yield of fumaric acid was gradually increased with the increase of concentration of maleic acid. When the concentration was below 80%, the product was paste-like and flowable, which was easy to pour out from reactor. The paste-like product was filtrated and washed by deionized water, the white powder was obtained. When the concentration was up to 90%, the product blocked to hard solid and was difficult to further separation and purification. Considering all aspects of the reaction, the reactant concentration of 80% and the reaction temperature of 190 °C were the optimum reaction conditions. Under this circumstance, the yield of the fumaric acid was 72%, at the same time, the color and form of products were acceptable.

The Effect of the Reaction Time. The effect of the reaction time was shown in Figure 5. At the concentration of maleic acid of 80% and the reaction temperature of 190 °C, the yield of the fumaric acid reached 69% at 0.5 h, and reached the highest value of 75% at 3 h. But no remarkable improvement of yield was observed by further prolonging reaction time. The result indicated the isomerization of the maleic acid without catalysts was efficient.

HPLC was used to analyze the content of filter liquor at different reaction times. According to Figure 6, when the reaction time prolonged, the quality of maleic acid decreases gradually. When the reaction time was 3 h, only a small amount of maleic acid was found in the filtrate and the quality of malic acid did not change much. It was meant that the reaction was, to a certain extent, basically the mutual conversion between maleic acid and fumaric acid, the best reaction time was 3 h.

The Effect of Stirring. In order to investigate the effect of stirring on yield, comparative experiments with stirring

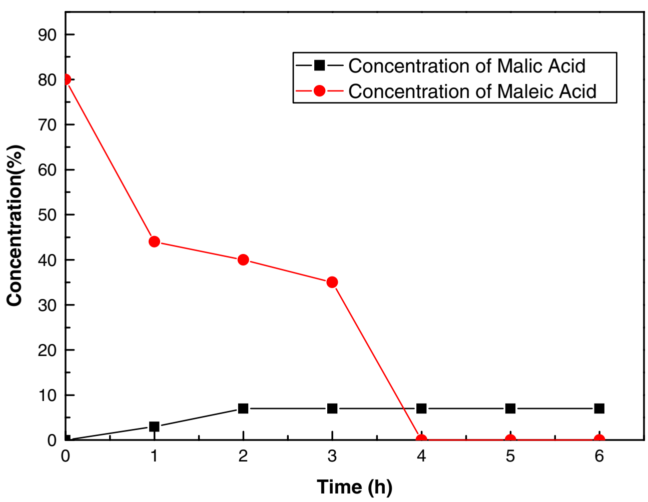


Figure 6. The concentration of maleic acid and malic acid with time in filtrate liquor.

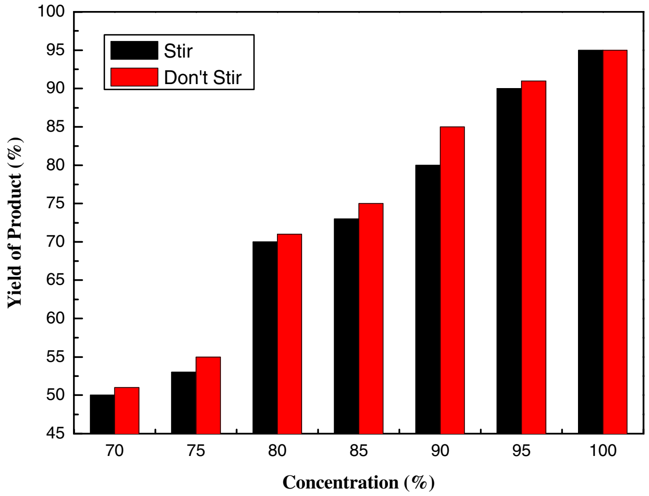


Figure 7. The yield of the products under the conditions of stirring and without stirring.

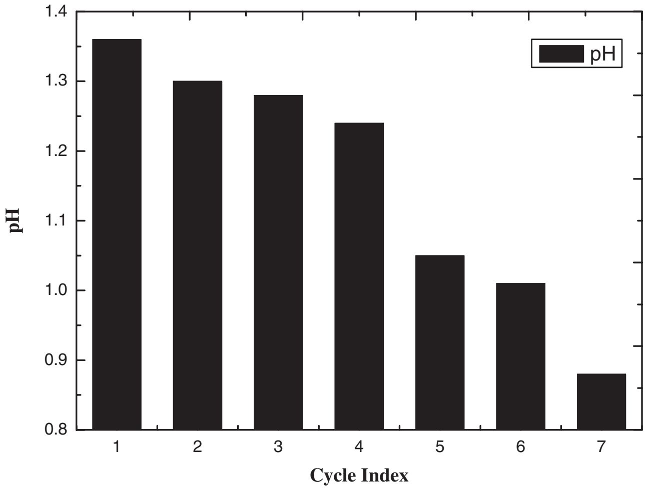


Figure 9. The pH of filter liquor for different cycle times.

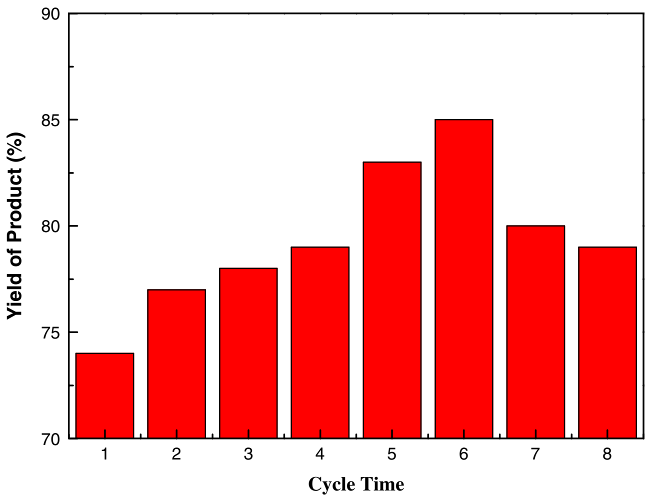


Figure 8. Effect of cycle times on the yield of reactants at 200 °C and the concentration of the fumaric acid production was 80%.

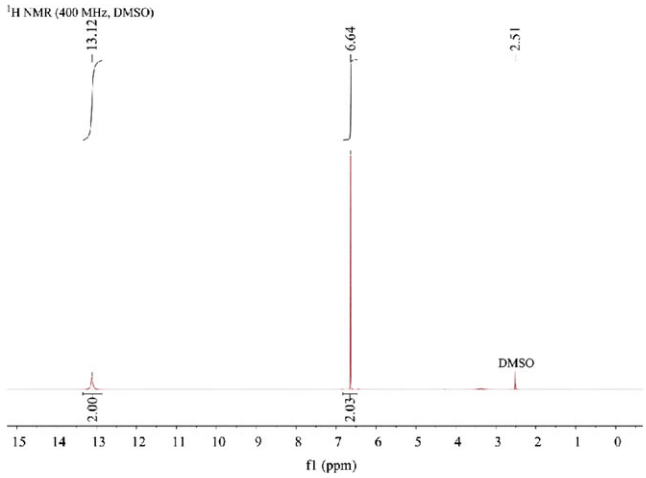


Figure 10. The ^{1}H NMR spectrum of the product with the filtrate circulates six times.

were carried out and results presented in Figure 7. The yield of fumaric acid decreased little when the reaction was performed with stirring. Isomerization of the maleic acid to fumaric acid is single reactant conversion reaction, so stirring has little effect on it. On the other hand, because of insolubility of fumaric acid in water, stirring made the solid product to fix on the upper wall of the reactor, which led to the lower yield with stirring.

Recyclability. One of the important characters of "green" process is zero emission (10 mL used for evaporative crystallization, 5 mL used for HPLC, and 15 mL used for solvent for the next experiment and the solution pH is 1.40), so in our study, filter liquor produced in separation and washing process were used as solution in next produce cycle instead of deionized water. The recyclability of filter liquor was investigated by repeating the cycle eight times at 190 °C and keeping the concentration of the maleic acid at 80% (Figure 8). The first time, the fumaric acid yield was close to 72%, and then increased constantly until the sixth time, at which the maximum value of 86% was obtained. The results were ascribed to the change of pH of the filter liquor. The pH of filter liquor decreased from 1.36 to 1.01 with the increase of recycle times (Figure 9). According to Hayon and Simic's[28] study, maleate anions were formed by an electric transfer process at acidic condition, which was not observed at higher pH. So lower pH was in favor of the conversion of maleic acid to fumaric acid.

However, the fumaric acid yield decreased to 79% after six cycles. This result was ascribed to the increase of the number of cycles leading to more and more imparities in filter liquor according to the principle of reversible reaction, the accumulation of malic acid is not conducive to the production of fumaric acid, which inhibited the occurrence of the reaction. But the yield of the fumaric acid at eighth cycle was still above 75%, and ^{1}H NMR spectrum of product in Figure 10 indicated that its purity was very high. So filter liquor recycle was a promising way to achieve zero emission.

Conclusion

Fumaric acid was prepared through the isomerization of maleic acid without catalysts. The concentration of the maleic acid, reaction temperature and pH of solution played important roles in the yield of the fumaric acid. When the filter liquor recycled six times and its pH was 1.01, reaction temperature was at 190 °C, the concentration of maleic acid was 80%, reaction time was 1 h, the 86% yield of fumaric acid was obtained.

The fumaric acid products yield could be guaranteed. The more acidic, the reaction is more complete, the greater the yield of fumaric acid. And the purity of the fumaric acid products did not change with the accumulation of the organic acid and the cyclic index and the pH of the filtrate. Finally, the potential for industrial application of this fumaric green production is very large, which greatly protects the environment. This can be used as green and efficient way maleate isomerizes to fumaric acid.

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