Glucose Conversion Process to Methyl Lactate Catalyzed by SnCl₄-based Homogeneous Catalysis

Xiao-Wei Zhuang, Yong-Shun Feng, Hui Qiao, Hai-Xia Yu, Wei-Ming Yang, and Xin Pan *

Biomass is a renewable alternative to fossil fuels and a valuable source of chemicals. In this study, a facile and efficient method was established to improve the selectivity of methyl lactate (MLA) for the homogeneous Lewis acid catalyzed chemical conversion of glucose and methanol. The effects of catalyst dosage, reaction temperature, and reaction time were systematically investigated, with an emphasis on the variation trends of MLA and other by-products. Through process optimization, the best catalyst molar ratio was 0.075 to 0.1, the reaction temperature was 170 to 180 °C, and the reaction time was 3 h. Under these conditions, the conversion of glucose in methanol exceeded 98%, and the yield of MLA was greater than 40%.

INTRODUCTION

Facing the global carbon emissions caused by fossil energy consumption, people are increasingly concerned about the transformation of renewable biomass to generate energy or value-added products (Maki-Arvela *et al*. 2020). Among various products obtained from biomass, methyl lactate (MLA) is an important chemical that can be used as a valuable solvent with high boiling point (Koutinas *et al*. 2017), detergent (Weltman *et al*. 1994), and synthetic raw material. For example, MLA can be polymerized to obtain polylactic acid (Kamble *et al*. 2012), hydrogenated to obtain propylene glycol (Simonov *et al*. 2012), and dehydrated to obtain acrylate (Pang *et al*. 2021).

There are two available methods for preparing methyl lactate. One method involves the fermentation of biomass into lactic acid (Ma *et al*. 2022), which is then esterified with methanol. In this process, H_2SO_4 is commonly used as a catalyst. However, H_2SO_4 is prone to intramolecular and intermolecular dehydration and carbonization of lactic acid, resulting in low product yield and a large amount of industrial waste (Maki-Arvela *et al*. 2014). Furthermore, the fermentation production process also has drawbacks such as strict fermentation conditions (Tang *et al*. 2016), low efficiency, high cost, difficult separation (Ahmad *et al*. 2020; Oscar *et al*. 2022), and multiple process steps (Demichelis *et al*. 2017).

The other method is the catalytic conversion of biomass sugars to methyl lactate (Yamaguchi *et al*. 2018; Zhao *et al*. 2021). The process of catalytic conversion of sugars to methyl lactate typically involves the hydrolysis of polysaccharides to produce fructose and glucose, which are isomerized into fructose (Lyu *et al*. 2019). Afterwards, fructose undergoes reverse aldol condensation to form a tricarbon compound, which is then

converted into methyl lactate through steps such as dehydration and hydrogen migration (Zhou *et al*. 2014; Lyu *et al*. 2019).

Many Lewis acids and bases have been studied as catalysts for the synthesis of lactic acid and methyl lactate (Tolborg *et al*. 2015; Tosi *et al*. 2019; Yue *et al*. 2021). These catalysts have been further combined with molecular sieve materials to form heterogeneous catalysts (Peiyan *et al*. 2020; Jimenez-Martin *et al*. 2022). However, such catalysts also have disadvantages when included in complex synthesis processes, such as high cost and harsh catalytic conditions (Murillo *et al*. 2021; Li *et al*. 2021; Sun *et al*. 2021). There is relatively little systematic study on the reaction parameters in the catalytic process of methyl lactate. Therefore, the purpose of this study is to investigate the catalytic performance of Sn^{4+} ions on the conversion of glucose to MLA at various dosages and time periods, as well as mild temperature.

EXPERIMENTAL

Materials

All reagents used in this study were analytical reagents ($\geq$ 99%). Glucose was used as a model compound for biomass sugar in all experiments. As Lewis acid catalyst, $SnCl_4.5H_2O$ purchased from Sinopharm Chemical Reagent Co., Ltd. (China) was used in this study.

Methods

Catalytic reaction procedure

About 5 g of glucose was completely dissolved in 5 mL of distilled water, and then diluted with 495 mL of methanol to prepare a 1% (W/V) glucose solution as the reaction substrate. Then, a 100 mg/mL of $SnCl_4$ solution prepared with methanol as the solvent was used as a catalyst additive.

A 20 mL Teflon-lined stainless steel autoclave reactor was charged with glucose (10 mL), and catalyst solutions. After the autoclave was sealed, the reactor was heated to the desired temperature. When the reaction was complete, the reactor was cooled using a cold-water bath down to the ambient temperature.

Catalytic parameter selection

The gradient of catalyst dosage was studied using a molar ratio range of 0.025 to 0.2 between catalyst and the reaction substrate, with an interval of 0.025. The reaction condition was 160 ℃, 3 h.

To study the influence of temperature on catalytic performance, a range of 140 to 190 ℃ was selected with an interval of 10 ℃. The reaction time was 3 h.

To study the impact of time on catalytic performance, a range of 1 to 6 h was used, with an interval of 1 h and a maximum duration of 16 h.

Product analysis

The products formed in the reaction solution were filtered with a 0.22-μm filter and then identified using a GC-MS (6890NGC/5973, Agilent, Santa Clara, CA, USA) and a high-performance liquid chromatograph (HPLC; LPG-3400SD, DIONEX, Sunnyvale, CA, USA) analysis system. Conversion of glucose was analyzed with the external standard method on the HPLC equipped with an Aminex HPX-87H column (300 mm × 7.8 mm)

and a refractive index detector (RI-201H, Shimadzu, Kyoto, Japan). An aqueous H_2SO_4 (0.005 M) solution was used as the mobile phase, with a flow rate of 0.6 mL/min (Lyu *et al.* 2018). The column temperature was 55 °C. The yield of MLA was analyzed using the external standard method on the gas chromatograph-mass spectrometer (GC-MS) with DB-WAX column (30 m× 0.25 mm). Helium was used as the carrier gas, with the flow rate of 1 mL/min, an injection volume of 1.0 μL, a split ratio of 19:1, and an injection temperature of 280 °C. The initial temperature of the oven was 50 °C for 4 min, then ramped to 180 °C at 8 °C/min for 5 min, and finally ramped to 250 °C at 10 °C/min for 8 min. The MS system was operated at 230 °C, and the quadrupole temperature was set at 150 °C. Identification was performed using the NIST MS Search Program (Version 2.2) and the NIST/EPA/ NIH Mass Spectral Library (NIST 8.0).

Glucose conversion and product yields were calculated using the following Eqs. 1 and 2 (Lyu *et al.* 2019):

$$\text{Glucose conversion} = 100 \times \frac{\text{Moles of glucose reacted}}{\text{Moles of starting glucose}} \qquad (1)$$

$$\text{MLA yield} = 100 \times \frac{\text{Moles of C in produced MLA}}{\text{Moles of C in glucose}} \qquad (2)$$

All reactions were repeated at least twice, and the difference between the two results was less than 3%.

RESULTS AND DISCUSSION

Effect of Catalyst Dosages and Product Analysis

After 3 h at 160 °C, Fig. 1a shows that the yield of MLA increased with the increase of catalyst dosage, and the molar ratio of catalyst to glucose was within 0.1. Among them, the yield of MLA increased the fastest from a molar ratio of 0.025 to 0.05, with an increase of 447%. As the amount of catalyst further increased, the increase in the yield of MLA gradually decreased, ranging from 2.1% to 12.4%. The peak of MLA reached 3.94 mg/mL when the molar ratio of catalyst was 0.1. As the amount of catalyst continued to increase, the yield of MLA subsequently began to decrease.

Figure 1b shows the conversion of glucose at 160 °C for 3 h under various molar ratios of catalyst dosage. As depicted in the figure, the glucose conversion rapidly increased from 83.5% to 96.8% when the molar ratio of catalyst dosage increased from 0.025 to 0.05. However, as the catalyst dosage continued to increase, the glucose conversion eventually stabilized. Figure 1c displays the conversion of glucose to MLA based on varying molar ratios of catalyst dosage. The graph indicates that the trend of MLA conversion rate was consistent with the variation in MLA content, with its peak occurring at a catalyst molar dosage of 0.10, resulting in an MLA yield of 34.8%. Hence, the subsequent experiment primarily aimed to examine the influence of temperature and time parameters on the yield of MLA, maintaining the catalyst molar ratio within the range of 0.075 to 0.125.

Figure 2 displays the gas phase mass spectrometry of various catalyst dosages. At a molar ratio of 0.025, the two main components in the mass spectrometry were MLA and methyl 4-pentynoate, yet their peak areas in GC-MS were minor. As the dosage of catalyst increased, the contents of MLA and by-products initially increased and subsequently decreased, suggesting a rather complex catalytic conversion mechanism of glucose.
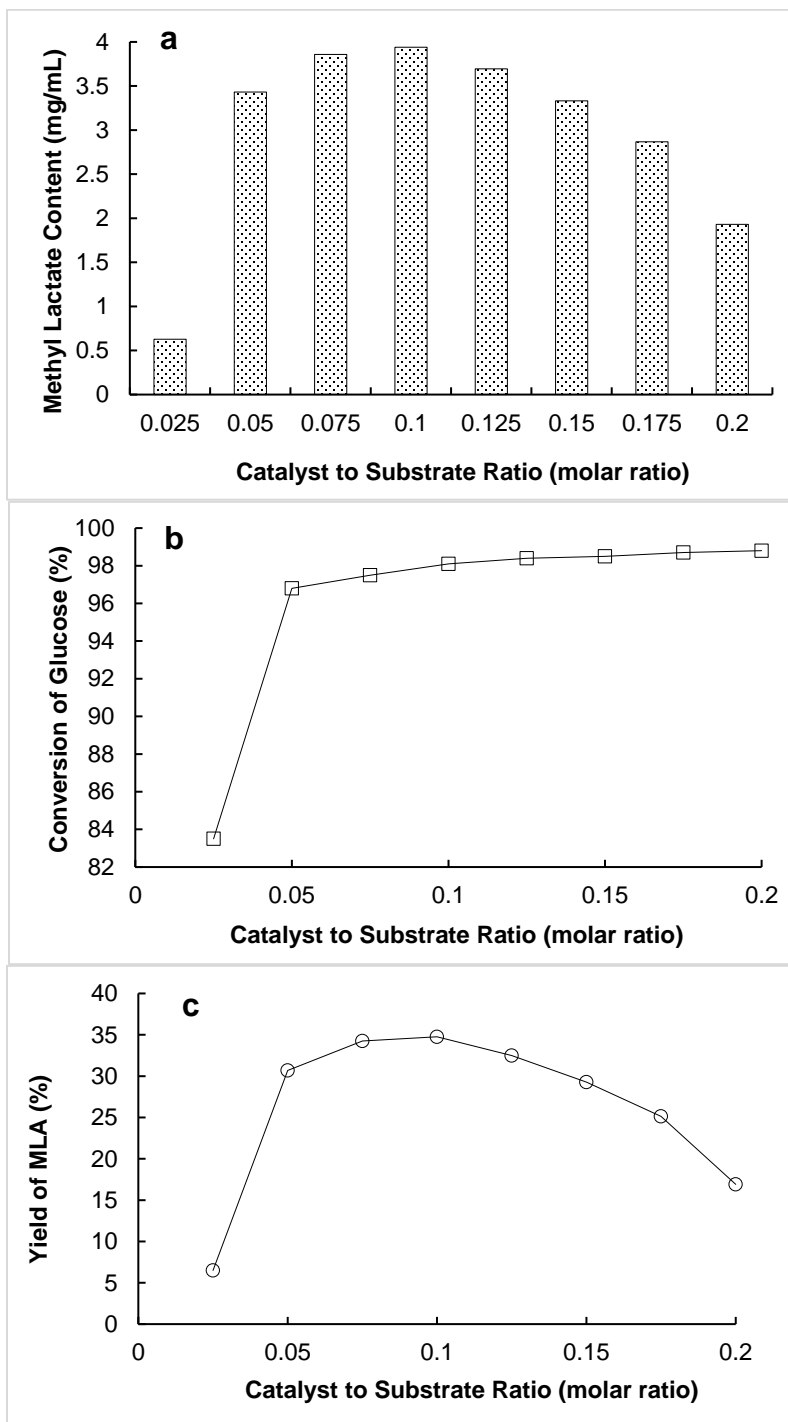
Fig. 1. The effect of different catalyst dosages on content of MLA (a), glucose conversion rate (b), yield of MLA (c)

Based on mass spectrometry data, it was observed that the components, glycolaldehyde dimethyl acetate (GDA), 4-oxo-pentatonic acid methyl ester (PAM), 1,2-dimethoxy-ethane (DE), 2-(2-furyl)-thiazolidine (FTH), and methyl 4-pentynoate (MPN), exhibited a similar trend to MLA. They first increased to the peak value and then decreased as the amount of catalyst increased. However, when it comes to individual components, the amount of catalyst required for the peak can be different. At a catalyst dosage of 0.05

molar ratio, glycolaldehyde dimethyl acetate and FTH reached their peak values, followed by a rapid decrease in glycolaldehyde dimethyl acetate. When the catalyst dosage was 0.1 in molar ratio, the component signals cannot be detected. When the molar ratio of catalyst dosage was 0.175, FTH could not be detected.

The variation trends of components DE and MPN were identical to those of MLA, suggesting that they may be co-products of glucose-catalyzed conversion to MLA. The peak area of component 4-oxo-pentatonic acid methyl ester in mass spectrometry continued to increase with the increase of catalyst dosage. When the content of glucose substrate remained constant, the composition content increased, whereas the content of MLA, DE, and MPN correspondingly decreased. Some speculate that there may be a polymerization pathway from MLA and other components to PAM under continuous high temperature and pressure conditions. There may be a possible pathway for MLA to be catalyzed by Lewis acid and Cl$^-$ under subcritical methanol conditions to undergo dehydration to prepare acrylate, which can undergo unsaturated C-C addition reaction with acetaldehyde to generate pentanoate components. An alternative pathway involves the initial conversion of glucose into xylitol, which subsequently undergoes dehydration and hydrogenation to yield pentanoate components. The exact pathway needs to be verified through further experiments.
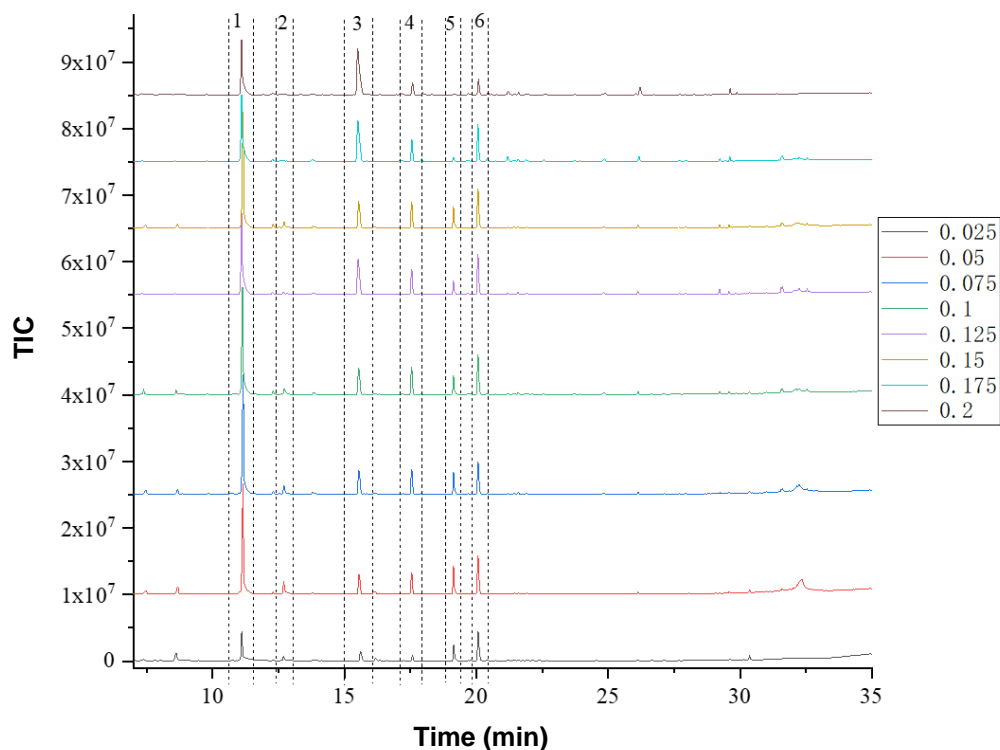

Fig. 2. Gas chromatography-mass spectrometry of different catalyst dosages at 160 °C for 3 h: 1: Methyl lactate; 2: Glycolaldehyde dimethyl acetal (GDA); 3: 4-oxo-Pentatonic acid methyl ester (PAM); 4: 1,2-dimethoxy-Ethane (DE); 5: 2-(2-furyl)-Thiazolidine (FTH); and 6: Methyl 4-pentynoate (MPN)

Effect of Different Temperatures on the Conversion of MLA

According to Fig. 3, at catalyst molar doses of 0.075 and 0.1, the yield of MLA increased with increasing temperature in the neighborhood of 180 °C. In the temperature

range of 140 °C to 180 °C, the linear regression equations for MLA were $Y_{0.075} = 0.568\ X - 43.169$, ($R^2 = 0.924$) and $Y_{0.1} = 0.568\ X - 58.12$, ($R^2 = 0.976$), respectively. Here, X represents the temperature parameter and Y represents the yield of MLA, indicating the significant role of temperature in affecting the conversion of glucose to MLA. However, when the temperature exceeded 180 °C, the yield of MLA decreased. Furthermore, an excessively high temperature resulted in increased demands for temperature and pressure resistance of the reaction vessel, thereby diminishing the cost-effectiveness of this method.
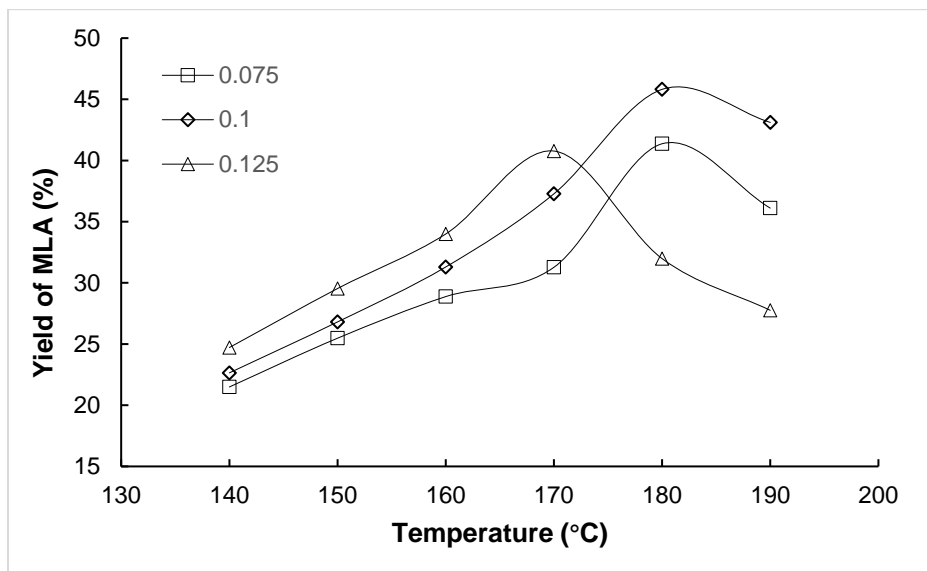

Fig. 3. The effect of different temperatures on the yield of MLA

When the catalyst molar ratio was 0.125, an increase in temperature factor within the range of 140 to 170 °C was positively correlated with the yield of MLA. However, once the temperature exceeded 170 °C, the MLA yield started to decrease. When the catalyst molar ratio was 0.1 and 0.075, the yield of MLA began to decrease when temperature exceeded 180 °C, which applied to all monohydric alcohols. Methanol exhibited the highest polarity. The reaction in this system was conducted at elevated temperatures (140 to 190 °C), during which methanol was in a subcritical state. The polarity of C-O and O-H bonds in subcritical methanol intensified, thereby augmenting the apparent polarity and acidity of methanol. When using a large amount of Lewis acid catalyst, methanol more readily attacked MLA and generated various by-products, suggesting that at higher catalyst concentrations, both high temperature and high-pressure can lead to further conversion of MLA. Therefore, one cannot solely enhance the temperature parameters to obtain higher MLA yield. As shown in Fig. 4, in addition to the MLA component, other components also demonstrated additional attenuation and conversion at higher temperatures and catalyst dosages. Of all the components, PAM and DE were less affected by temperature, whereas MPN was the component most sensitive to temperature. Hence, an appropriate temperature parameter setting can be employed to decrease the content of by-products.

Effect of Different Times on the Conversion of MLA

In this section, a systematic study was conducted to examine the impact of time, catalyst concentration, and reaction temperature on the formation of MLA. As depicted in Figs. 5 to 7, the variation trend of the yield of MLA over time was not similar under

different catalyst dosages. When the catalyst molar ratio was 0.075, the yield of MLA reached its peak at 190 °C for 2 h and at 180 °C for 3 h, whereas it took 5 h to reach its peak at 140 to 170 °C. Subsequently, the MLA yield began to decrease and eventually reached a balance. This suggests that MLA is not the ultimate stable product under Sn-based catalysts, thus it is subject to further transformation over time.
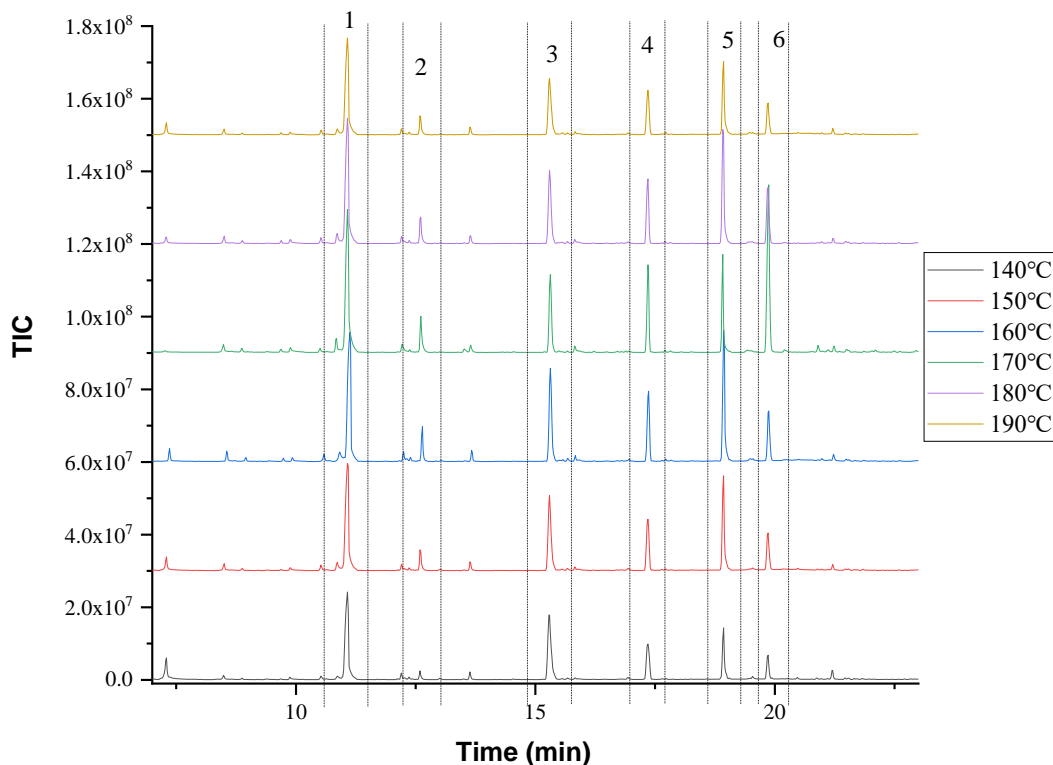

Fig. 4. Gas chromatography-mass spectrometry at different temperatures with catalyst dosage of 0.125 (molar ratio) at 3 h: 1: MLA; 2: GDA; 3: PAM; 4: DE; 5: FTH; and 6: MPN
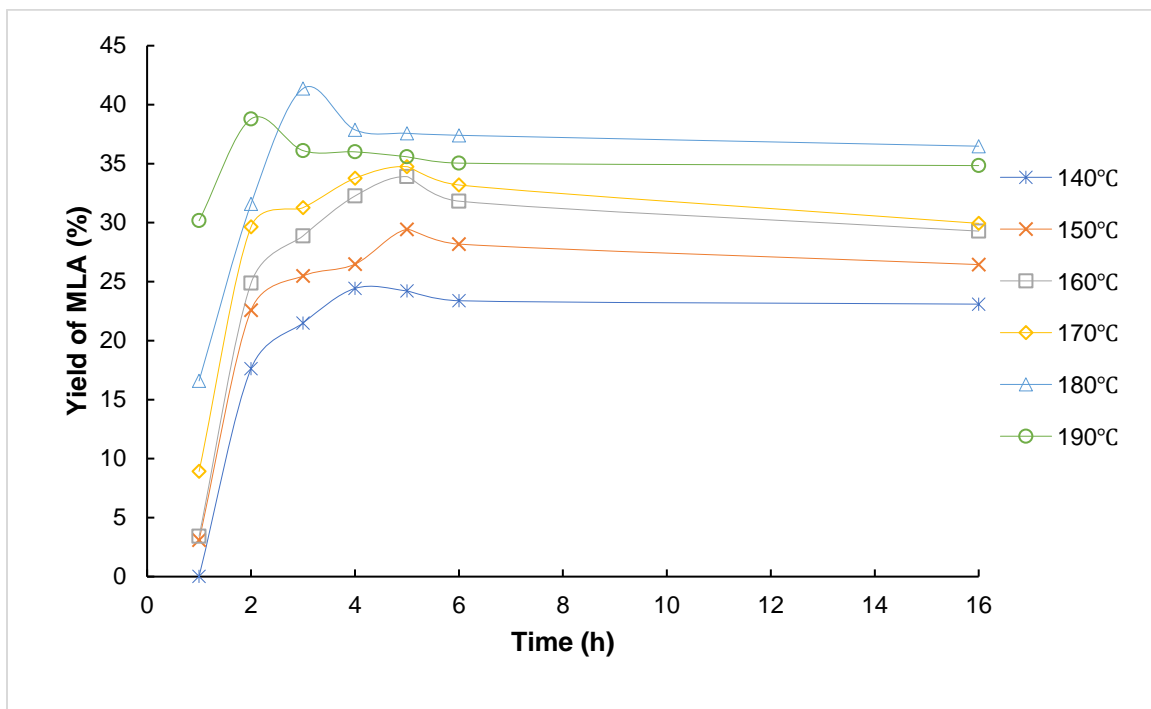
Fig. 5. The effect of reaction time on the yield of MLA at different temperatures with catalyst dosage of 0.07 5 (molar ratio)
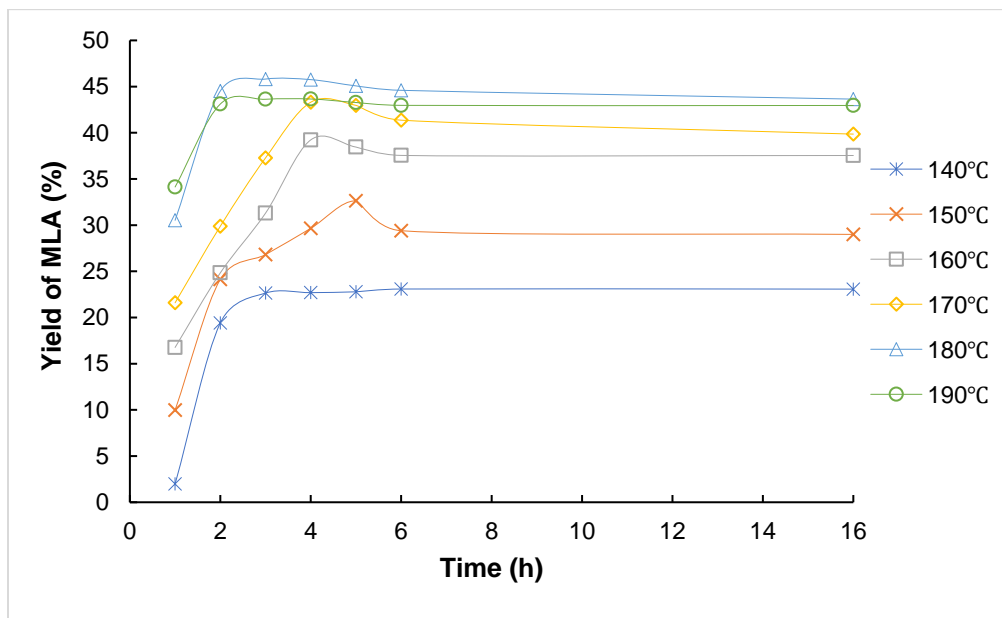

Fig. 6. The effect of reaction time on the yield of MLA at different temperatures with catalyst dosage 0.1 (molar ratio)
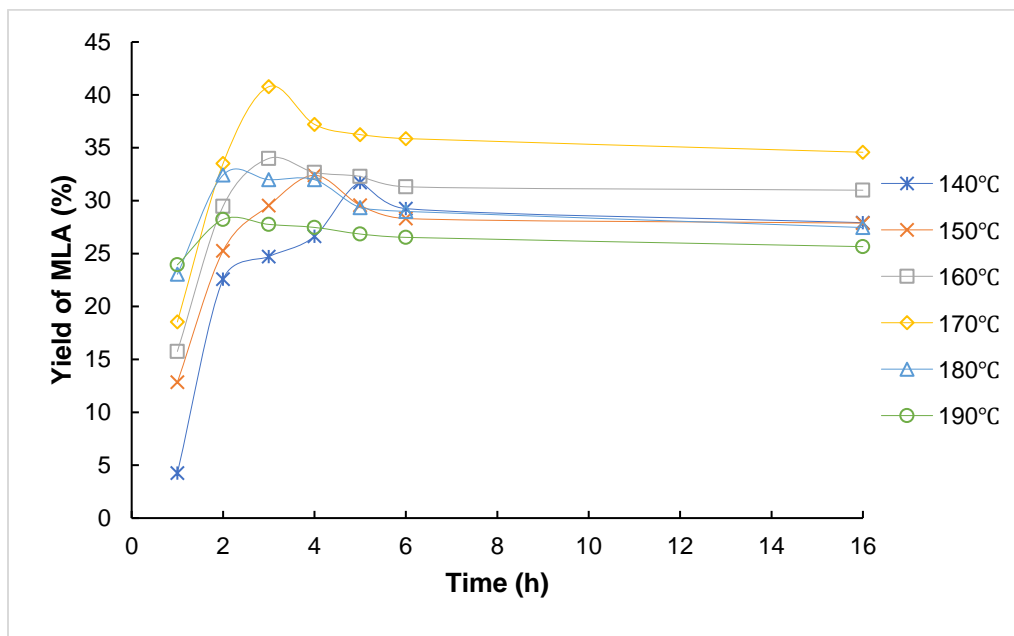
Fig. 7. The effect of reaction time on the yield of MLA at different temperatures with catalyst dosage of 0.125 (molar ratio)

As depicted in Fig. 6, when the catalyst molar ratio was 0.1, the trend of MLA yield at 180 to 190 °C was similar to that at a catalyst molar ratio of 0.075, but the peak value at 180 °C was 10.76% higher than that at a catalyst dosage of 0.75, reaching 45.8%. It took 4 h to reach its peak at 150 to 170 °C, which was 1 h shorter than the catalyst molar ratio of 0.075. At 140 °C, it took 5 h to reach its peak. Based on Fig. 7, it can be observed that the molar ratio of catalyst was 0.125, and the impact of reaction time and temperature on the yield of MLA differed compared to the molar ratio of catalyst 0.075 and 0.1. At a molar ratio of 0.125, the peak value in all treatments was at 170 °C for 3 h, with an MLA yield of 40.8%. Based on the analysis of Figs 5 to 7, it can be seen that the higher the temperature under the same catalyst conditions, the faster the reaction rate. However, as the amount of catalyst increased, the temperature required for the maximum yield of MLA decreased, indicating that in subcritical methanol, the increase in methanol polarity greatly accelerated the conversion of glucose to MLA under Sn catalysis. Moreover, MLA became less stable in this system and further degraded into other by-products, suggesting that the yield of MLA from glucose conversion was governed by the interplay of catalyst dosage, time, and temperature. Therefore, it is necessary to systematically control the three factors of time, temperature, and catalyst dosage, so as to obtain high MLA yield and low by-products as soon as possible.
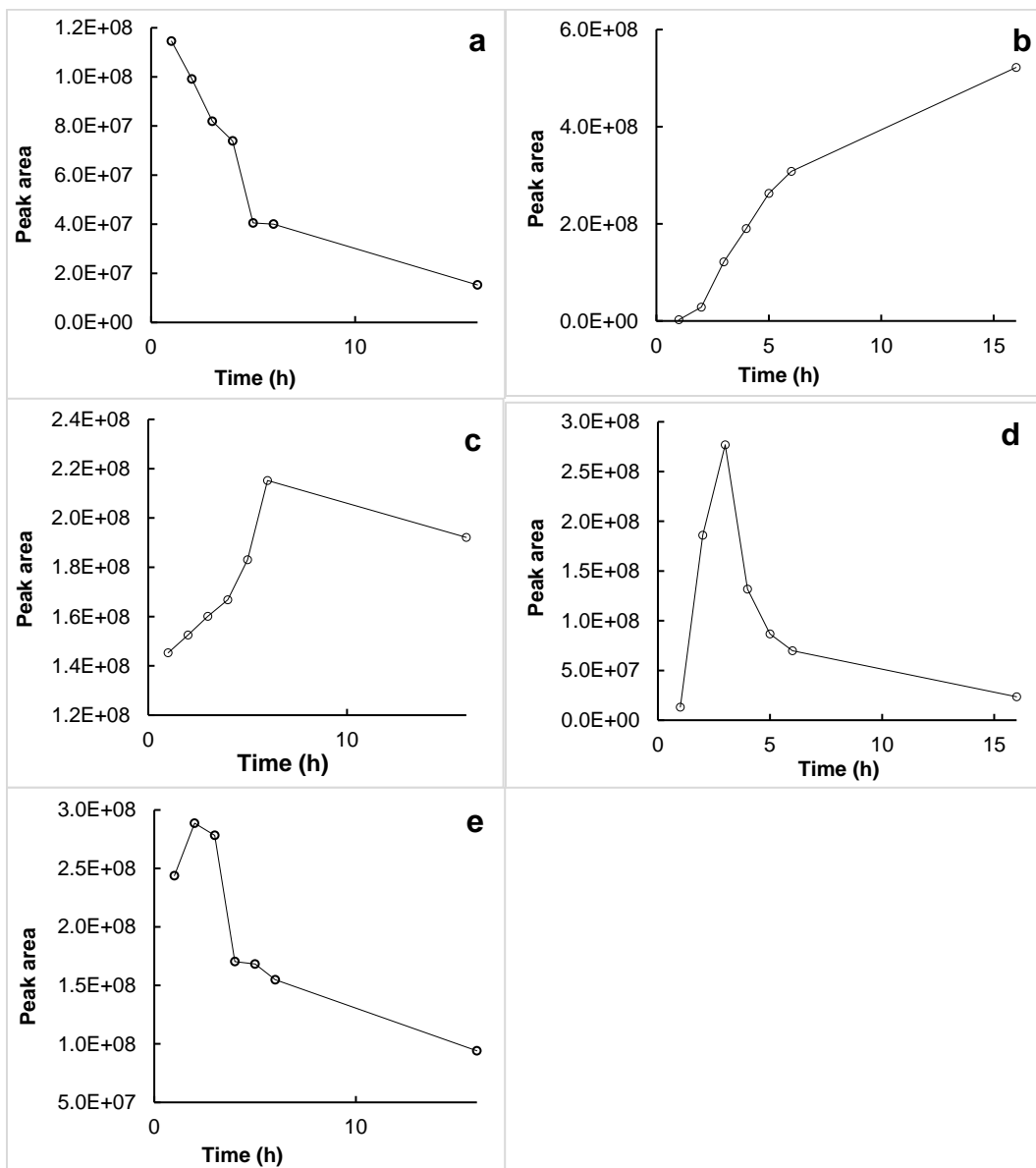
Fig. 8. Mass spectrometry peak area of the main by-products varies with reaction time at a catalyst dosage of 0.075 (molar ratio) at 190 °C for glucose.
a: GDA; b: PAM; c: DE; d: FTH; and e: MPN

Fig. 9. Mass spectrometry peak area of the main by-products varies with reaction time at a catalyst dosage of 0.1 (molar ratio) at 190 °C for glucose.
a: GDA; b: PAM; c: DE; d: FTH; and e: MPN

Fig. 10. Mass spectrometry peak area of the main by-products varies with reaction time at a catalyst dosage of 0.125 (molar ratio) at 190 °C for glucose.
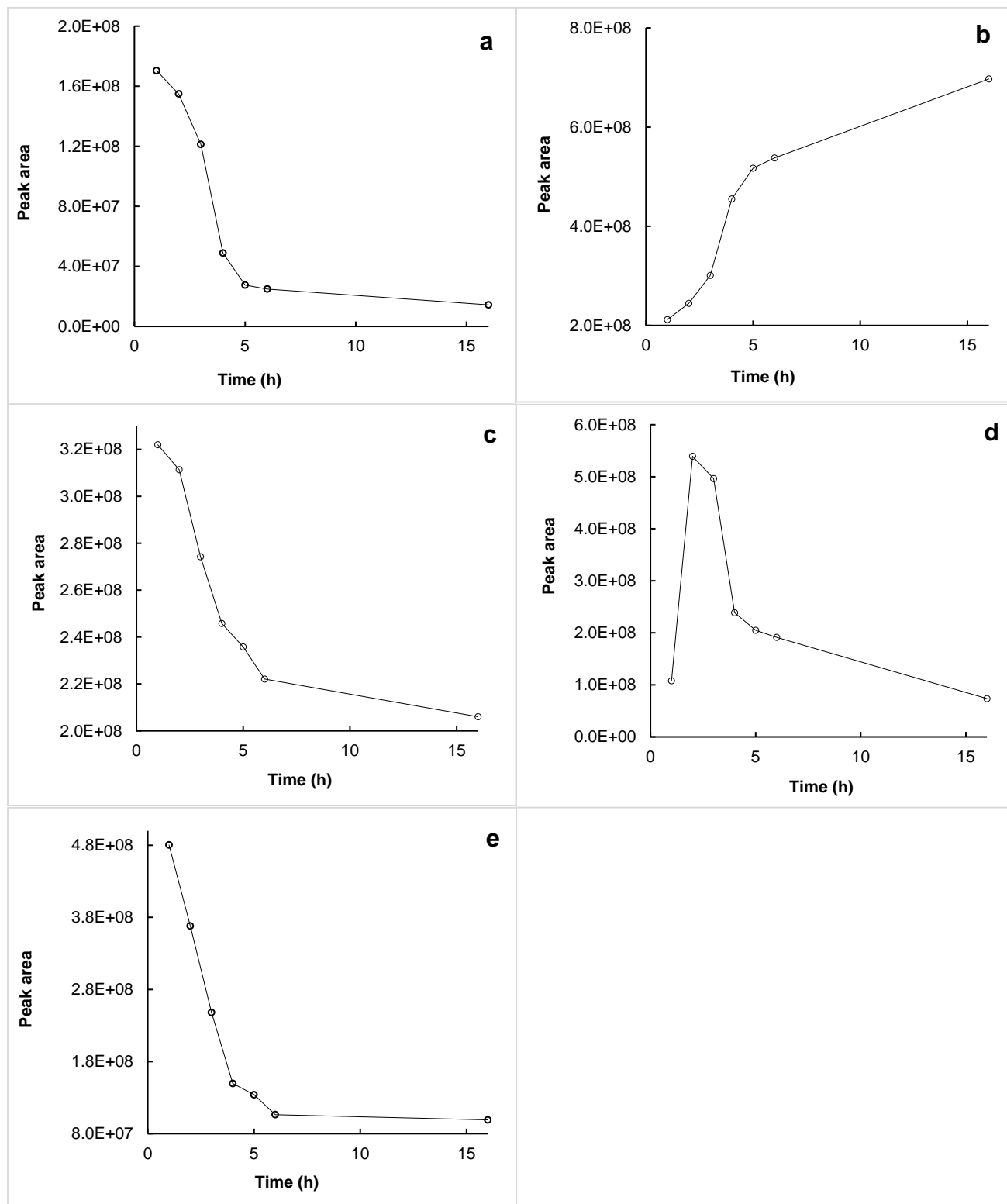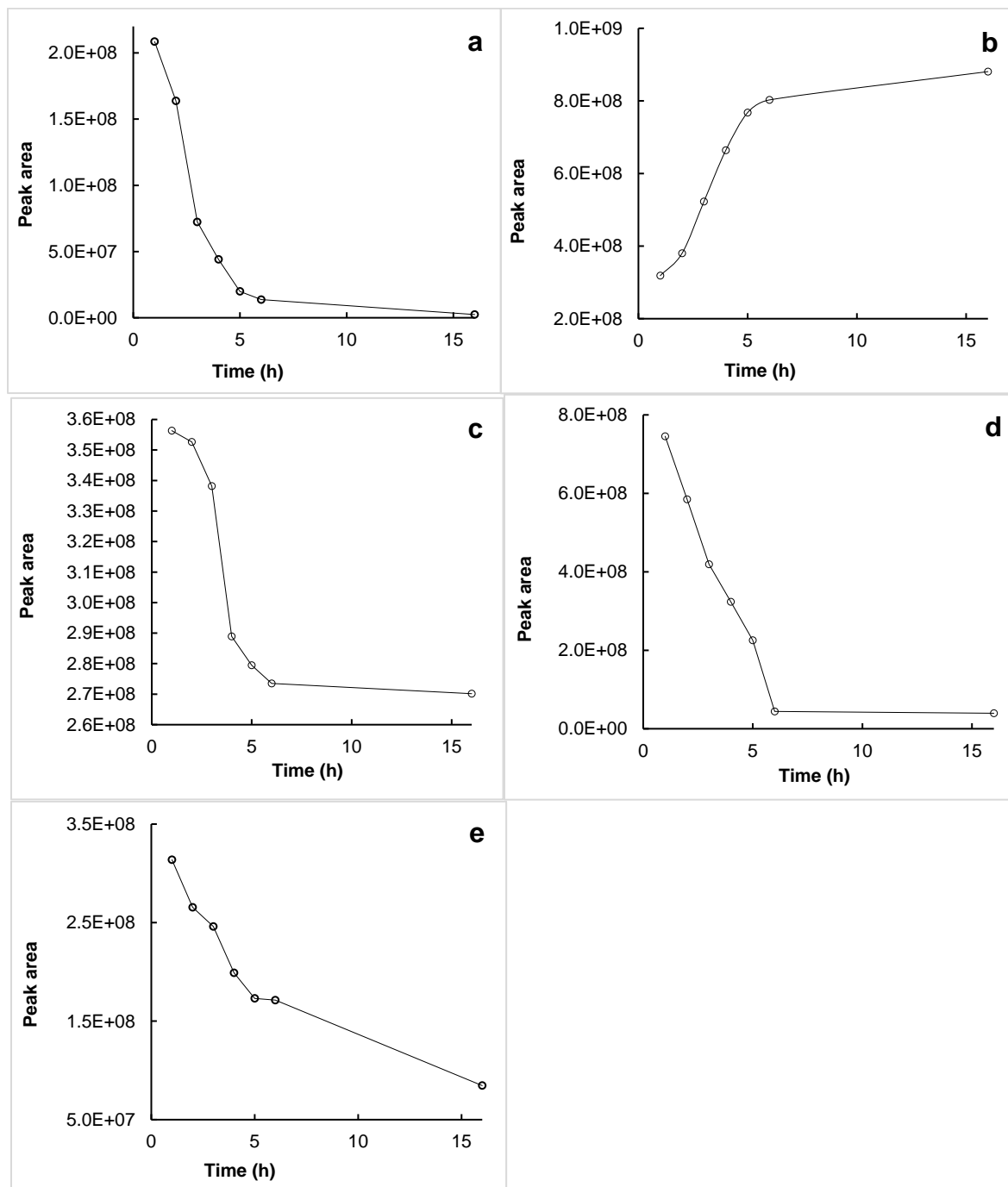a: GDA; b: PAM; c: DE; d: FTH; and e: MPN

Figures 8 to 10 show the effect of time at different molar doses at 190 °C on by-products of glucose conversion. From the figure, it can be seen that the time factor is a very important regulatory parameter in the entire catalytic conversion reaction of glucose, and the optimal reaction time depends on temperature and catalyst dosage.

As the reaction time increased, the peak area of GDA exhibited a tendency towards attenuation. Furthermore, with an increase in catalyst dosage, the rate of GDA attenuation

accelerated. Conversely, the trend of PAM in the system was opposite to that of GDA, indicating an increase in peak area of this component with extended reaction times. This finding corroborates the hypothesis that PAM is synthesized from GDA and acrylic esters esters from MLA, which can also account for the reduction of GDA and the elevation of PAM in the composition.

The mass spectrum peak areas of components DE and MPN exhibited an initial increase, followed by a decrease with increasing reaction time when the catalyst mole ratio was 0.075. However, when the catalyst mole ratios were 0.1 and 0.125, the DE and MPN variation trend was similar to those of GDA, showing a negative correlation with time. This may be attributed to the fact that DE and MPN are intermediate substances in the subcritical catalytic conversion of glucose, whose component content is influenced by the conversion rate of their previous conversion products on one hand, and the rate of their further conversion into smaller molecules on the other. At the catalyst mole ratio of 0.075, the catalytic rate of the entire reaction system was lower than that of the catalysts with mole ratios of 0.1 and 0.125, resulting in a longer duration of glucose catalytic conversion into DE substances. In addition, the slow degradation rates of DE and MPN themselves will lead to an increase in the component contents of DE and MPN over a certain period of time. However, at high catalyst doses, DE and MPN completed all the conversion and accumulation within one hour, and they decreased over time due to their own degradation. At catalyst mole ratios of 0.075 and 0.1, the component FTH exhibited a trend of initial increase and subsequent decrease. Differences were observed a follows: at a ratio of 0.075, FTH reached its peak within 3 hours; at a ratio of 0.1, it took 2 hours. However, at a ratio of 0.125, all conversion accumulation was accomplished within 1 hour, resulting in a continuous downward trend in the graph. Therefore, by adjusting the time parameters, the yield of by-products can be reduced.

When combined with the reaction time and temperature parameters, the results revealed that increasing the temperature within 180 ℃ not only accelerated the conversion of glucose to MLA, but it also boosted the yield of MLA. The adjustment of time parameter figures prominently in the catalytic conversion of glucose. The optimal duration of the reaction varies with the temperature and the quantity of catalyst. Considering the influence of temperature, time, and catalyst dosage on the yield of MLA, the optimal catalyst molar ratio was 0.075 to 0.1, the reaction temperature was 170 to 180 ℃, and the reaction time was 3 h. Under these conditions, the yield of MLA was maximized to 45.8%, and the overall process required relatively low equipment requirements. Compared to the catalytic conversion of glucose to lactic acid in aqueous phase, the target product MLA in this reaction can be easily separated from the by-products through distillation, and high-purity MLA can be obtained through molecular distillation.

CONCLUSIONS

1. Through comparative experiments with various catalyst doses, it was found that the effect of catalysts on the conversion of glucose to MLA was not linear. The appropriate dosage range was a molar ratio of catalyst to substrate between 0.075 to 0.10.

2. Temperature is an important factor affecting the conversion of glucose MLA, but it is also coupled with the amount of catalyst used. Higher catalyst doses and temperatures may result in a reduction in MLA yield. At appropriate catalyst doses, higher

temperatures can increase the yield of MLA, but excessively high temperatures not only will result in dismal process economy, but it also will impose higher demands on the reaction vessel. The optimal processing temperature is 170 to 180 °C.

3. This study revealed that the influence of the time factor on the MLA conversion reaction results in the optimal time to reach the peak MLA yield under different temperature and catalyst dosage conditions not being completely consistent, and its parameters are related to temperature and catalyst dosage. After comprehensive investigation, including temperature, time, and catalyst dosage, the optimal process parameters are considered as a reaction time of 3 h, a reaction temperature of 170 to 180 °C, and a catalyst molar ratio of 0.075 to 0.1. Under these conditions, MLA can reach a maximum yield of 45.8%.

ACKNOWLEDGEMENTS

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