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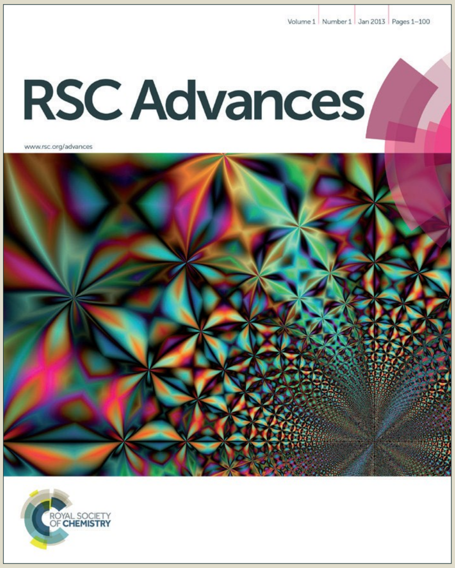

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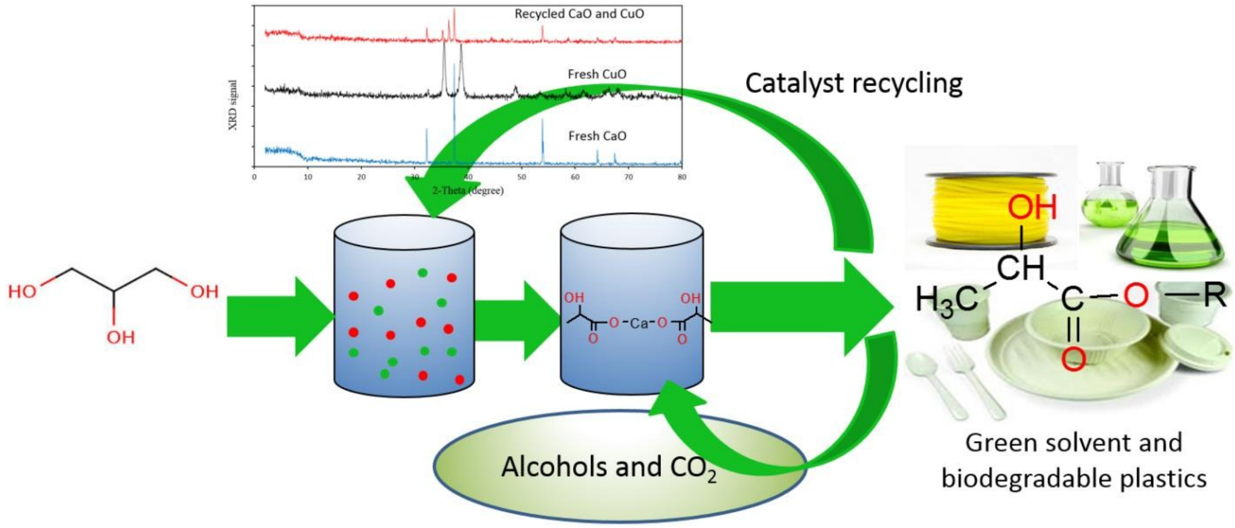
GRAPHICAL ABSTRACT

An environmentally benign process for alkyl lactate production from glycerol using solid catalysts with alcohols and carbon dioxide



Tandem catalytic conversion of glycerol using solid catalysts followed by transesterification to produce alkyl lactate

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ABSTRACT: This study investigated alkyl lactate production from glycerol by tandem processes which included glycerol conversion to calcium lactate using solid catalysts and subsequent transesterification of calcium lactate to alkyl lactate using methanol/ethanol and carbon dioxide. The effect of reaction conditions on alkyl lactate production was systematically investigated. A central composite design (CCD) and response surface methodology were used to design the experiments and evaluate the optimum process conditions. At the optimum condition, the methyl lactate yield reached 57 mol% with a glycerol conversion of 94 mol% using refined glycerol. A yield of approximately 42 mol% for ethyl lactate was obtained using refined glycerol at the optimum condition. Similar glycerol conversion and alkyl lactate yields were obtained using crude glycerol, indicating that the impurities in the crude glycerol had no significant effects on alkyl lactate production. The examination of regenerated catalysts that had been reused twice showed no negative effects on glycerol conversion and methyl lactate production. Compared to the traditional lactic acid and alkyl lactate production, this two-step process for alkyl lactate production from glycerol is both economical and environmentally benign since no gypsum was produced and the solid catalysts can be regenerated and reused.

KEYWORDS: Glycerol, Alkyl lactate, CaO, Methanol, CuO, Carbon dioxide

1. Introduction

Biodiesel is a renewable fuel produced from the transesterification of vegetable oil and animal fat. During biodiesel production, one mole glycerol is formed as a co-product with one mole of triglyceride feed. With expanded biodiesel production, a large amount of glycerol is produced and available in the market that resulted a significantly decrease of price of glycerol. Due to its high availability and low price, glycerol has been selected as one of the top 12 platform chemicals from biomass.[1]

Lactic acid has been a commodity chemical used in food, chemical and pharmaceutical industries traditionally. Alkyl lactate such as methyl lactate and ethyl lactate are derivatives of lactic acid widely used as a green solvent, an additive and an intermediate chemical in the biodegradable polymer industry.[2] High purity methyl lactate is also used to produce highly pure lactic acid, which has broad applications in dairy products and pharmaceutical products.[3] Recently, lactic acid has been drawing great interest in producing biodegradable plastics.[2] With the extension of applications, the demand for lactic acid in the chemical industry has significantly increased.

Lactic acid can be produced through both fermentation of carbohydrates and chemical conversion starting from glycerol.[1, 4-8] Lactic acid produced by fermentation needs to add $Ca(OH)_2$ or NaOH to maintain a neutral pH and precipitate the formed lactic acid. A large amount of $Ca(OH)_2$ is consumed in the process and this leads to large amounts of $CaSO_4$ produced as a byproduct.[9] Recent investigation of lactic acid production from glycerol under hydrothermal conditions with homogeneous base catalysts such as NaOH and KOH showed the product existed as a lactate form due to an instant reaction of lactic acid and base during the production process.[1, 5, 10] The high concentration of NaOH or KOH used in the process also causes severe corrosion—even to stainless steel reactors. It is worth noting that lactic acid produced from the fermentation and chemical synthesis of carbohydrates or glycerol is of low purity. To obtain a highly pure lactic acid, crude lactic acid needs to be esterified with methanol or ethanol to form methyl or ethyl lactate and subsequent hydrolyzation of the methyl/ethyl lactate.[11-14] So, direct formation of alkyl lactate from glycerol is desirable when helping to reduce the tedious process of lactic acid production in fermentation and in chemical synthesis and waste generation.

Direct synthesis of alkyl lactate has been investigated using simple sugars as starting materials with heterogeneous catalysts.[15-18] Among these studies, West et al. reported dihydroxyacetone [10] and glyceraldehyde [19] in the methanol solvent converting to methyl lactate. This conversion utilized the zeolite H-USY as a catalyst. Final analysis reported over 90% selectivity and yield for methyl lactate.[15] Wang et al. also converted dihydroxyacetone [10] and glyceraldehyde [19] with alcohol to alkyl lactates using Brønsted acid with ion-exchanged montmorillonite (Sn-Mont) as a catalyst and obtained 89–93% yield of alkyl lactates in the conversion of DHA.[17] DHA and GLA are C-3 sugars and have served as intermediate chemicals in the hydrothermal conversion of glycerol to lactic acid with alkali.[4, 7, 20] Yoon et al. reported directly converting glycerol to alkyl lactate in published patent. But the catalysts they used are the mixture of base such as CaO and MgO with NaOH or synthesized catalysts of Na/NaOH/Al_2O_3, Na/MgO, and Sn/zeolite. The strong alkali used in the process or catalyst synthesis are not desirable.[21] Purushothaman et al. reported a one-pot conversion of glycerol to methyl lactate in methanol and air but the precious golden are required as catalyst. [22]

CaO as a solid-base catalyst has been investigated in biodiesel production.[19, 23-25] In our previous study, we investigated CaO as a solid-base catalyst for converting glycerol to racemic lactic acid with a 40.8 mol% yield of lactic acid and a glycerol conversion of 97.8 mol% thereby achieving at the optimum condition.[20] However, in this study lactic acid existed in the form of calcium lactate salt at the end of the reactions and still required recovery and purification of lactic acid and generated $CaSO_4$ waste.

The objective of this study was to investigate alkyl lactate production from glycerol using a tandem process. This developed process included glycerol conversion using solid catalysts (CaO and CuO) to calcium lactate, and subsequent calcium lactate conversion to methyl/ethyl lactate with CO_2 and methanol/ethanol. Process conditions such as reaction temperature and time, catalyst and methanol/ethanol loading in refined and crude glycerol were systematically studied. Direct use of industrial crude glycerol was also investigated in order to investigate the effects of impurities and the possibility of using crude glycerol as a starting material. The regeneration and reusability of catalysts were also investigated in this study.

2. Materials and methods

2.1 Materials

Refined glycerol (99.5%) used as the starting material was first investigated in this study. CaO and CuO were used as solid catalysts. CaO was calcined at 910°C in a muffle furnace for 3h before used. Anhydrous methanol (99.99%) and ethanol (99.99%) were as solvents and reactants in the process of this study. Lactic acid (90%), methyl lactate (>96%), ethyl lactate (>96%), and propylene glycol (>99.5%) were used for product calibration of HPLC. All these chemicals, refined glycerol, and catalysts were purchased from Thermo Fisher Scientific Inc. (Waltham, MA, USA). Carbon dioxide in the form of dry ice used in this study was purchased from a local supplier.

2.2 Reactor

The reactions were performed in batch tube reactors made of stainless steel. The volume of the tuber reactor was 2.72 mL with an outside diameter (OD) of 9.525 mm (0.375 inch), an inside diameter (ID) of 7.036 mm (0.277 inch), and a length of 70 mm. The process of glycerol conversion and alkyl lactate production were carried out in an oil bath.

2.3 Experimental procedure

The first-step of the process was glycerol conversion to calcium lactate using solid catalysts of CaO and CuO. The second-step of the process was preparing calcium lactate to react with alcohol and carbon dioxide to form alkyl lactate. After reaction, the mixture of products was washed out by DI water and centrifuged. For testing the recyclability of catalysts, the solids from centrifugation (mainly $CaCO_3$, CuO and Cu) were calcined and reused in glycerol conversion. To analyze the products, the pH of the collected supernatant was adjusted to around 3 by adding diluted sulfuric acid (the concentration of diluted sulfuric acid is 10%). All unconverted calcium lactate was converted back to lactic acid while sulfate salt precipitated in the solid form. If a large amount of lactic acid is detected, it means low conversion of calcium lactate to methyl/ethyl lactate. To the contrary, if a small amount of lactic acid is detected, it indicates that there was a high conversion of calcium lactate to methyl/ethyl lactate.

2.3.1 Glycerol conversion to calcium lactate

In our previous research, the optimum condition for calcium lactate was at the molar ratio CaO to glycerol of 1, the molar ratio CuO to glycerol of 0.2, and 33.3% water content of glycerol at the reaction temperature of 230 °C. [26] So the first-step process of calcium lactate formation was performed at this condition. First, CaO, CuO, glycerol, and water were well mixed. About 0.5 g of well-mixed reactant was added to the tube. Before sealing the tube, argon gas was purged to repel the air from the tube. Then the tube reactor was immersed in a pretreated oil bath at the desired temperature of 230 °C for 30 min. After reaching the reaction time, the reactor was quenched in cold water immediately to stop any further reaction.

2.3.2 Calcium lactate conversion to methyl lactate

The quenched reactor from the first-step process was opened, and methanol and dry ice were added in the second-step process in which the calcium lactate was converted to methyl lactate. In this study, dry ice was the carbon dioxide source. The reaction was performed in the same oil bath with desired temperature and time. During the reaction, the tubes were shaken by a shaker (Wrist Action Model 75, Burrell Scientific, Inc.) to assure adequate mixing of reactants. After the reaction, the reactor was quenched in cold water immediately to stop the reaction and the reactant was washed out by DI water to prepare for analysis.

To optimize the process conditions of calcium lactate conversion and methyl lactate production, a central composite design (CCD) was used. Three independent variables, reaction temperature (X_1, °C), reaction residence time (X_2, min), and molar ratio of methanol to glycerol (X_3) were chosen along with one dependent variable of methyl lactate yield. For statistical calculations, the variables X_i were coded as x_i according to Equation 1 expressed as

$$x_i = (X_i - X_0)/\Delta X \qquad (1)$$

where x_i is dimensionless value of an independent variable, X_i is the real value of an independent variable, X_0 is the real value of the independent variable at the center point, and ΔX is the step change. The central point of independent variables was set at 180 °C, 4 hrs, and 8 mole/mole of methanol/glycerol and the step changes were chosen at 20 °C, 2 hrs and 4 mole/mole of methanol/glycerol. A total of 18 experiments with 6 axial points (α=1.68) and 4 replications at the center points in a 2^3-factorial CCD were employed for the optimization (Table 1). The second degree polynomial (Equation 2) was calculated to estimate the response of dependent variable. Hence, the response is expressed as

$$Y_i = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1{}^2 + b_{22}X_2^2 + +b_{33}X_3^2 + b_{12}X_2X_1 + b_{13}X_3X_1 + b_{23}X_2X_3 \qquad (2)$$

where Y_i represents the predicted response. X_1, X_2 and X_3 are independent variables, b_0, b_1, b_2, b_3, b_{11}, b_{22}, b_{33}, b_{12}, b_{13}, and b_{23} are regression coefficients.

Table 1. Experimental design for optimizing the process condition and results

ID#	Reaction temperature (°C)	Residence time (hrs)	Methanol: glycerol (mole/mole)	Unconverted calcium lactate (%)	Methyl lactate yield (%)	PG yield (%)	Carbon closure (%)
1	160	2	4	59.11	19.8	6.29	87.21
2	200	2	4	43.67	23.53	6.8	75.58
3	160	6	4	49.67	18.41	4.14	75.3
4	200	6	4	40.19	27.91	2.84	72.86
5	160	2	12	44.22	26.24	6.02	82.16
6	200	2	12	15.96	48.3	9.47	84.35
7	160	6	12	25.59	44.08	8.98	85.19
8	200	6	12	13.63	56.75	4.79	77.76
9	146	4	8	55.41	13.85	2.9	73.94
10	214	4	8	23.33	54.48	8.09	90.09
11	180	0.63	8	55.47	27.67	10.76	97.92
12	180	7.37	8	22.75	58.22	9.61	94.75
13	180	4	1.3	69.82	8.38	10.64	99.14
14	180	4	14.7	15.6	57.19	7.38	86.42
15	180	4	8	22.62	48.72	11.14	89.92
16	180	4	8	36.27	41.01	10.74	92.31
17	180	4	8	37.4	41.94	9.46	93.2
18	180	4	8	36.03	43.95	6.32	89.94

The statistical analysis of the model was performed by Design-Expert 8 software. And the coefficient of determination (R^2) and F test were used to determine the quality of fit of the second order equation. The effect of each independent variable and their interactions were determined. F test was used to determine the model parameter's significance (α = 0.05).

2.3.3 Calcium lactate conversion to ethyl lactate

Similar process with methyl lactate production was used for ethyl lactate production. The experiments investigating ethyl lactate production with ethanol and carbon dioxide were conducted at three different conditions based on results of methyl lactate and preliminary experiments: 180 °C (reaction temperature), 4 hrs (reaction time) and 14.68 (molar ratio of ethanol to glycerol); 200 °C, 6 hrs and 12; and 220 °C, 4 hrs and 12.

2.3.4 Catalyst regeneration and reuse

In our previous research, CaO was difficult to be regenerated and reused. To test the regenerated CaO, we added sodium hydroxide to convert calcium lactate to $Ca(OH)_2$ and sodium lactate.[20] However, this process is not practical for industrial process as the recovery of lactic acid was still required. In this study, most calcium was converted to $CaCO_3$ by adding carbon dioxide that could be easily regenerated to CaO by simple calcination and then reused in the process.

After reaction, the solution was centrifuged and the precipitates were collected to investigate the catalyst regeneration and reusability. Due to the low amount of solids in each run, the solids were collected from several runs and mixed together before regeneration. The mixed solids were washed 3 times by DI water and then dried overnight in an oven at the temperature of 110 °C. The dried solids were then calcined in the air at 910 °C for 3 hrs. The calcined solids were ground to powder using mortar and pestle, and then passed through a 60 mesh sieve before they were recycled or used again in the process. In this research, the CuO was not separated during the process, so the calcined solids were a mixture of CuO and CaO. The calcined solids were weighed to determine how many catalysts can be recycled. We assumed that CuO could be totally recycled. About 10–15% of CaO could not be recycled because there were small amount of calcium lactate that was not converted to methyl lactate and $CaCO_3$ in the second-step reaction. However, we did not add fresh CaO to the regenerated catalyst.

The catalysts were regenerated and reused twice. Each time, regenerated catalysts were tested for the glycerol conversion and methyl lactate production in the tandem process. The amount of regenerated catalyst (mixture of CaO and CuO) used in the process was calculated based on the molar ratio of CuO (in regenerated catalyst) to glycerol at 0.2. The reaction temperature and time were same with the process using raw catalysts. The second-step process was conducted at a reaction temperature of 180 °C, a reaction time of 4 hrs, and a molar ratio of methanol to glycerol at 14.7:1 because at this condition, most calcium lactate can be converted to methyl lactate according to results of previous condition optimization.

The spent catalyst and regenerated catalysts were characterized by Powder X-ray diffraction (XRD). Powder X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert PRO PW3050 X-ray diffractometer using Cu K α radiation (0.154 nm) and a graphite generator. The tube voltage and the current were at 45 kV and 40 mA, respectively. And scan range was 2º–80º with the scan rate at 0.5º/min.

2.3.5 Sample analysis

The sample after reaction was washed out with DI water; then, centrifuged at a relative centrifugal force (RCF) of 4070 g for 5 min. The clear liquid in the upper layer was collected and the pH value was adjusted to around 3 with diluted H_2SO_4 in order to convert the unconverted calcium lactate to lactic acid. After that the sample was fed through an ion-exchange column packed with DOWEX 50WX8-400 Resin (Sigma Aldrich). The samples after ion-exchange were analyzed by HPLC equipped with SH 1011 column with the mobile phase of 0.5 mmol H_2SO_4.

The lactic acid, glycerol, and PG were identified by A Waters 410 RI detector (Waters Chromatography Division, Millipore Corp., Milford, MA), and the methyl/ethyl lactate were identified by a UV detector at 210 nm. External calibration was used to quantify each component in the products. It is noteworthy that the purchased lactic acid usually contained a small amount of lactic acid oligomers because of its high concentration. Therefore, before conducting calibration using HPLC, the standard lactic acid was first diluted to a concentration of about 2%, then hydrolyzed with 0.025 M H_2SO_4 at a temperature of 80 °C for 8 hrs.

Glycerol conversion, unconverted calcium lactate (equal to lactic acid determined by HPLC), methyl/ethyl lactate yield and propylene glycol yield were calculated by the following equations:

$$C_{glycerol}(mol\%) = \frac{n_{feed} - n_{quantified}}{n_{feed}} \times 100\% \qquad (3)$$

where $C_{glycerol}$ is glycerol conversion (mol%), n_{feed} is the moles of the starting glycerol, $n_{quantified}$ is the remaining glycerol in the collected sample quantified by HPLC.

$$y_{product}\ (mol\%) = \frac{n_{product}}{n_{feed}} \times 100\% \qquad (4)$$

where $y_{product}$ is the yield of a specific product formed (methyl/ethyl lactate or propylene glycol, mol%) or unconverted calcium lactate detected after reaction , $n_{product}$ is the moles of the specific product (methyl lactate or propylene glycol) or unconverted calcium lactate detected after reaction, and n_{feed} is the moles of the starting glycerol.

2.4 Crude glycerol conversion to methyl/ethyl lactate

Crude glycerol from a biodiesel plant, which contained 88.5 wt% of glycerol, 7.4 wt% of water, 2.4 wt% soap, and 1.4 wt% of methanol was used to investigate the effects of impurities on glycerol conversion and alkyl lactate production. According to the optimization for the second-step process in prior experiments, the reaction of methyl lactate was conducted at a reaction temperature of 180 °C and 4 hrs, and a molar ratio of methanol to glycerol at 14.7:1. The reaction of ethyl lactate was conducted at the reaction temperature of 220 °C and 6 hrs, and molar ratio of ethyl to glycerol at 12.

3. Results and discussion

3.1 Response surface analysis

The details of reaction conditions for the second-step process and product yields are shown in Table 1. In this tandem process, glycerol conversion was observed from 89.39 to 98.42%. The propylene glycol yield was about 3% to 10% and varied according to the different process conditions. However, the unconverted calcium lactate and methyl lactate yield greatly changed with the process conditions. The unconverted calcium lactate ranged from 13.63 to 69.82 while the methyl lactate yields ranged from 8.38 to 58.22%.

Using results of the experiment, a second order regression equation for methyl lactate yield (Equation 5) was obtained with the function of reaction temperature *(*X_1, °C), time (X_2, min) and molar ratio of methanol to glycerol ((X_3, mole/mole); hence,

$$Y_{Methyl\ lactate} = -403.23 + 3.93X_1 + 2.95X_2 + 7.46X_3 - 0.0097X_1^2 - 0.27X_3^2 \qquad (5)$$

It was also found that the model terms X_{22}, X_{12}, X_{13}, and X_{23} were insignificant when Equation 2 was used to fit the data for methyl lactate yield. Equation 5 was obtained with its significant terms (P-value < 0.0001) by using forward statistical analysis from Equation 2. The ANOVA for the response surface model of methyl lactate yield is shown in Table 2.

Table 2. The ANOVA for the response surface reduced quadratic model of methyl lactate yielded ($Y_{Methyl\ lactate}$)

Source	Sum of squares	DF	Mean square	F value	p-value Prob > F
Model	3917.17	5	783.43	18.73	< 0.0001
X_1: Reaction temperature (°C)	990.25	1	990.25	23.67	0.0004
X_2: Reaction time (hrs)	476.38	1	476.38	11.39	0.0055
X_3: Mole ratio of methanol to glycerol	2061.94	1	2061.94	49.29	< 0.0001
A^2	200.89	1	200.89	4.80	0.0489
C^2	254.35	1	254.35	6.08	0.0297
Residual	501.95	12	41.83		
Lack of Fit	466.52	9	51.84	4.39	0.1253
Pure Error	35.43	3	11.81		
Total	4419.13	17			

The correlation coefficients of determination (R-square) for Equations 5 was 0.89, implying that the reduced quadratic model for methyl lactate accurately represented the experiment data and the relationships among independent variable. Fig. 1 show the predicted methyl lactate using Equations 5.

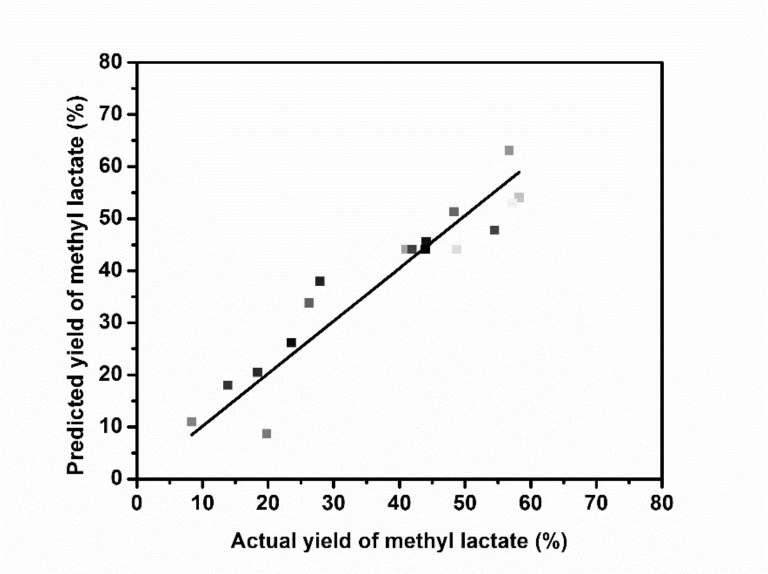

Fig. 1. Comparison plots of predicted and actual methyl lactate using Equation 5

3.2 The effects of process conditions on methyl lactate yield

Methyl lactate yield significantly increased with the increase of reaction temperature, time, and molar ratio of methanol to glycerol. Fig. 2A shows the effects of reaction time and temperature at the constant molar ratio of methanol to glycerol of 8:1. At the constant molar ratio of methanol to glycerol, methyl lactate yield increased with reaction temperature and time. The maximum yield of methyl lactate was obtained 53.5% at the reaction temperature of 200 °C and the reaction time of 6 hrs. Fig. 2B shows the effects of reaction temperature and molar ratio of methanol to glycerol at the constant reaction time of 4 hrs. The methyl lactate yield increased with the reaction temperature and molar ratio of methanol to glycerol; the maximum yield was 55.49% obtained at the reaction temperature of 200 °C with a methanol to glycerol molar ratio of 12:1. Fig. 2C shows the effects of reaction time and molar ratio of methanol to glycerol on the methyl lactate yield at the constant reaction temperature of 180 °C. The methyl lactate yield also increased with the increase of reaction time and molar ratio of methanol to glycerol and maximum yield was 56.78% at the reaction time of 6 hrs and methanol to glycerol ratio of 12.

These results suggested that the high reaction temperature, time, and molar ratio of methanol to glycerol favor the methyl lactate production. From Fig. 2, we also found that the increasing rate of methyl lactate yield trends to slow down when increasing the reaction temperature, time and molar ratio of methanol to glycerol, implying that the formation of methyl lactate is close to equilibrium at the higher reaction temperature, time, and molar ratio of methanol to glycerol.

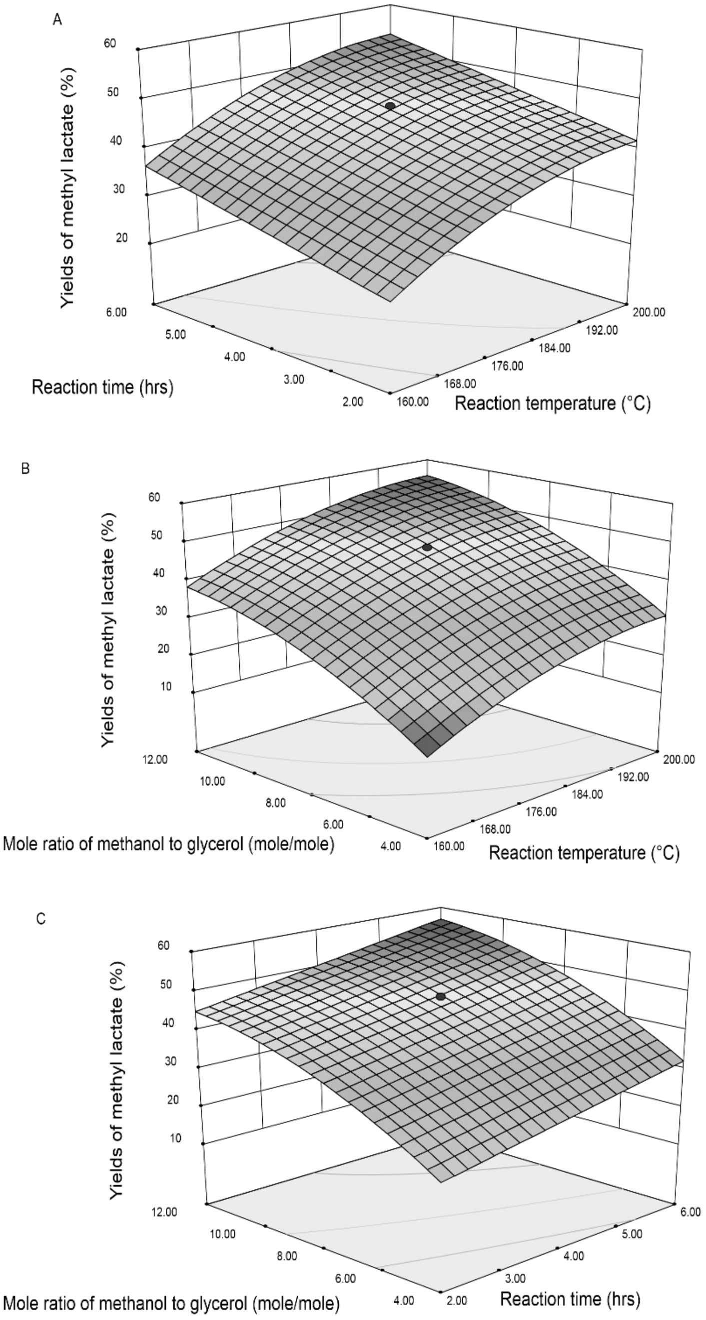

Fig. 2. Response surface profiles for the yield of methyl lactate. **A** is at the constant molar ratio of methanol to glycerol of 8:1; **B** is at the constant reaction time of 4 hrs; **C** is at the constant reaction temperature of 180 °C.

Barve et al. pointed out how the low concentration of calcium lactate in the methanol favors the conversion of calcium lactate to methyl lactate, which gives the high yield of methyl lactate obtained at the high molar ratio of methanol to glycerol.[27] ANOVA analysis for the obtained models for methyl lactate production in Tables 2 also suggests that the molar ratio of methanol to glycerol has more effect on the methyl lactate yield than on the other two factors. Methyl lactate shows great change with an increase of methanol to glycerol molar ratio at a constant reaction temperature or time (Fig. 2). This figure suggest that the high molar ratio of methanol and glycerol help to achieve the maximum methyl lactate yield. In this study the highest molar ratio of methanol to glycerol investigated was at 14.73. And at this molar ratio of methanol to glycerol with mild reaction temperature and time (180 °C and 4 hrs) the higher methyl lactate yield was obtained at 57.19%. Therefore, the following studies on catalysts regeneration and reuse test was conducted at this process condition.

3.3 Ethyl lactate production

Fig. 3 shows glycerol conversion, ethyl lactate yield, unconverted calcium lactate, and propylene glycol yield at various temperatures in ethyl lactate production. The glycerol conversion was about 88% to 96% which is similar with those observed in methyl lactate production. The ethyl lactate yield showed an increasing trend with the second-step reaction temperature. The ethyl lactate yield was 22.3% at a reaction temperature of 180 °C. When the reaction temperature increased to 200 °C, the ethyl lactate yield greatly increased to 42%. By further increasing the temperature to 220 °C, the ethyl lactate yield showed a slight increase. In contrast, unconverted calcium lactate, which was 46.5%, was obtained at the reaction temperature of 180 °C. This indicates that most of the calcium lactate obtained from the first-step reaction was not converted to ethyl lactate in the second-step reaction condition. When the reaction temperature increased to 200 °C and 220 °C, the calcium lactate greatly decreased. These results suggest that the high temperature favors the calcium lactate conversion to ethyl lactate. The PG yield at this condition was about 8.11%, which closely compares to the yield of PG in methyl lactate production.

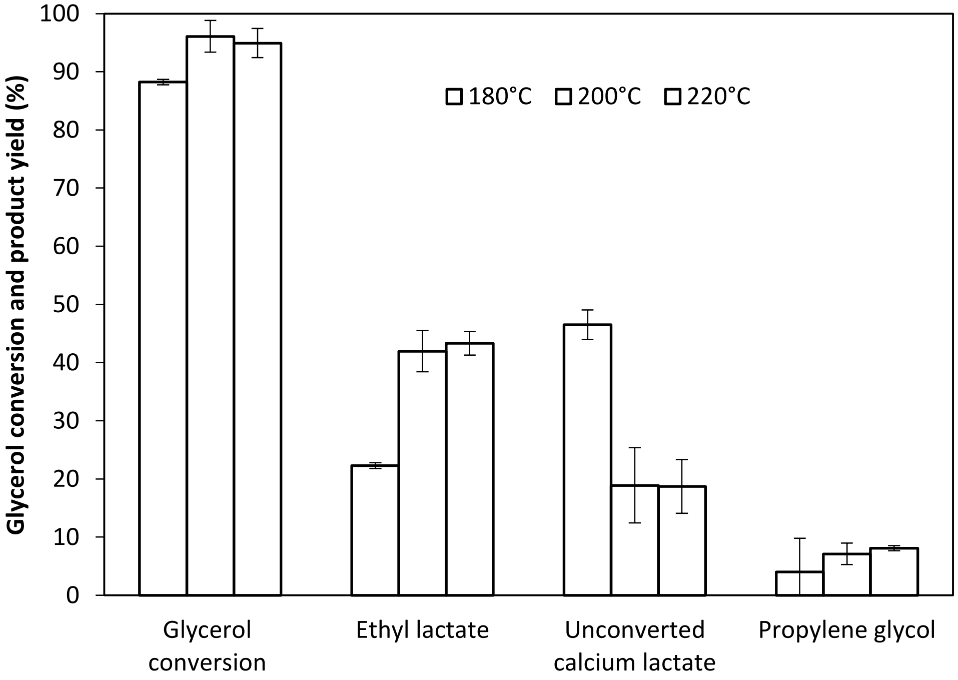

Fig. 3. Comparison of glycerol conversion, ethyl lactate yield, unconverted calcium lactate, propylene glycol yield at the different reaction temperature (second-step reaction) using refined glycerol with 33.33% water (first-step reaction was conducted at the reaction temperature of 230 °C and 30 min. where CaO:glycerol=1mol/mol and CuO:glycerol=0.2mol/mol)

3.4 The effects of recycled catalysts on glycerol conversion and methyl lactate production

Fig. 4 shows the comparison of glycerol conversion, methyl lactate yield, unconverted calcium lactate and propylene glycol yield using fresh catalysts and regenerated catalysts. Regenerated catalysts showed a similarity of glycerol conversion with fresh catalysts. The regenerated catalyst had no negative effects on the glycerol conversion. The methyl lactate yield obtained from glycerol conversion using regenerated catalysts were very close with the yield from fresh catalyst. Both unconverted calcium lactate and propylene glycerol yields significantly decreased when reused two times of catalysts. The total amount of methyl lactate and unconverted calcium lactate obtained from the reused catalysts especially for 2nd use of the catalyst was reduced greatly. This means that the regenerated catalyst had a noteworthy effect on the calcium lactate selectivity in the first-step process. During the catalysts regeneration, we found that only about 85% of fresh catalysts were regenerated. About 15% of fresh catalyst from CaO interaction was maintained in the unconverted calcium lactate. Before the regenerated catalysts were reused, we did not add fresh CaO in the process. That might limit the formation of calcium lactate in the first-step process due to the reduced CaO in the regenerated catalyst. We did not reduce the methanol loading in the second-step process which could have lowered the concentration of calcium lactate and favor the calcium lactate conversion. In this study, a certain amount of calcium lactate was not converted to methyl lactate. This unconverted calcium lactate could be recycled in the process thereby helping to recycle the CaO catalyst.

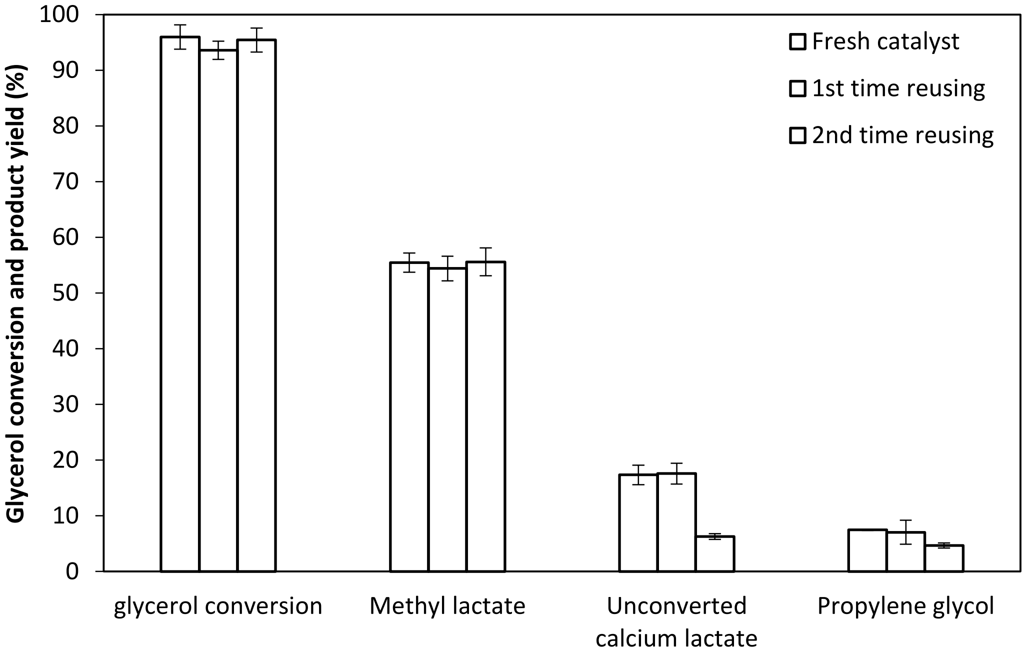

Fig. 4. Glycerol conversion, methyl lactate yield, unconverted calcium lactate and propylene glycol yield using regenerated catalysts.

The XRD pattern for the spent catalyst is shown in Fig. 5A. No peak associated with CaO was observed on the XRD, suggesting that there was no CaO in the spent catalyst or it only existed in an amorphous form. The peaks associated with CuO and Cu were detected, indicating that CuO occurred with a partial reduction during the reaction. Peaks associated with $CaCO_3$ were observed in the spent catalyst, which confirmed the transesterification of calcium lactate with CO_2 to form $CaCO_3$. XRD patterns of regenerated catalysts were shown in Fig. 5B. Peaks associated with CaO and CuO were observed in the 1^{st} to 3^{rd} regenerated catalysts. This result confirmed that the regenerated catalysts are still composed of CaO and CuO. The peak intensity of CaO and CuO during different times of regeneration was not reduced significantly, indicating that the regenerated catalyst maintained a similar crystalline proportion during recycles.

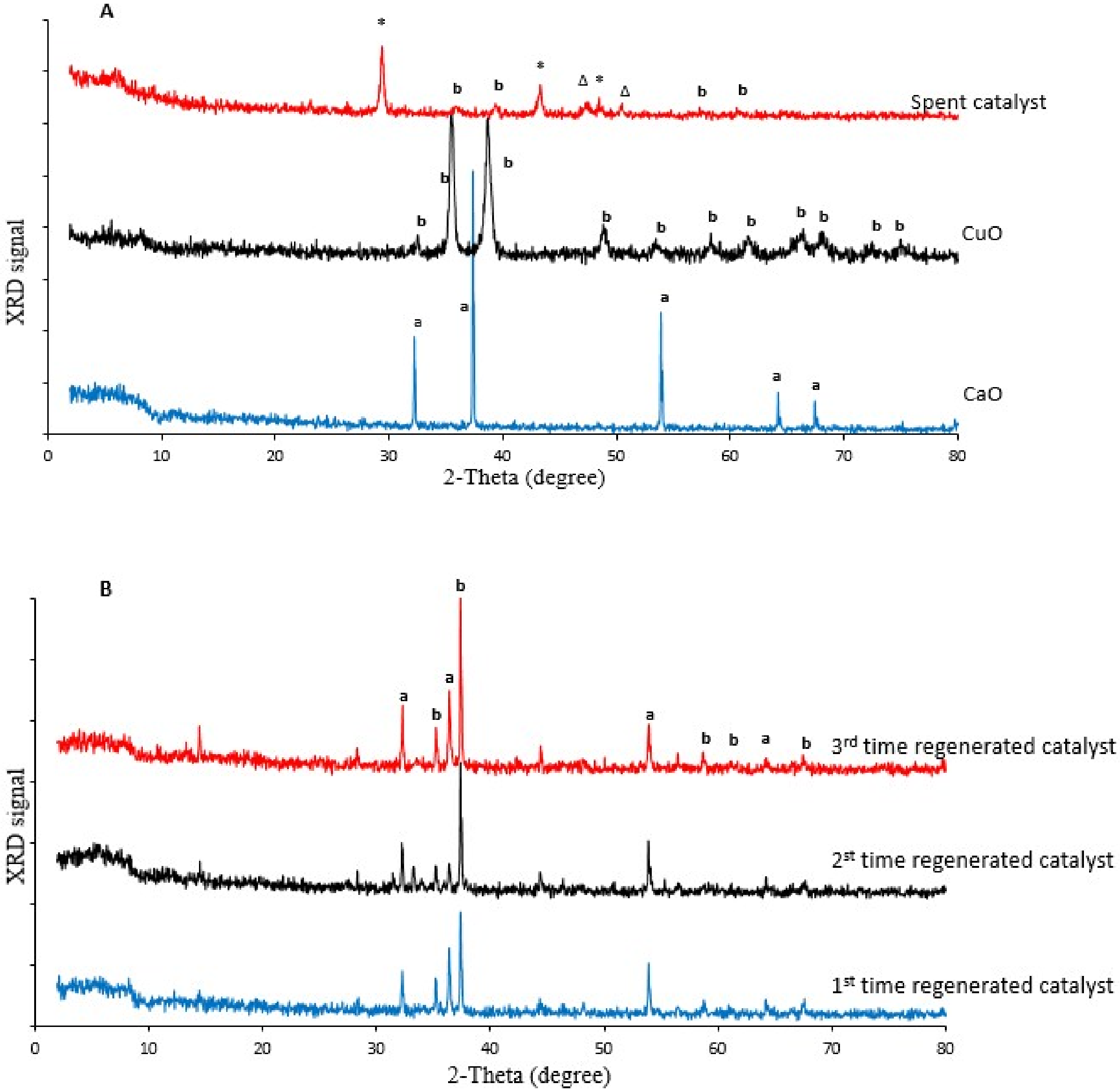

Fig. 5. XRD patterns of CaO, CuO and spent catalyst **(A),** and regenerated catalysts **(B)**. The peaks marked with "a" are the characteristic peaks of CaO; The peaks marked with "b" are the characteristic peaks of CuO; The peaks marked with "*" are the characteristic peaks of $CaCO_3$; The peaks marked with "Δ" are the characteristic peaks of Cu.

3.5 Methyl and ethyl lactate production from crude glycerol

The crude glycerol was used as starting material to produce methyl/ethyl lactate. Fig. 6 compares glycerol conversion with product yield between using refined glycerol and crude glycerol. Crude glycerol conversion and methyl lactate were similar to that of refined glycerol in both methyl and ethyl lactate production. The unconverted calcium lactate in methyl lactate production was slightly higher than that from refined glycerol. But the unconverted calcium lactate in ethyl lactate was similar to that of refined glycerol. These results revealed that the impurities in the crude glycerol had no significant effects on either the glycerol conversion or the methyl/ethyl lactate production and the crude glycerol can be directly used as a feedstock in methyl and ethyl lactate production.

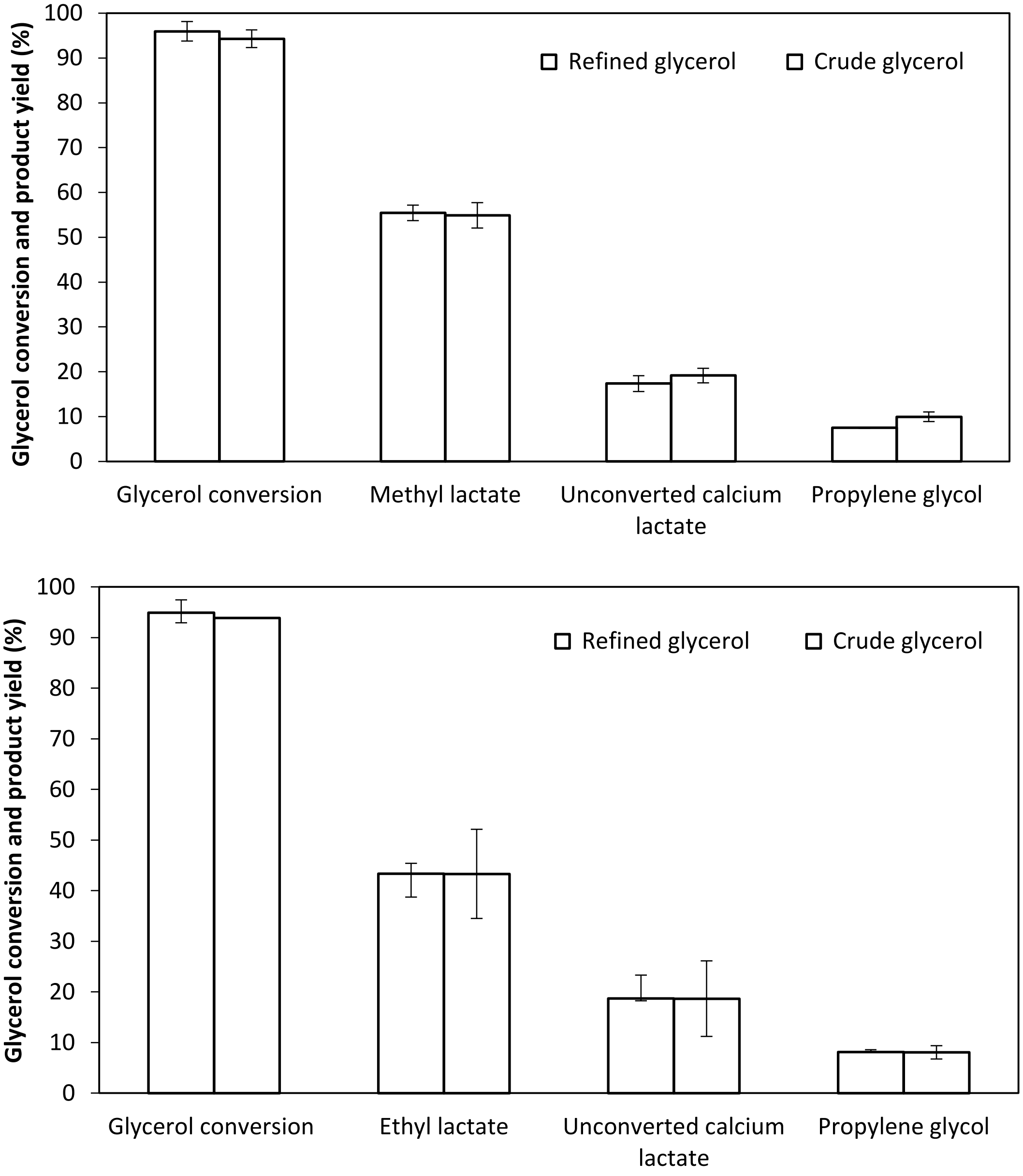

Fig. 6. Comparison of glycerol conversion and product yield between refined glycerol and crude glycerol for methyl and ethyl lactate production

3.6 Reaction mechanisms of methyl/ethyl lactate production

Glycerol conversion to methyl/ethyl lactate includes two steps. The first step is glycerol conversion to calcium lactate using the catalysts of CaO and CuO. Multiple reactions occurred during the glycerol conversion to calcium lactate. The reaction mechanism of this step has been proposed in our previous report.[20] The initial reaction occurs between the H proton of the hydroxyl group of glycerol and CaO to form glyceroxide anion and CaO hydrogen cation ($CaOH^+$). Glyceroxide anion and CaO hydrogen cation ($CaOH^+$) further react to form glyceraldehyde via dehydrogenation. In its basic condition, glyceraldehyde is converted to 2-hydroxypropenal via dehydration and 2-hydroxypropenal further forms pyruvaldehyde via keto-enol tautomerization. Pyruvaldehyde undergoes a benzilic acid rearrangement and finally forms the calcium lactate with CaO. Hydrogen generated in the process can also react with 2-hydroxypropenal and pyruvaldehyde to form propylene glycol especially when CuO catalyst exists in the process.

The second step is calcium lactate reaction with CO_2 and methanol or ethanol to form methyl/ethyl lactate and calcium carbonate, which will precipitate out of the solvent. Barve et al. investigated methyl lactate production from alkali metal salts of carboxylic acids using carbon dioxide and alcohol.[27] They proposed a reaction mechanism of esterification of calcium lactate using CO_2 and methanol made up of three steps: 1) the formation of carbonic acid by the reaction of water with CO_2, 2) the formation of lactic acid and $CaCO_3$ by the reaction of calcium lactate with carbonic acid, and 3) the esterification of lactic acid with methanol. However, in our process, CaO used was excessive, which might also induce methanol to form methoxy anion, which further reacts with CO_2 to form intermediates.[28] These intermediates might react with calcium lactate to form methyl lactate and $CaCO_3$. The possible reactions is shown in equations 6-9, and the proposed reaction pathway from glycerol to methyl lactate is shown in Fig. 7.

$$CH_3OH + CaO \rightarrow CH_3O^- + Ca(OH)^+ \tag{6}$$

$$CH_3O^- + CO_2 \rightarrow CH_3OC(O)O^- \tag{7}$$

$$Ca(OH)^+ + CH_3OH \rightarrow CH_3^+ + CaO + H_2O \tag{8}$$

$$CH_3^+ + CH_3OC(O)O^- + (CH_3CH(OH)COO)_2Ca \rightarrow 2CH_3CH(OH)COOCH_3 + CaCO_3 \quad (9)$$

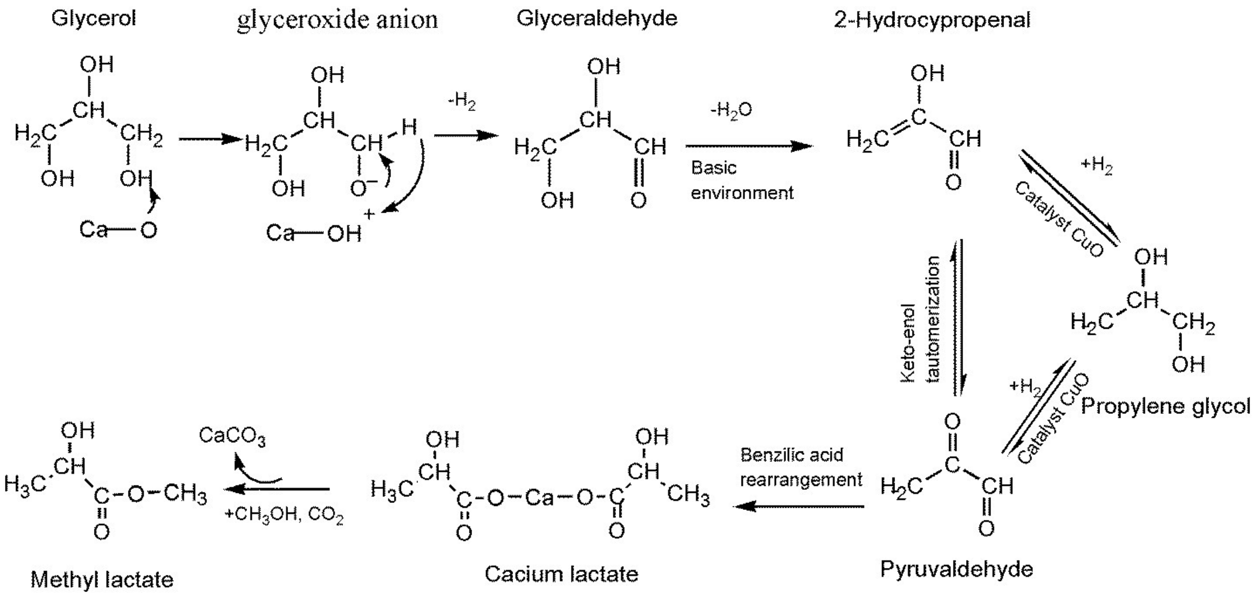

Fig. 7. Proposed reaction pathway from glycerol to methyl lactate using CaO and CuO as catalysts with methanol and carbon dioxide

4. Conclusions

In this study, a two-step process for methyl lactate production from glycerol using solid catalysts, methanol and carbon dioxide were developed, and the process conditions were investigated. The reaction temperature, time and molar ratio of methanol to glycerol had significant effects on the methyl lactate yields. The relatively high methyl lactate yield, which was more than 55%, was obtained at the reaction temperature of 180-200 °C, reaction time of 4-7 hours and methanol to glycerol molar ratio of 8:1 to 14.7:1. The test for regenerated catalysts suggests that the catalysts can be reused with little effect on the methyl lactate yield. The ethyl lactate production was also investigated, and about a 42% yield was obtained using refined glycerol at the optimum condition. The studies on crude glycerol conversion to methyl/ethyl lactate revealed a similar methyl and an ethyl lactate yield when using refined glycerol, which was achieved at the optimum condition. The impurities in the crude glycerol had no significant effects on alkyl lactate production. Compared with traditional methyl lactate production, this two-step process for methyl and ethyl lactate production from glycerol is economic and environmentally sustainable since no gypsum was produced and both CaO and CuO can be regenerated and recycled.

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