Conversion System Using Subcritical Water to Convert Biomass to Utilizable Substances

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ABSTRACT

Effective utilization of glycerol, which is one of wastes when biodiesel fuel is produced, is focused on in this study. A converted reaction from glycerol to lactic acid in subcritical water was investigated. By using a flow-type reactor, the yield of 90 mol% was achieved within 2 minutes without any metal catalyst. The productivity was 30 times higher than that with a batch-type reactor. From an analysis for activation energy of the conversions from glycerol or two intermediates, alternative reaction pathway was supported. Due to the reaction pathway, the high productivity by the flow-type reactor was understandable.

KEYWORDS

Subcritical water, glycerol, lactic acid, biodiesel fuel

INTRODUCTION

Biomass would be one of the important resources to produce utilizable substances. Solid and liquid wastes would be also the important resources. In Okayama city and Kyoto city in Japan, wasted food oil were collected and converted to biodiesel fuel (BDF) by an alkali-catalyzed method. Not only wasted food oil but also oil form plant such as rapeseed oil, one of biomass, is used to produce BDF in the world. It is expected that the production of BDF from the oils will become more important and be spread. When the BDF is produced, glycerol with alkali is also produced as a by-product. Utilization of wasted glycerol should be important due to the increasing of the BDF production. Glycerol can be converted to lactic acid with a metal catalyst (Shen *et al.* 2010, Roy *et al.* 2011, and Maris *et al.* 2007). This conversion can occur without any metal catalyst in hydrothermal conditions (Kisitda *et al.* 2005 and Zang *et al.* 2012). Lactic acid is the important monomer to produce polylactic acid (PLA), which is one of the resources to form bioplastic. So, the establishment of an effective system for the conversion from wasted glycerol to lactic acid is really desired. In this study, we focused on hydrothermal reaction using subcritical water.

Water can maintain its liquid state in a temperature range from 100 to 374^{o}C under pressurized conditions. This water is called as subcritical water and has two characteristics different from water at ambient temperature and pressure. One of the characteristics is a low relative dielectric constant. It is a reason why solubility of hydrophobic substances such as fatty acid to subcritical water was increased while temperature increased. The other is a high ion product. It makes subcritical water to act as an acidic or basic catalyst. Due to this property, subcritical water could convert glycerol to lactic acid without any metal catalyst. In this study, the converted reaction from glycerol to lactic acid in subcritical water was investigated. Especially, a flow-type reactor was focused on because the reactor could realize a continuous production.

MATERIALS AND METHODS

Figure 1 illustrates the schematic diagram of the flow-type reactor. A coiled stainless tube (sus316, 0.8 mm i.d.) was set in an oven (GC-7A, Shimadzu, Kyoto, Japan) and in a water bath. The temperatures were set at 300-350^{o}C and 20^{o}C, respectively. The tube was connected to a pump (LC-20A, Shimadzu) which feed a solution containing glycerol and NaOH. The concentrations of glycerol and NaOH were set from 0.5 to 2.0 mol/L. A back-pressure valve was connected at the end of the tube and controlled the pressure in the tube at 20 MPa. The flow rate of the solution was controlled then the residence time of the solution in the tube which was set in the oven was 15-300 seconds. The concentrations of substances in the effluents were measured by a high performance liquid chromatography (HPLC) with a UV-Vis detector. The pH of the effluent solution was measured by a pH meter.

For experiments to investigate the reaction pathway, glyceraldehydes or pyruvaldehyde instead of glycerol was dissolved in the feeding solution.

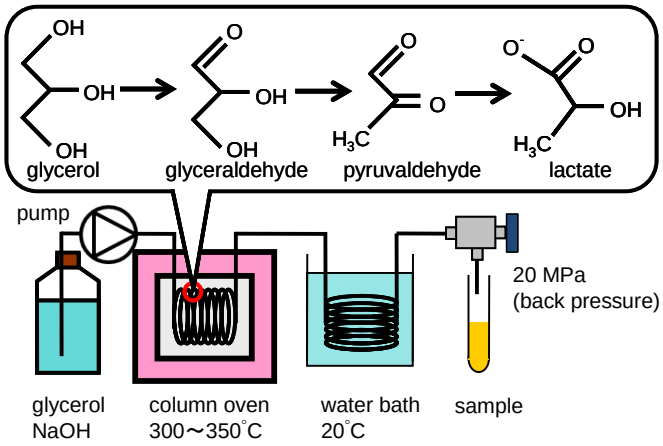

Fig. 1 ***Schematic diagram of the flow-type reactor and a reaction pathway***

RESULTS AND DISCUSSION

1. Conversion of glycerol to lactic acid

Figure 2 shows the relationship between yield of lactic acid and residence time of the reaction solution in this flow-type reactor. Within 2 min, 90 mol% was achieved. The longer residence time gave lower yields due to degradation of lactic acid. Table 1 shows the yields with various reaction conditions in some papers. In these papers, some metal catalysts were used for the conversion of glycerol to lactic acid. Au-Pt/TiO2 could have realized the conversion below 100^{o}C

(Shen et al, 2010), however, the yield was 42 mol%, which was lower than the one in this study. Roy et al. (2011) and Maris et al. (2007) also used metal catalysts for the conversion. The yields were higher than the one in Shen et al. (2010), however, they needed longer reaction time. Kishida et al. (2005) and Zang et al. (2012) realized the conversion without any metal catalyst and with shorter reaction time. They used a batch-type reactor as same as the others (Entry 1-6). The batch-type reactor has a disadvantage for continuous operation. For the continuous production, a flow-type reactor is better. In this study, the 90 mol% yield was achieved within 2 min in the flow-type reactor.

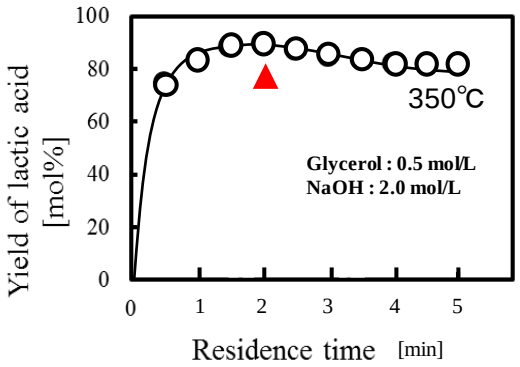

Fig. 2 Relationship between the yields of lactic acid and residence time in the flow-type reactor.

Table 1 Conversion of glycerol to lactic acid using various catalysts [a]

Entry	Reaction condition	Substrate NaOH/Glycerol	Temp. [°C]	Reaction time [min]	Yield [%]	Ref.
1	Hydrothermal	1.25M/0.33M	300	60	90	Kishida 2006
2	Hydrothermal	1.25M/0.33M	300	60	75	Zhang 2012
3	Cu_2O, NaOH/N_2-14bar	1.1 M	240	360	73.1	Roy 2011
4	Au-Pt/TiO_2 (Au:Pt=1:1, 2.5×10^{-3} mmol), 1atm O_2	0.88M/0.22M	90	—	42	Shen 2011
5	Ru/C, 40 bar H_2	0.8M/1wt%	200	180	55	Maris 2007
6	Hydrothermal	2 M/0.5M	350	2	90	This study

a Reaction conditions: conversion and yield of lacitic acid was determined by HPLC.

2. Reaction pathway and activation energy

Kishida et al. (2006) showed a reaction pathway as shown in Fig. 3. We performed the experiments to convert two intermediates, glyceraldehyde and pyruvaldehyde, to lactic acid in the flow-type reactor. Figure 4 showed the concentrations of lactic acid produced by the converted reaction from the intermediates at 350°C. Lactic acid was

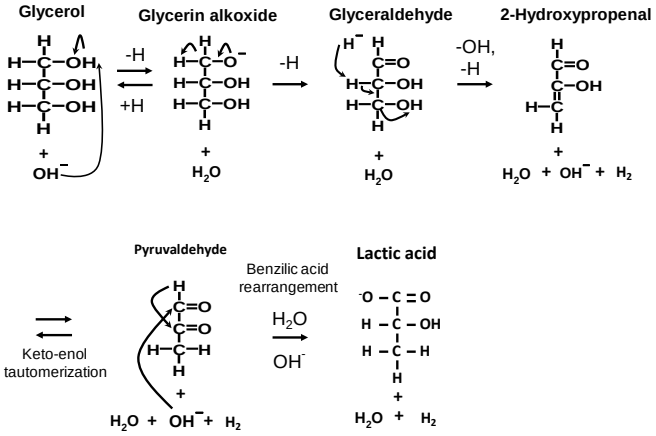

Fig. 3 A reaction pathway which was proposed by Kishida *et al.* 2006

given within the shorter residence time for both reactions.

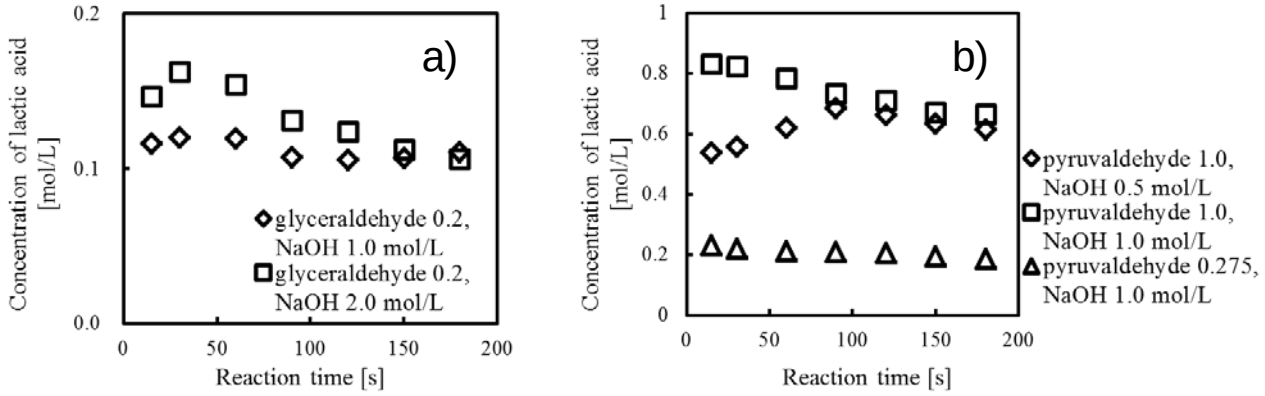

Fig. 4 Concentrations of lactic acid with the converted reaction from glyceraldehydes (a) and pyruvaldehyde(b)

We estimated the initial reaction rate, v_0, at various temperatures to produce the lactic acid from glycerol, glyceraldehydes, and pyruvaldehyde when the concentration of NaOH was fixed at 2.0 mol/L. Arrhenius plots for the converted reactions was shown in Fig. 5(a). The activation energies could be estimated from the slopes. Figure 5(b) shows the activation energy. The highest value was achieved for the converted reaction from glycerol. The value for the one from glyceraldehyde was lower and the one from pyruvaldehyde was very low. These results mean that the reaction step to produce glyceraldehyde from glycerol would be the rate-limiting step for the production of lactic acid from glycerol if the reaction pathway is according to Kishida's model as shown in Fig. 2. However, the value of the activation energy was still lower than that in Kishida et al. (2006). It suggested that the converted reaction could proceed in a different pathway in the higher temperature. Zhang et al. (2012) proposed a different pathway as shown in Fig. 6. According to the pathway, glycerol is not converted via glyceraldehyde but via acetol to pyruvaldehyde and H_2 gas comes out just before changing to pyruv- aldehyde. In the batch reactor, the pressure could not be controlled and there was a gas phase. It could not suppress the occurrence of H_2 gas, which inhibited mass transfer of the substrates in the liquid phase. There is a possibility that the inhibition of the mass transfer raised up the value of the activation energy.

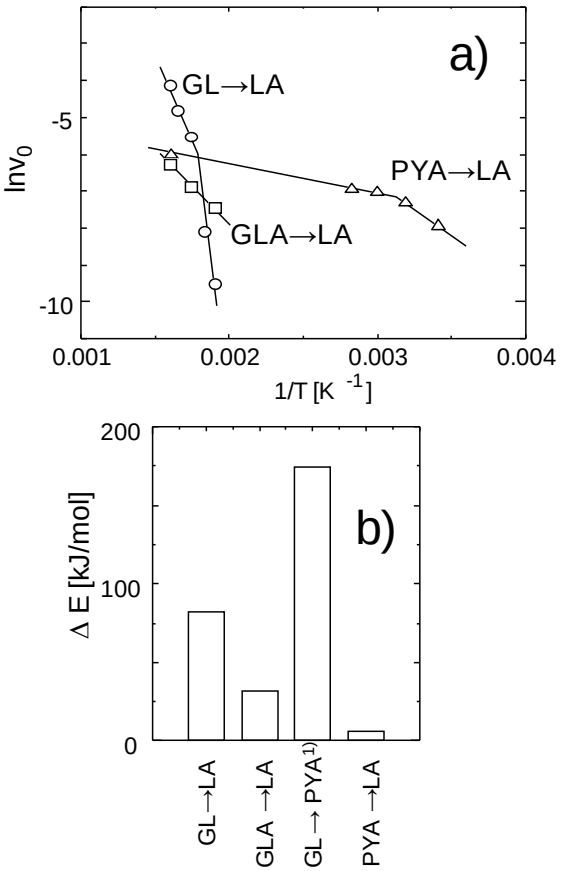

Fig. 5 Arrhenius plots (a) and activation energies (b) for each converted reaction. GL: glycerol, GLA: glyceraldehydes, P YA: pyruvaldehyde, LA: lactic acid. 1) Kishida *et al.* 2006

In the flow-type reactor, the pressure was well controlled at 20 MPa. The high pressure could suppress the occurrence of H_2 gas then decrease the value of activation energy. From these reasons, the high productivity would be achieved by the flow-type reactor.

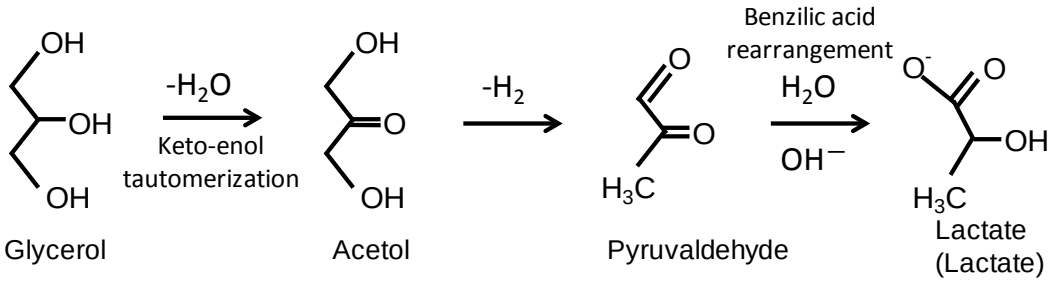

Fig. 6 A reaction pathway which Zhang et al. (2012) proposed.

CONCLUSIONS

The high productivity of conversion from glycerol to lactic acid was achieved in the flow-type reactor. Due to the investigation for conversion from the intermediates, the reaction pathway via acetol would be considerable. This consideration supports the reasons for the high productivity.

REFERENCES

Kishida, H., Jin, F., Zhou, Z., Moriya, T. and H. Enomoto, Conversion of Glycerin into Lactic Acid by Alkaline Hydrothermal Reaction, *Chem. Lett. 34, 1560-1561 (2005).*

Kishida, H., Jin, F., Moriya, T. and H. Enomoto, Kinetic Analysis of Converted Reaction from Glycerol to Lactic Acid with Alkali Hydrothermal Treatment, *Kagakukougaku Ronbunshu (in Japanese), 32, 535-541 (2006).*

Maris, E.P. and R.J. Davis, Hydrogenolysis of glycerol over carbon-supported Ru and Pt catalysts, *J. Catal. 249, 328-337 (2007).*

Roy, D., Subramaniamm, B. and R.V. Chaudhan, Cu-Based Catalysts Show Low Temperature Activity for Glycerol Conversion to Lactic Acid, *ACS Catal. 1, 548-551 (2011).*

Shen, Y., Zhang, S., Li, H., Ren, Y. and H. Liu, Efficient Synthesis of Lactic Acid by Aerobic Oxidation of Glycerol on Au–Pt/TiO_2 Catalysts, *Chem. Eur. J. 16, 7368-7371 (2010).*.

Zhang, Y., Shen, Z., Zhou, X., Zhang, M. and F. Jin, Solvent isotope effect and mechanism for the production of hydrogen and lactic acid from glycerol under hydrothermal alkaline conditions, *Green Chem. 14, 3285-3288 (2012).*

Conversion System Using Subcritical Water to Convert Biomass to Utilizable Substances

—Conversion from wasted glycerol to lactic acid—

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Okayama University
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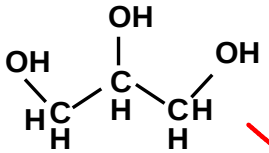
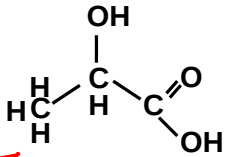
Background (about my researches)

Wasted oil



Wasted glycerol



Lactic acid

Poly lactic acid

Subcritical Water

Low Relative dielectric constant
High Ion Products

Bio Diesel Fuel
(BDF)

Biodegradable
plastic

Lignocellulose

Shell

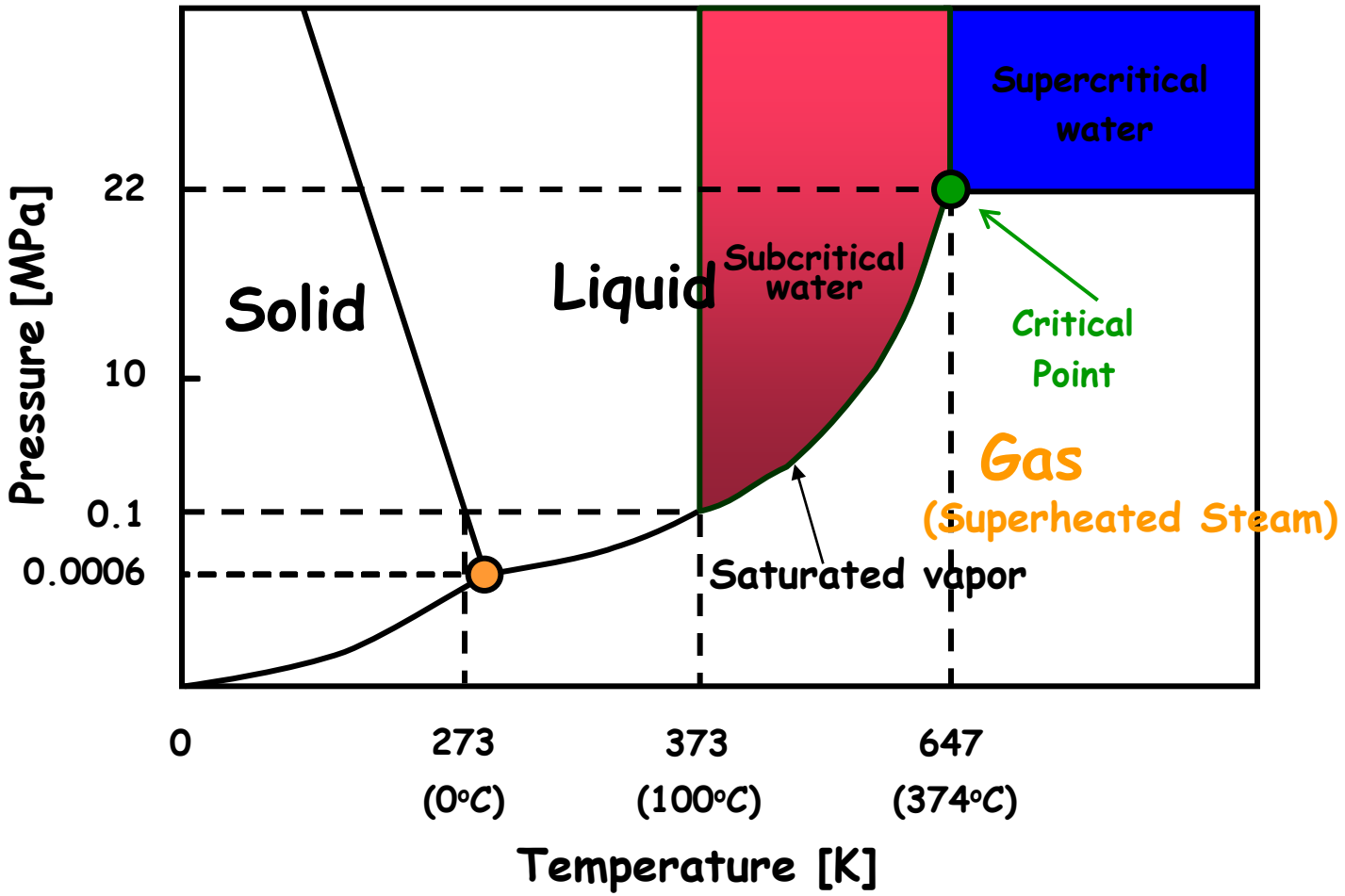
Heated & pressurized

Water

Carya cathayensis sarg

Starch foam

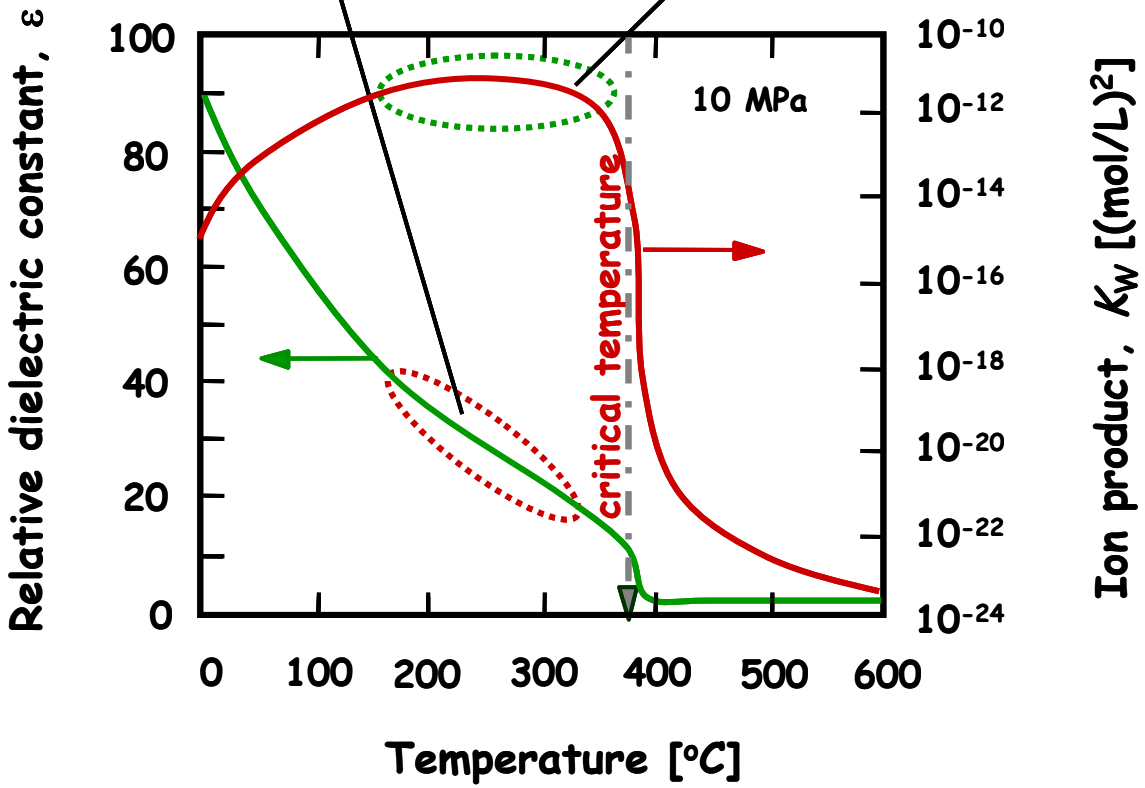
Phase diagram of water



Characteristics of subcritical water (SCW)

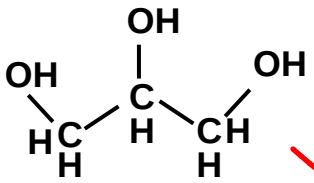
Low relative dielectric constant
(Same properties as an organic solvent)
Good solvent for hydrophobic substances

High ion product
(High concentrations of H^+, OH^-)
Act as a catalyst



Background

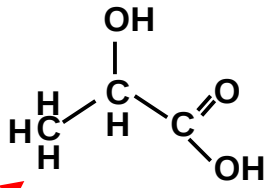
Wasted oil



Wasted glycerol

Subcritical Water

Low Relative dielectric constant
High Ion Products



Lactic acid

Poly lactic acid

Bio Diesel Fuel
(BDF)

Biodegradable
plastic

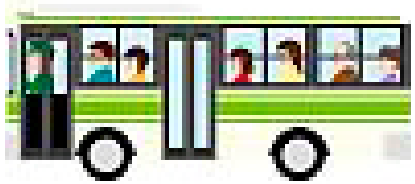
Glycerol is a by-product when BDF is produced

Rapeseed Oil

or

Waste Oil

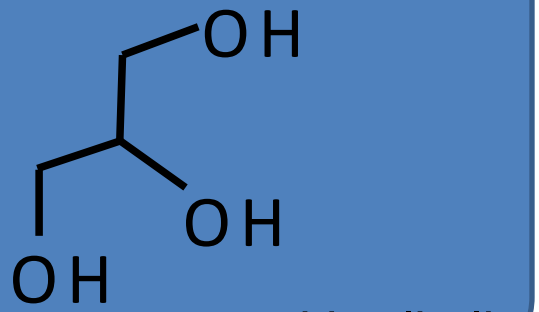
\+ Methanol as a substrate
Alkali as a catalyst



Bio-Diesel Fuel (BDF)

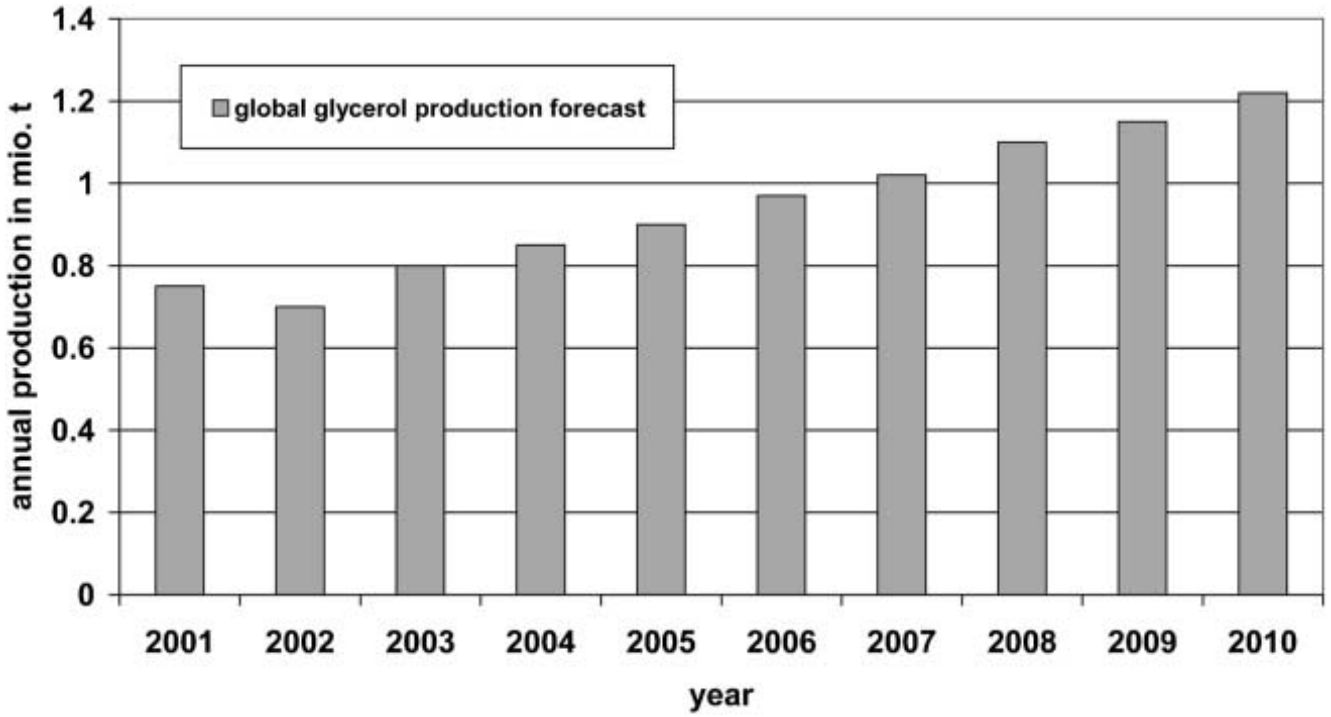
\+

Glycerol as a by-product



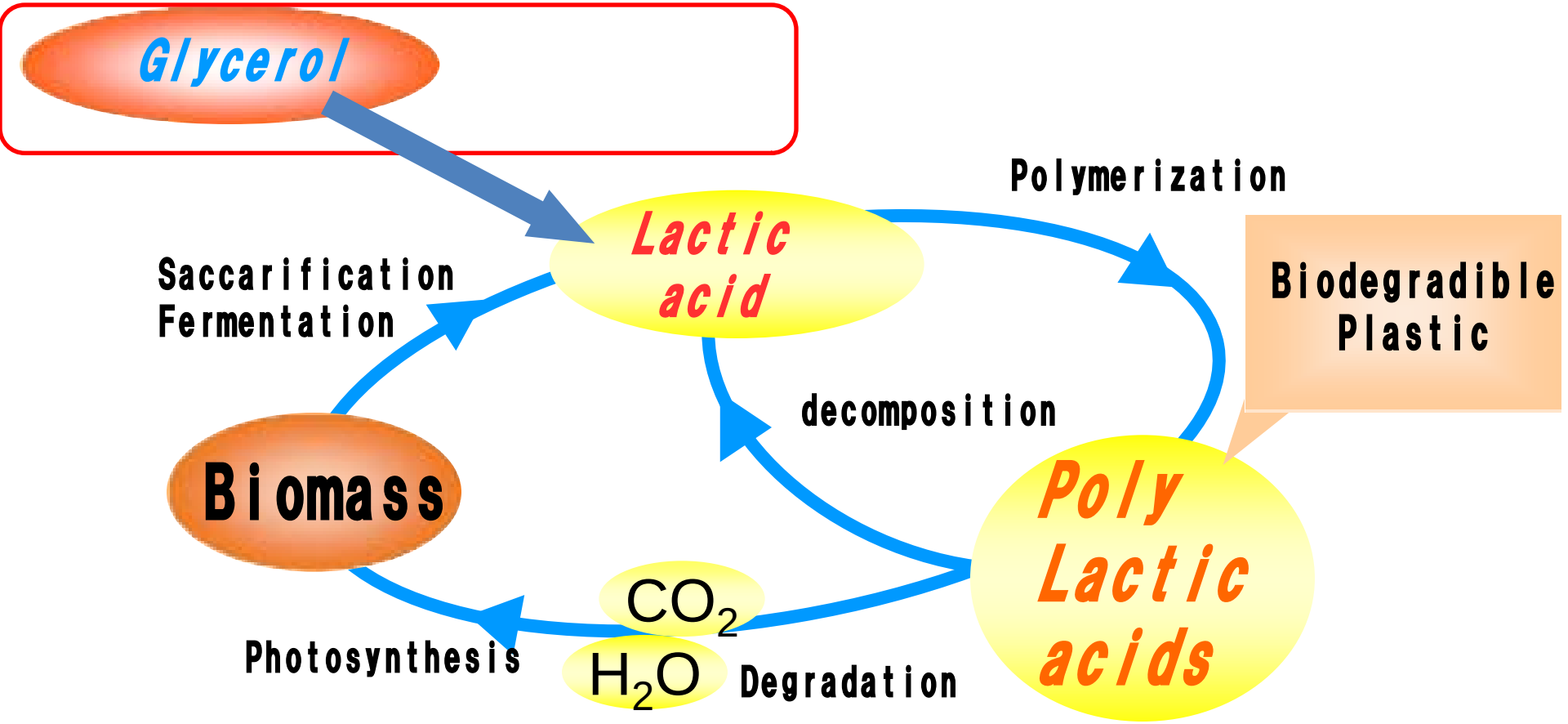
With Alkali

Global production of glycerol



L. Ott *et al*., *Green Chem*., **8**, 214–220, (2006)

Carbon neutral



Type of reactor

Batch-type

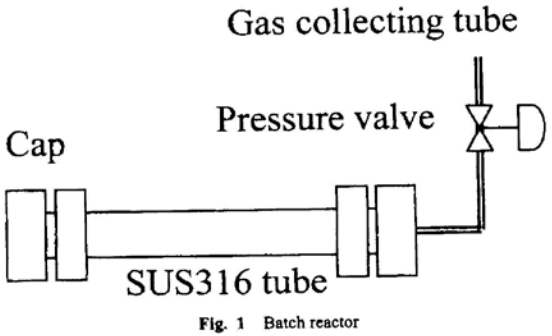
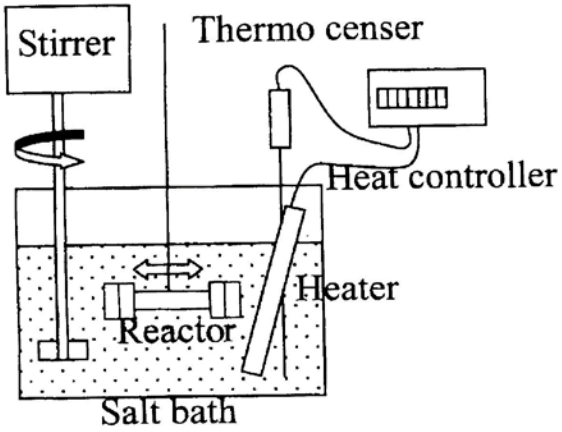
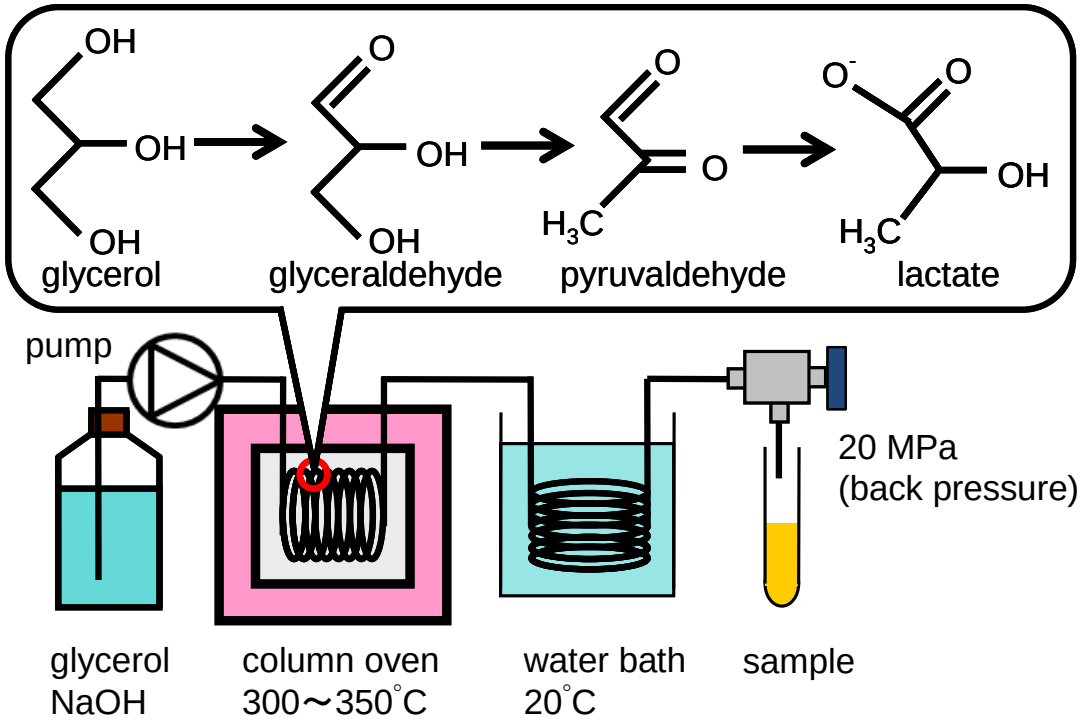


Fig. 1 Batch reactor



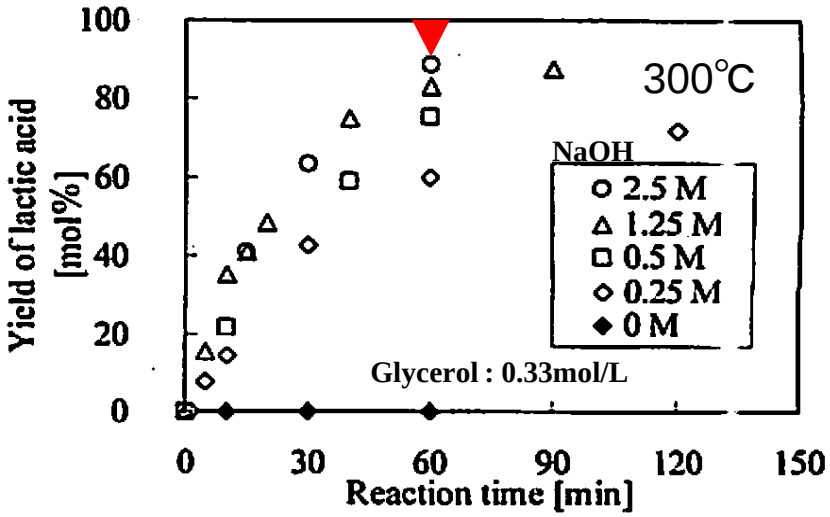
Kishida *et al. Kagakukougaku Ronbunshu* inJapanese, **32**, 535 (2006)

Flow-type



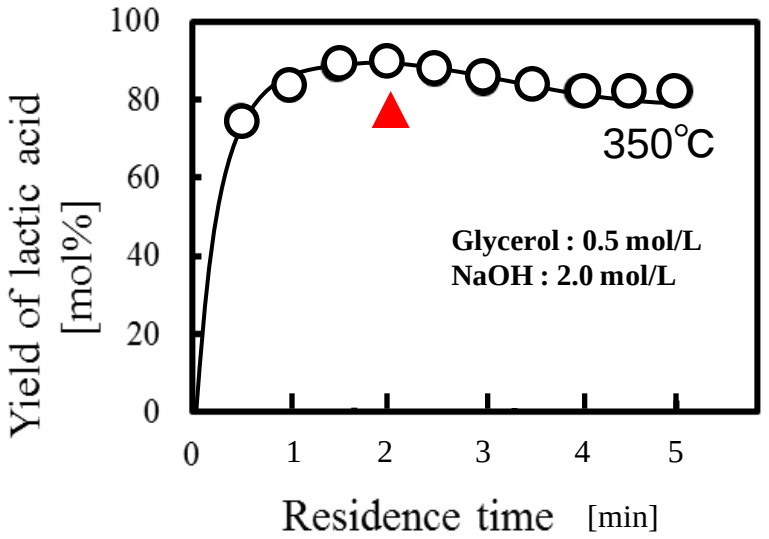
Flow-type was effective.

Batch-type



60 min

Flow-type



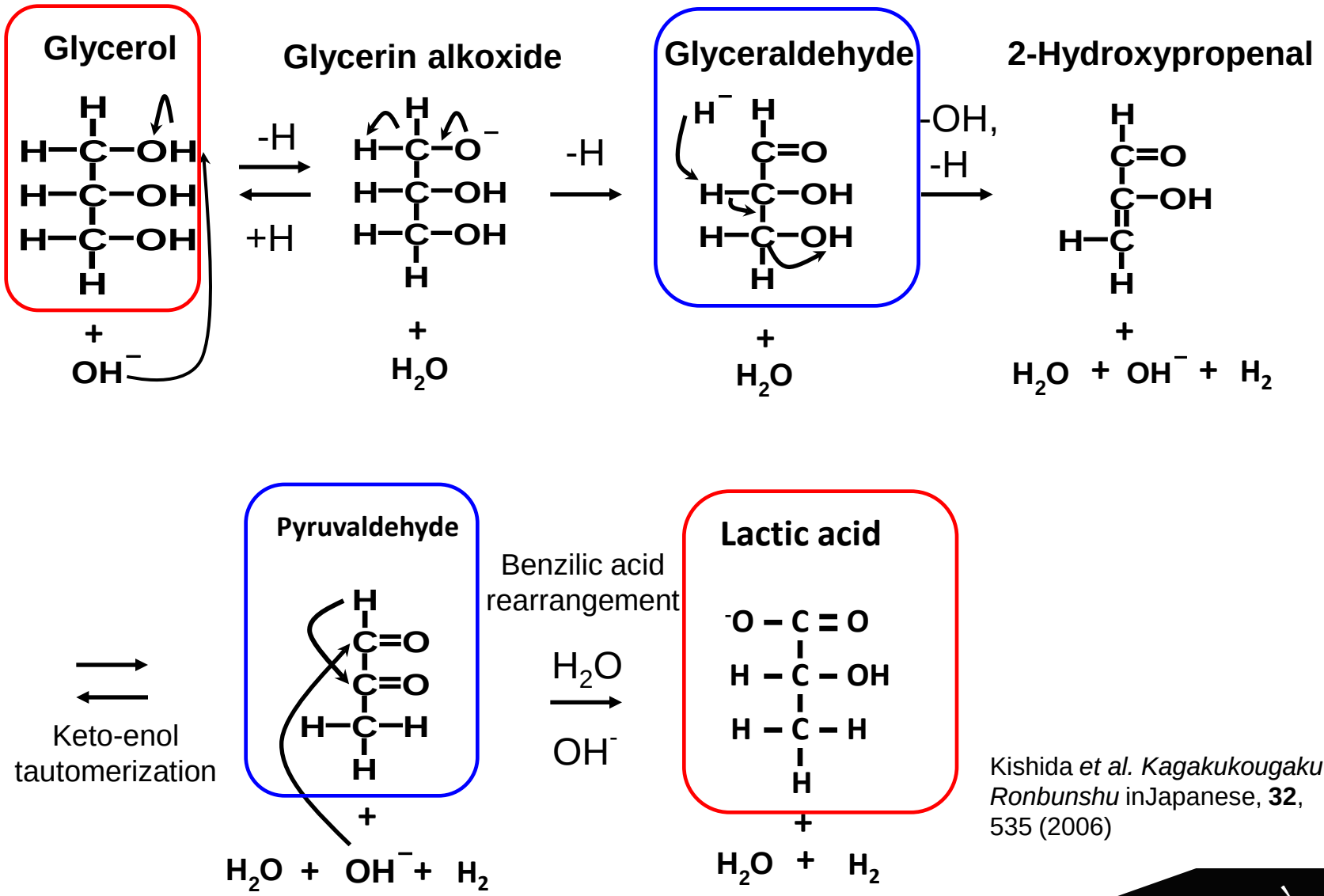
2 min

Maximun yield : 90 mol%

30 times shorter

Kishida *et al. Kagakukougaku Ronbunshu* inJapanese, **32**, 535 (2006)

Proposed mechanism for the conversion



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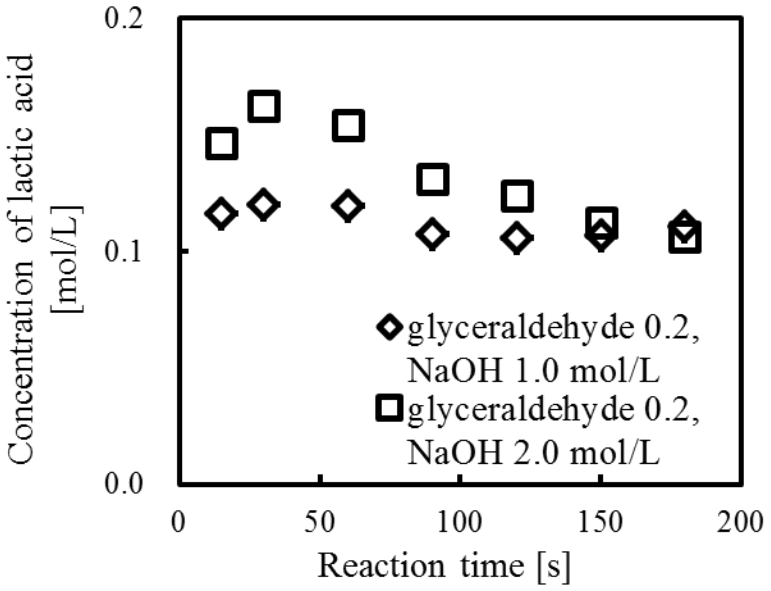
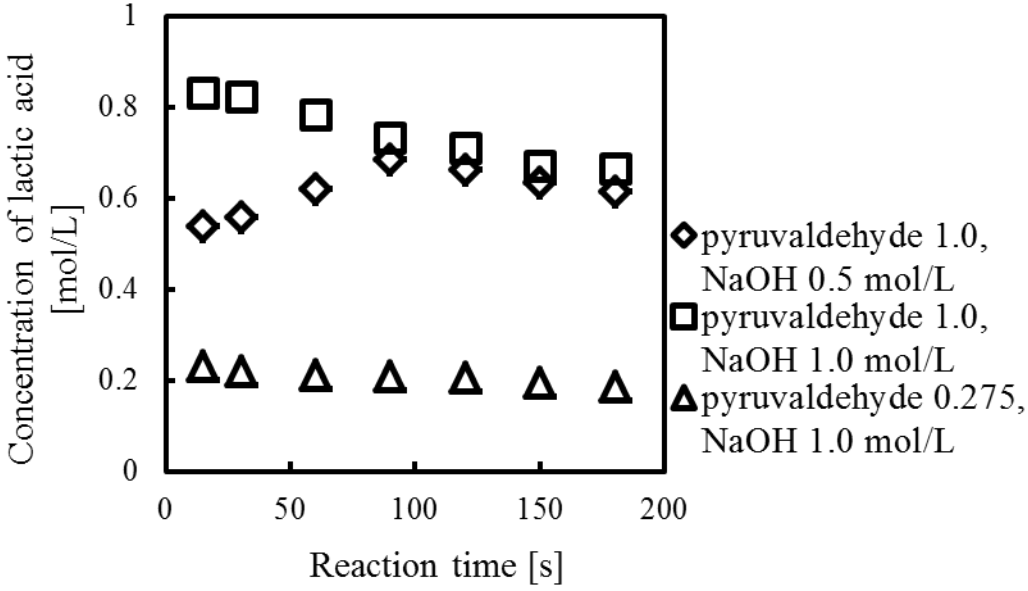
Conversion from intermediates to lactic acid

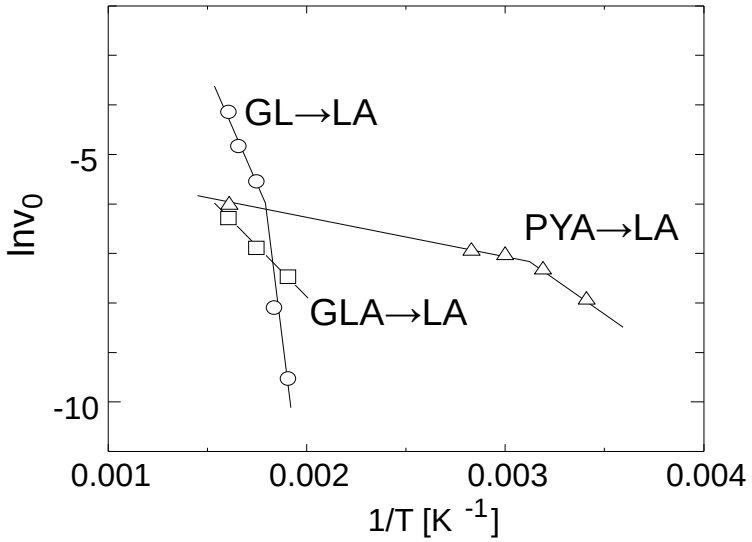
From glyceraldehyde

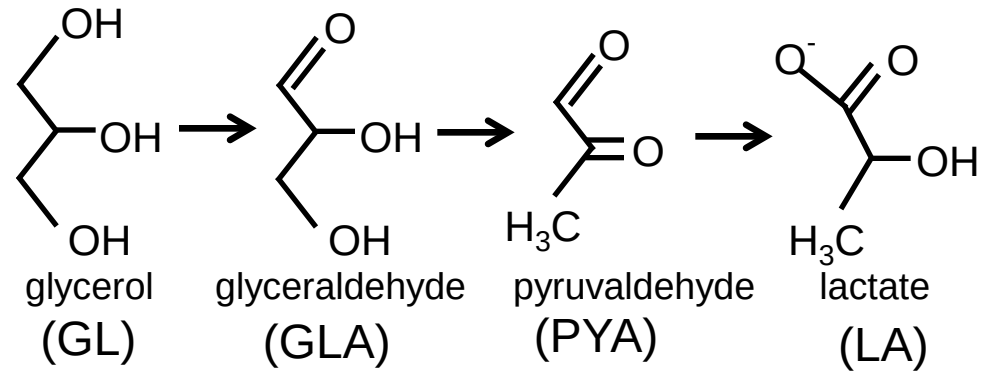


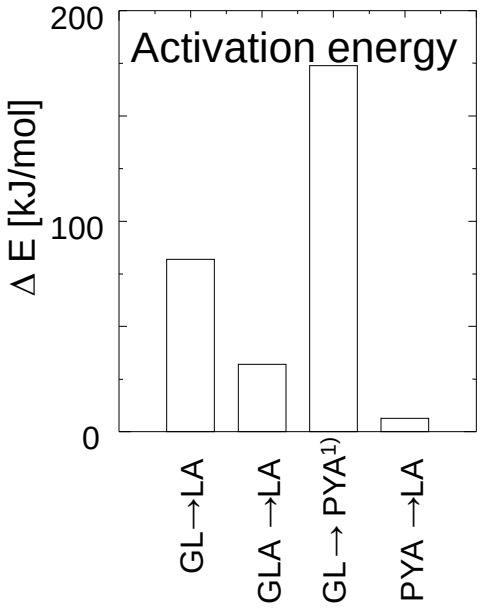
From pyrvaldehyde



Reaction rates and activation energy







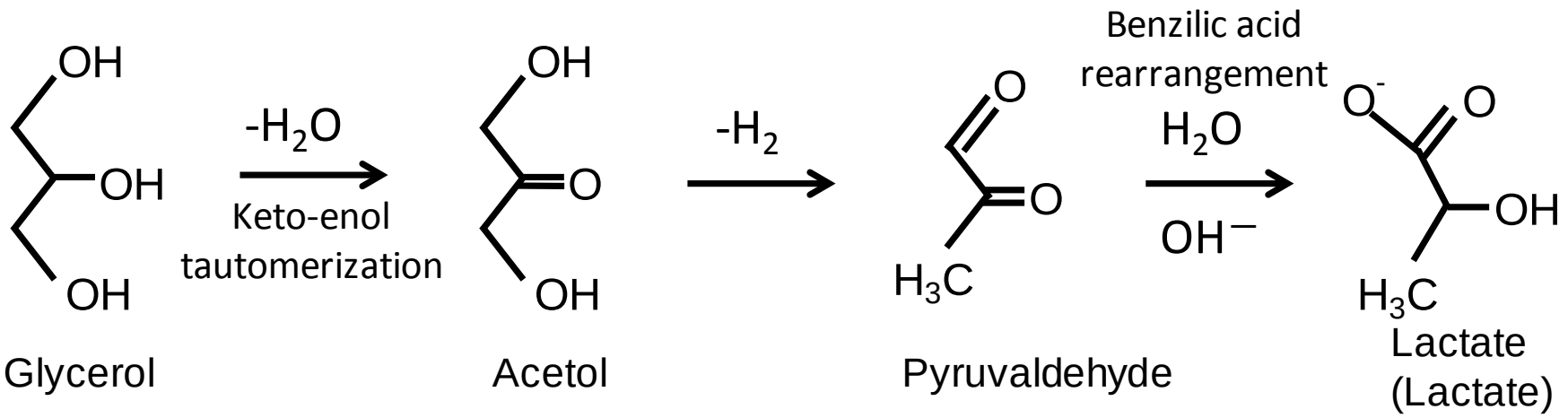
A lower activation energy was shown in this study.

The rate-limiting step should be the step from GL to GLA.

There is a possibility that the pathways were incorrect.

1) Kishida *et al. Kagakukougaku Ronbunshu* inJapanese, **32**, 535 (2006)

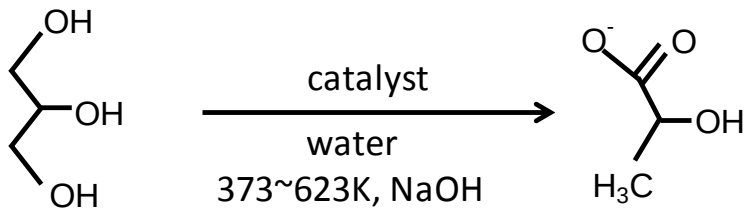
A new proposed pathway



Y. Zhang et al., Green Chem. 14, 3285, (2012)

We are going to prove which this pathway is correct or not.

Conversion of glycerol to lactic acid using various catalysts



Entry	Reaction condition	Substrate NaOH/Glycerol	Temp. [°C]	Reaction time [min]	Yield [%]	Ref.
1	Hydrothermal	1.25M/0.33M	300	60	90	Kishida et al. 2006
2	Hydrothermal	1.25M/0.33M	300	60	75	Zhang et al. 2012
3	Cu_2O, $NaOH/N_2$-14bar	1.1 M	240	360	73.1	Roy et al. 2011
4	Au-Pt/TiO_2 (Au:Pt=1:1, 2.5×10^{-3} mmol), 1atm O_2	0.88M/0.22M	90	—	42	Shen et al. 2011
5	Ru/C, 40 bar H_2	0.8M/1wt%	200	180	55	Maris et al. 2007
6	Hydrothermal	2 M/0.5M	350	**2**	90	This study

Reaction conditions: conversion and yield of lacitic acid was determined by HPLC.

Conclusion

The yield to produce lactic acid was 90mol%.

The maximum yield was achieved within 2 min with the flow-type reactor.

The flow-type reactor would have an advantage for the short time-operation.