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Concentrated Lactic Acid Production from Invert Sugar in Alkaline Solution

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High concentration of lactic acid production is not practical in industry, which is currently produced by fermentation. This work investigated lactic acid synthesis derived from invert sugar in an alkaline solution at low temperature under atmospheric pressure. 30 % invert sugar was continuously added into 3.5 - 8.5 M concentrated sodium hydroxide solutions in a semi-batch reactor at 30 – 80 °C. The central composited design (CCD) was used for design experiments and three variables such as reaction temperature, initial concentration of sodium hydroxide (NaOH) and feed time being investigated. The reaction temperature and initial concentration of NaOH were more pronounced on the yield. At 70 °C, 8.5 M NaOH, and feed time of 6 h. 76 % lactic acid yield was achieved. An independent study at 70 % invert sugar and 15 M NaOH solution caused runaway in a batch reactor, while the yield in a semi-batch reactor was 62 %.

1. Introduction

Lactic acid is widely used for food, pharmaceutical and chemical industries. Moreover, it attains more attention because it is a monomer for bio-plastic production as polylactic acid (PLA). PLA has many applications, some of the common uses as films, bottles, containers and medical devices. Lactic acid can be produced from fermentation or chemical synthesis. Currently, fermentation is commonly used for lactic acid production because it can get above 90% lactic acid yield. Drawbacks of fermentation are control of growth of microorganism, long fermentation time, medium sterilization, inhibitor removal from low-cost agricultural biomass. Moreover, the concentration of raw material (sugar) and lactic acid product are low, because of end-product inhibition. Therefore, it requires a large amount of energy for water removal in product purification.
Many researchers used agricultural or industrial wastes such as cellulose, starch, sugar cane bagasse, rice straw and molasses to be raw materials for lactic acid production (Komasu et al., 2014; Niemela, 1990; Sjostrom, 1991) because they are abundant and cheap. However, the cost of pretreatment is expensive and when it is used for chemically lactic acid production, the reaction conditions have been severely applied (Niemela, 1990; Sjostrom, 1991). In this work, sucrose was selected as the raw material since it is plenty and low price in Thailand and several countries. Sucrose can be easily hydrolyzed to a mixture of glucose and fructose, namely invert sugar, which is a good raw material for lactic acid production.
Previously, alkaline degradation of monosaccharides and sugar was studied (de Bruijin et al., 1986; de Bruijin et al., 1987; Rattanajairakul, 2016; Shaffer and Friedemann, 1930; Yang and Montgomery, 1996). Several researchers found that it resulted many products such as formic acid, acetic acid, glycolic acid, saccharinic acids (<C6 polyhydroxy acids), >C6 polyhydroxy acids, and lactic acid (de Bruijin et al., 1986; Yang and Montgomery, 1996). They reported that lactic acid was the main product from this reaction. These previous works conducted the reactions at high temperature (more than 100 °C) and use low concentration of sugars in their experiments. This limits the applicability of this reaction as a simple lactic acid production process.
In this work, the lactic acid will be produced in semi-batch reactor that has not been investigated before, and shown that semi batch reactor can be used with high concentration of sugar to produce high concentration lactic acid production. The objectives of this work are production of concentrated lactic acid by alkaline degradation and find the effect of variables on yield of lactic acid with response surface methodology (RSM).

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2. Materials and Method

2.1 Materials

Sucrose was food grade (> 99.9% purity) obtained from a local supermarket in Thailand. It was hydrolyzed to invert sugar by acid hydrolysis. Sodium hydroxide (> 99%) was commercial grade from Korea. Other chemicals were analytical grade or HPLC grade from RCI Labscan. An in-house 300 ml glass reactor for lactic acid synthesis was equipped with the glass jacket for temperature controlling by flowing controlled-temperature water from a circulating bath, PolyScience model 9602. Inside the glass reactor, there were 4 glass baffles and a magnetic stirring bar to enhance well mixing. Temperature inside the reactor was monitored by a thermometer. To run in the semi-batch mode a metering pump, Dosser model MPA 0120PV, was used to feed invert sugar solution into the reactor.

2.2 Method

2.2.1 Preliminary Experiments

2.2.1.1 Effect of batch and semi-batch reactors

100 ml of 30 % w/v invert sugar was used to react with 100 ml of 8.5M NaOH in batch and semi-batch reactors at 50 °C to produce lactic acid. Samples from the batch reactor were taken after reacted for 0.5 and 2 h. Samples from semi-batch reactor (at invert sugar feed rate of 0.2 ml/min) were taken at feed time (time after feeding sugar) of 8.3 and 10 h. Other samples from semi-batch reactor (at invert sugar feed rate of 1 ml/min) were taken at feed time of 1.7 and 3 h. Samples were analyzed by HPLC and calculated % yield of lactic acid by eq. (1)

$$\% \text{ yield} = (C_{\text{lactic acid}} / C_{\text{initial sugar}}) \times 100 \qquad (1)$$

2.2.1.2 Effects of initial concentration of NaOH and reaction temperature in semi-batch reactor

100 ml of 30 % w/v invert sugar was continuously fed into the semi-batch reactor filled with 100 ml of 3.5, 5.5, 8.5 and 10 M NaOH at 50 °C. Samples were taken for analysis, after feed time of 8.3, 10 and 24 h. Semi-batch procedures were repeated at 30, 50, 70 and 90 °C by using 100 ml of 8.5 M NaOH.

2.2.2 Experimental Design

Central Composite Design (CCD) was used to investigate selected variables that affect lactic acid yield in semi-batch reactor with minimum numbers of runs. A five-level, three-factor CCD was practiced, requiring 20 runs. The variables and their levels were prearranged previously in our laboratory The actual variables and their corresponding coded levels are shown in Table 1. The experimental results were analyzed using Minitab. Lactic acid yield (Y) from CCD was fitted to a second-order polynomial given by eq. (2)

$$Y = \beta_0 + \beta_1 T + \beta_2 C + \beta_3 F + \beta_{11} T^2 + \beta_{22} C^2 + \beta_{33} F^2 + \beta_{12} (T^*C) + \beta_{13} (T^*F) + \beta_{23} (C^*F) \qquad (2)$$

where β_0, is intercept. β_1, β_2 and β_3, are linear coefficients. β_{11}, β_{22} and β_{33} are square coefficients. β_{12}, β_{13} and β_{23} are interaction coefficients.

Table 1: Variables and levels for CCD

Variables	Code	$-\alpha$	-1	0	1	$+\alpha$
Temperature (°C)	T	17.3	30	50	70	82.7
Initial concentration of NaOH (M)	C	1.9	3.5	6	8.5	10
Feed time (h.)	F	0.73	2	4	6	7.3

2.2.3 Analytical Procedure

Samples were taken, acidified to pH 2, and analyzed for lactic acid concentration by High Performance Liquid Chromatograph (HPLC) of Thermo Spectra SYSTEM with Platisil 5 μm ODS column using UV-VIS detector at 210 nm. The mobile phase was 5 mM sulfuric acid in deionized water at flow rate of 0.8 ml/min. Reducing sugar content was determined by DNSA method.

3. Results and Discussion

3.1 Lactic acid synthesis in batch and semi-batch reactors

The reaction of alkaline and sugar was studied in batch and semi-batch reactor and the results were depicted in Figure 1.

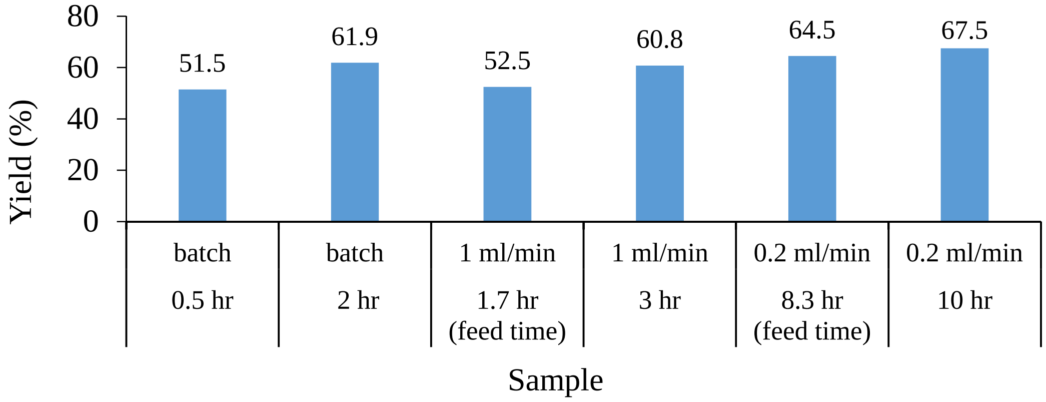


Figure 1: Batch and semi-batch modes on yield of lactic acid

The lactic acid yield of a short feed time (1.7 h.) in semi-batch mode was comparable with the batch mode, which was about 61-62 %. However, slower feed rate or increasing feed time by 5-times (8.3 h.) in the semi-batch reactor had a higher yield of 67.5 %. Longer feed time always had dilute sugar concentration surrounding by high concentration of NaOH inside the semi-batch reactor in which side reactions were prevented. There was no reducing sugar left in both batch and semi-batch reactor at one hour after feed time. Such a high yield of lactic acid in alkaline medium in this work has not been reported before, since all of past works performed in the batch mode (Shaffer and Friedeman, 1930; Yang and Montgomery, 1996). In previous research, the yield of lactic acid in batch reactor were about 50 % g lactic acid/g glucose when 50 mmol glucose and 0.5-10 mol KOH were used at 40 °C of temperature reaction (Shaffer and Friedemann, 1930). Yang and Montgomery (1996) also found that the yield of lactic acid decreased when the concentration of glucose increased, the highest yield of lactic acid was 25 % mol lactic acid/mol glucose at 100 °C. Rattanajairakul (2016) showed that the control of low glucose concentration in the batch system will improve the yield of lactic acid. Moreover, our results demonstrated that lower feed flow rate of sugar provided higher yield. Low sugar concentration enhances lactic acid yield, since it is fragmented in alkaline to C_3 sugars and converted to lactic acid. High concentration of sugar results to saccharinic acids by series of reactions, namely enolization/isomerization, β-elimination and benzillic acid rearrangement (de Bruijin et al., 1986). In order to have low sugar concentration in the reactor, the gradually feed of sugar by semi-batch mode definitely enhances the yield.

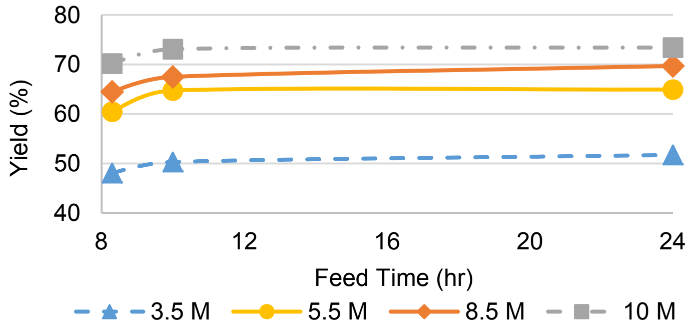


Figure 2: The effect of initial concentration of NaOH on yield of lactic acid in semi-batch reactor at 0.2 ml/min

3.2 Effects of alkaline concentration and temperature

Several bases were used for alkaline degrade reaction such as sodium hydroxide (NaOH), potassium hydroxide (KOH), calcium hydroxide ($Ca(OH)_2$) (Niemela, 1990; Rattanajairakul, 2016; Shaffer and Friedemann, 1930; Yang and Montgomery, 1996). NaOH and KOH had much higher lactic acid yield than

$Ca(OH)_2$, since they are more alkaline (high hydroxide ion concentration) due to complete dissociation and $Ca(OH)_2$ has a very low solubility in aqueous solution (Rattanajairakul, 2016). Therefore, more concentrated NaOH need to be studied in semi-batch reactor for further yield improvement.

The effect of initial concentration of alkaline was investigated and shown in Figure 2. As NaOH concentration increases, the yield of lactic acid increases as well in agreement with previous research (de Bruijin, 1986; Niemela, 1990; Shaffer and Friedemann, 1930). De Bruijin et al. (1986) and de Bruijin et al. (1987) proposed a mechanistic picture of alkaline degradation as in Figure 3. At high alkaline concentration, invert sugar degrades to trioses which will be converted mainly to lactic acid via pyruvaldehyde by benzilic acid rearrangement. Trioses polymerize back to fructose and can form psicose, which both hexose sugars enolize/isomerize to 2,3-enediol. 1,2-enediol, from glucose and fructose enolize/isomerize, and previous 2,3-enediol are converted to C_6 α-dicarbonyl by β-elimination which proceed further to saccharinic acids by benzillic acid rearrangement. On the other hand, pyruvaldehyde and C_6 α-dicarbonyl can convert to $>C_6$ carboxylic acids when under low concentration of alkaline resulting much lower lactic acid yield. Above 2.5 M NaOH, there is no $>C_6$ carboxylic acids formation (de Bruijin et al., 1986) Although high concentration of 10 M NaOH has a high lactic acid yield, the following study will be investigated mostly at lower than 10 M of NaOH. The effect of temperature from 30 to 90 °C was studied as shown in Figure 4.

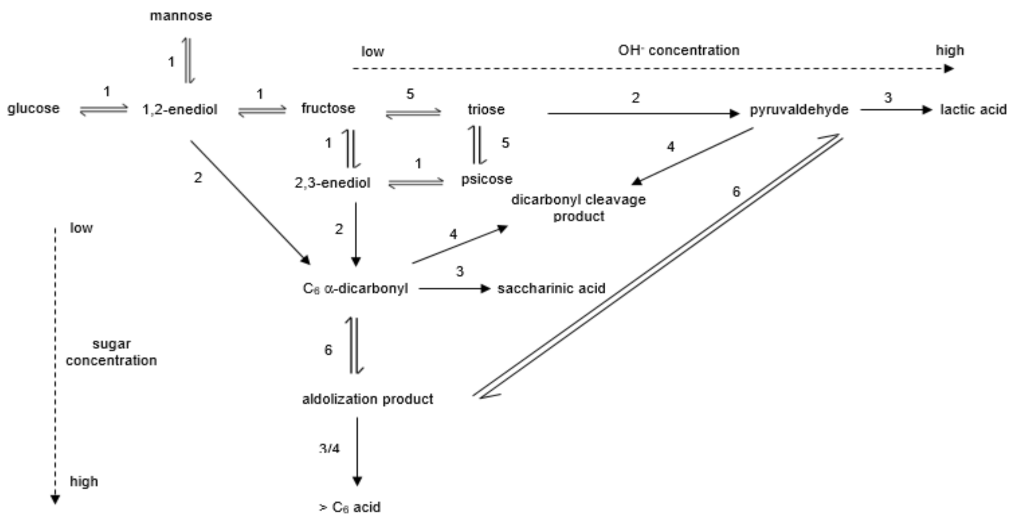


Figure 3: Mechanistic picture of alkaline degradation of monosaccharides : 1.enolization/isomerization, 2.β-elimination, 3.benzillic acid rearrangement, 4.α-dicarbonyl cleavage, 5.aldolization and retro-aldolization, 6.extended aldolization and retro-aldolization of dicarbonyl compounds

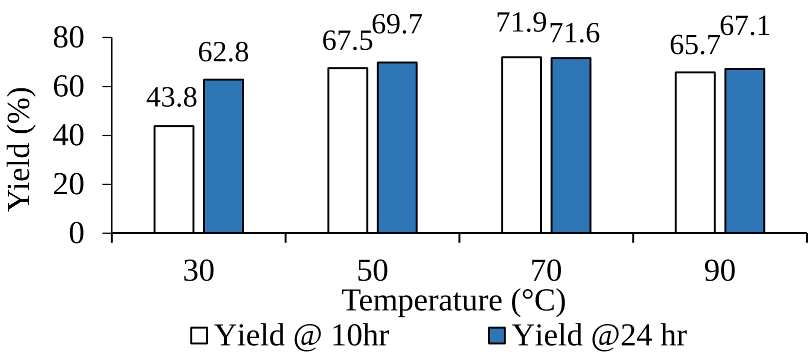


Figure 4: The effect of temperature on lactic acid yield in semi-batch

Temperature is an important factor for lactic acid production. Reaction at 30 °C had a low yield since slow reaction rate, the yield changed from 43.8 to 62.8 % at 10 and 24 h., respectively. However, at 90 °C the yield decreased to about 67 %. At high temperature, formation of C_7 or high molecular weight species takes place. This is a result of recombination in fragments of pyruvaldehyde and C_6 α-dicarbonyl (de Bruijin et al., 1986;

Shaffer and Friedemann, 1930). In next study, the reaction is set at mild temperature, so temperature will be varied from 30 to 82.7 °C.

3.3 RSM of concentrated lactic acid synthesis

From above study, the three variables affected on lactic acid yield. In CCD, twenty experiments were tested and twenty results were shown in Table 2. Such a low yield was found at low temperature and low NaOH concentration (exp.18 and 20). Reaction temperature and NaOH concentration had a large pronounced effect on the yield at the medium point of each variable (exp.3 and 6, and exp. 5 and 8, respectively). Feed time obviously had much less effect on the yield of lactic acid. These results were analyzed by ANOVA and used to demonstrate each effect, the square and interaction terms on the lactic acid yield. It was found that the factors that had no significant effect on yield (P-value > 0.05) were F^2 and interaction terms. Thus, those terms were neglected. The regression model in code coefficient was given by eq. (3). Coefficient of determination (R^2) indicates the fit of the above quadratic regression equation. The regression model for lactic acid production in equation (3) has a satisfied R^2 value of 0.914

$$Y = 58.21 + 20.77 *T + 10.39 *C + 5.01 *F - 6.45*T^2 - 6.58 *C^2 \quad (3)$$

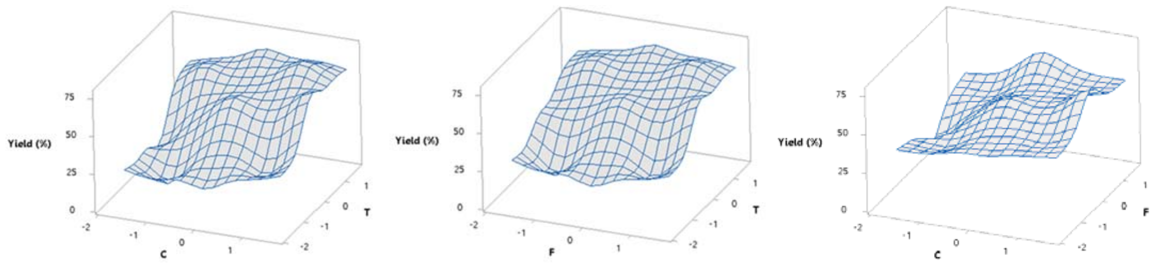
Table 2: Data statistic of model variables

Run	Real variables			Lactic acid yield (%)
	Temperature (°C)	Concentration of NaOH (M)	Feed time (h.)	
1	50.0	6.0	4	59.96
2	50.0	6.0	7.3	64.19
3	17.3	6.0	4	20.26
4	50.0	6.0	4	61.40
5	50.0	1.9	4	17.92
6	82.7	6.0	4	68.54
7	50.0	6.0	0.73	41.78
8	50.0	10.0	4	70.17
9	50.0	6.0	4	60.34
10	70.0	3.5	6	65.44
11	70.0	3.5	2	57.55
12	50.0	6.0	4	59.63
13	50.0	6.0	4	62.03
14	70.0	8.5	6	76.62
15	30.0	8.5	6	30.23
16	50.0	6.0	4	59.49
17	70.0	8.5	2	69.77
18	30.0	3.5	2	7.62
19	30.0	8.5	2	20.33
20	30.0	3.5	6	13.14

Figure 5 depicted response surface plot of lactic acid yield based on each effect. Higher reaction temperature from 30 to 70 °C had a large increasing effect on the yield and it has a small effect from 70 to 83 °C. Increasing temperature speed up the desired reaction rate as usual, but at above 70 °C, there is a competitive side reaction that yields C_7 or high molecular weight of carboxylic acids (de Bruijin et al., 1986; Shaffer and Friedemann; 1930). NaOH concentration had some degree of increasing yield, especially at the mean reaction temperature, since high NaOH concentration prevents aldolization to produce >C_6 polyhydroxy acids (de Bruijin et al., 1986; de Bruijin et al., 1987; Yang and Montgomery, 1996). While the feed time had a little effect in this experimental range, since there was always very low sugar concentration surrounding by such a high NaOH concentration within a small well-mixed semi-batch reactor. A much slower feed rate in run 2 was observed to be better yield than the very rapid one in run 7 at medium temperature and NaOH concentration. The optimum condition for lactic acid production was at 70 °C, 8.5 M NaOH, and feed time of 6 h.

3.4 Effect of very high concentration of reactants

Higher concentration of invert sugar and NaOH has less water in raw material and it will be more economics at the purification step. 70 % invert sugar and 15M NaOH was selected to this study. First, the batch reactor was studied. 100 ml of 15M NaOH was heated at 50 °C and 100 ml of 70 % invert sugar was added once into the concentrated NaOH solution. It was an immediately runaway with an explosion of the mixture. The reaction is highly exothermic (114 kJ/mol glucose or 633 J/g glucose) and it is unable to perform this high concentration reaction in the batch process, especially in the industrial scale. Heat of dilution of NaOH caused temperature rise by 20 °C, according to data from Wilson and McCabe (1942). This reaction was further assessed by slowly feeding 100 ml of 70 % invert sugar at the rate of 0.2 ml/min to react with 100 ml of 15M NaOH filled in the semi-batch reactor. The lactic acid yield was 62 %, without any temperature shooting. Therefore, the semi-batch mode by a continuously differential volume feeding of sugar solution can be used for very high concentration of lactic acid production via alkaline degradation.



(a) (b) (c)

Figure 5: Response surface plot of the effect of (a) temperature versus NaOH concentration (b) temperature versus feed time (c) NaOH concentration versus feed time on lactic acid yield

3. Conclusions

Lactic acid can be produced by a simple alkaline degradation at mild condition. The yield was about 60-70 % depends on the condition of experiments. Temperature and initial concentration of NaOH had more significant effect on the yield of lactic acid, while feed time had a small effect. However, the semi-batch mode is suitable for this reaction, especially at very high concentration of reactants that batch practice is impossible. This process is a good alternative for current lactic acid production.

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