Selective production of 1,3-butadiene using glucose fermentation liquor

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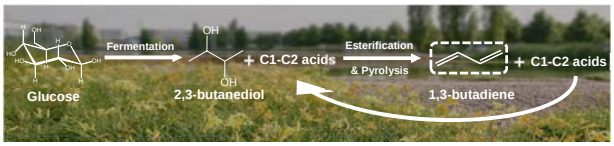
Complete List of Authors:	Yi, Jongheop; Seoul National University, School of Chemical and Biological Engineering Baek, Jayeon; Seoul National University, School of Chemical and Biological Engineering Kim, Tae Yong; Seoul National University, School of Chemical and Biological Engineering Kim, Wooyoung; GS-Caltex Corporation, Lee, Hee Jong; GS-Caltex Corporation,

➢ **Table of contents entry**



An alternative biomass-based route to petrochemical process for the production of 1,3-butadiene has been developed using glucose fermentation products.

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ARTICLE TYPE

Selective production of 1,3-butadiene using glucose fermentation liquor

Jayeon Baek,[‡a] Tae Yong Kim,[‡a] Wooyoung Kim,[b] Hee Jong Lee[b] and Jongheop Yi[*a]

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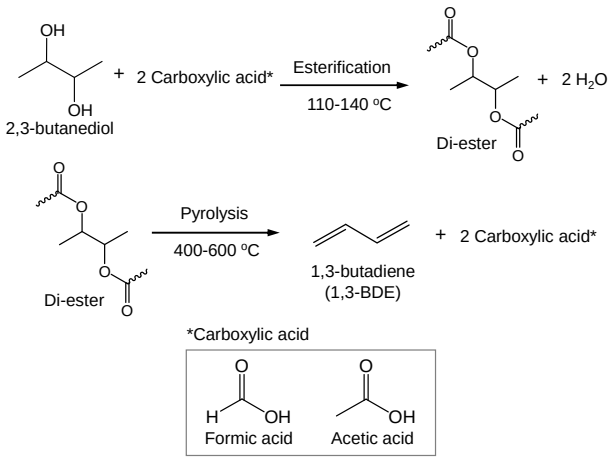
The production of 2,3-butanediol from glucose fermentation products and its subsequent esterification and conversion to 1,3-butadiene is reported. The addition of formic acid and acetic acid (C1-C2 acids) to the esterification reaction mixture resulted in yields of the di-esters of 70 % and 85 %, without the loss of C1-C2 acids during the reaction. In the pyrolysis step, a highly selective (94 % and 82 % for formic acid 2-formyloxy-1-methyl-propyl ester and acetic acid 2-acetoxy-1-methyl-propyl ester) C-O cleavage to 1,3-butadiene over di-esters were achieved without catalyst. In the case of acetic acid, 100 % was recovered, whereas in the case of formic acid, only 20 % was recovered. Based on these results, it can be concluded that, using glucose fermentation liquor as the starting material with external addition of acetic acid (2,3-butanediol : formic acid : acetic acid = 1: 0.5 : 2.5), 70 % yield of 1,3-butadiene can be achieved where the loss of formic acid is compensated by the acid in the starting material.

Introduction

The worldwide lack of petroleum has stimulated a search for alternative sources of clean energy. The use of biomass for this purpose, turning 'consumptive use' into 'recyclable use', is an ideal goal for the future. The use of feedstock derived from biomass, e.g., sugars, vegetable oil, lignocellulosic biomass, and algae emits the greenhouse gas, carbon dioxide, but it can be reused in the photosynthetic process and could result in the creation of a carbon-neutral and sustainable society.[1]

Glucose, a monosaccharide produced by plants could be efficiently utilized after a fermentation process as the carbon source for microorganisms.[2] Glucose can be converted into 2,3-butanediol by fermentation in which the major byproducts are formic acid and acetic acid (C1-C2 acids), although the proportion of these byproducts can vary, depending on the conditions of the fermentation.[3] The use of 2,3-butanediol is expected to steadily increase because its derivatives can be used in the production of synthetic rubber, plasticizers, and fuel additives. Therefore, the development of a suitable technology for the conversion of 2,3-butanediol into other value-added products such as 1,3-butadiene would be highly desirable.[4,5] 1,3-Butadiene is currently produced by the steam cracking of paraffinic hydrocarbons, the catalytic dehydrogenation of n-butane and n-butene, and the oxidative dehydrogenation of n-butene, all of which are based on a petrochemical process.[6]

Herein, we report on a process for the production of 1,3-butadiene from the mixture of 2,3-butanediol and C1-C2 acids which are representative products in glucose fermentation. Importantly, this process can replace some petrochemical-based processes. We proved that esterification would occur between the 2,3-butanediol and C1-C2 acids to form di-esters (product **4** and **7**). In addition, the C-O cleavage in the di-ester (product **4** and **7**) sequentially proceeds during the pyrolysis process, which results in the selective formation of 1,3-butadiene (Scheme 1). A similar procedure was reported in 1945 by S. Marshak and co-workers, however, the experimental details concerning it are not available.[7]



Scheme 1 Conversion of biomass-derived 2,3-butanediol and carboxylic acid to 1,3-butadiene.

To the best of our knowledge, the present work is the first report of esterification followed by pyrolysis for the formation of 1,3-butadiene by reacting 2,3-butanediol with products produced by the fermentation of glucose. This process would result in diminished cost and energy which are consumed in the pre-separation of reactants including 2,3-butanediol and C1-C2 acids. In addition, 1,3-butadiene (gas phase) can be easily isolated from the glucose fermentation products.

Results and discussion

The composition of glucose fermentation liquor by Klebsiella

Table 1 Composition of microbial fermented liquor[a]

(Unit: g/kg)

2,3-butanediol	Formic acid	Acetic acid	Acetoin	Lactic acid	Succinic acid	Ethanol
480.13	122.64	13.91	5.08	34.10	36.93	0.00

(Unit: ppm (w))

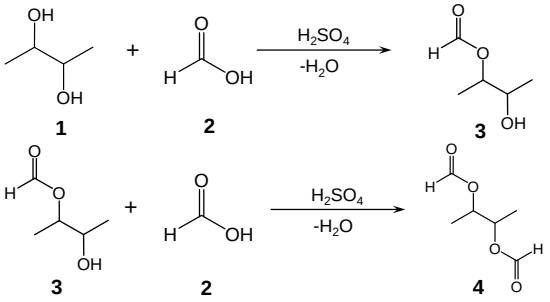
Cl^-	PO_4^{3-}	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
2,850	70,962	48,760	n.a.	n.a.	n.a.	n.a.	n.a.

[a] See the reference for the detailed information concerning the microbial fermentation of glucose using Klebsiella oxytoca KCTC12133BP (Korean Collection for Type Cultures, Daejeon, Korea).[8]

oxytoca KCTC12133BP (Korean Collection for Type Cultures, Daejeon, Korea) is presented in Table 1. The microbial fermentation experiment and the analysis was conducted by GS-Caltex Corporation. As can be seen from Table 1, the glucose fermentation liquor is comprised of 2,3-butanediol as the main product, followed by formic acid, acetic acid, lactic acid, succinic acid (C1-C4 acids), and acetoin, along with some inorganic salts. The molar ratio of 2,3-butanediol, formic acid, and acetic acid is typically 1 : 0.5 : 0.1 in the liquor where the amount of 2,3-butandiol is dominant. It should be noted that the isomer ratio between *meso* and *racemic* 2,3-butanediol used for the esterification coincide with the that of glucose fermentation product (*meso* : *racemic* = 9 : 1, Fig. S1-S7, ESI†).

The esterification process was evaluated as the first step using sulfuric acid as a catalyst. After the reaction, the sulfuric acid can be recovered in the course of the extraction procedure. The stoichiometric molar ratio between 2,3-butanediol and C1-C2 acids is 1:2, as shown in Scheme 1. However, taking the relatively low boiling point of formic acid (100.8 °C) and acetic acid (118 °C) into account, excess C1-C2 acids were used in the esterification; 2,3-butanediol (**1**) : formic acid (**2**) = 1 : 4 and 2,3-butanediol (**1**) : acetic acid (**5**) = 1 : 2.5 molar ratio. To force the equilibrium to the right, a Dean-Stark trap was used to remove water from the reaction mixture.

Esterification of 2,3-butanediol with formic acid



Scheme 2 Esterification of 2,3-butanediol (**1**) with formic acid (**2**) using sulfuric acid.

The esterification between 2,3-butanediol (**1**) and formic acid (**2**) occurs sequentially, in which the formic acid 2-hydroxy-1-methyl-propyl ester (**3**) is formed first and another 2,3-butanediol (**1**) reacts with product **3** to produce formic acid 2-formyloxy-1-methyl-propyl ester (**4**) (Scheme 2). This reaction process can be confirmed by time-on-stream reaction experiments (Fig. 1) as the continuous decrease in formic acid 2-hydroxy-1-methyl-propyl ester (**3**) is correlated with the gradual increase of 2,3-butanediol (**1**) conversion and formic acid 2-formyloxy-1-methyl-propyl ester (**4**) formation until 7 h of reaction time. The desired product

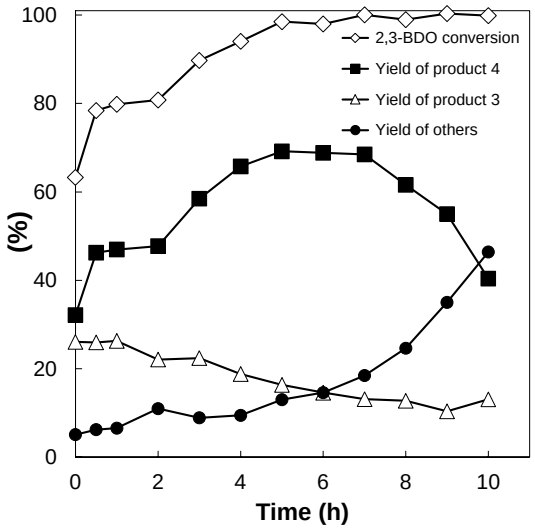
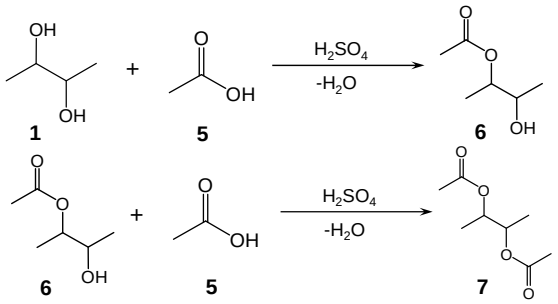


Fig. 1 Time-on-stream of esterification of 2,3-butanediol with formic acid. Reaction conditions: **1** (0.22 mol), **2** (0.88 mol) and 0.2 mL of H_2SO_4. The temperature of the reaction mixture gradually increased during the course of the run from about 110 °C to 130 °C. The conversion of 2,3-butanediol and selectivity was determined by GC-FID.

formic acid 2-formyloxy-1-methyl-propyl ester (**4**) for 1,3-butadiene was obtained with 70 % selectivity as well as formic acid 2-hydroxy-1-methyl-propyl ester (**3**) with 17 % selectivity as an intermediate within 5 h at 130 °C (Fig. 1). The calculated m/z for the formic acid 2-formyloxy-1-methyl-propyl ester (**4**) was 147.0657 and measured as 147.0659 and the structure was additionally confirmed by ^1H NMR and ^{13}C NMR (Fig. S8 and S9, ESI†). As the reaction proceeded, the color of the reaction mixture changed from light yellow to light brown (Fig. S12, ESI†). This color change can be attributed to the increased production of formic acid 2-formyloxy-1-methyl-propyl ester (**4**). While the composition of formic acid 2-hydroxy-1-methyl-propyl ester (**3**) and unknown products changed during the course of the reaction of 5 h to 7 h, the yield of the targeted formic acid 2-formyloxy-1-methyl-propyl ester (**4**) was maintained at a constant level of 70 %, indicating that the formation and degradation rates of formic acid 2-formyloxy-1-methyl-propyl ester (**4**) are equal. After 7 h of reaction time, however, the yield of other compounds originating from 2-formyloxy-1-methyl-propyl ester (**4**) rapidly increased as the decreased amount of product **4** was transformed into other products. Hence, the optimum time for the esterification between 2,3-butanediol and formic acid was 5 h at 130 °C. After the reaction, the loss of excess formic acid was calculated to be 2 %. For the subsequent experimental pyrolysis process, we used an esterification mixture that was produced after a reaction time of 5 h.

Esterification of 2,3-butanediol with acetic acid



Scheme 3 Esterification of 2,3-butanediol (**1**) with acetic acid (**5**) using sulfuric acid.

We further investigated the esterification of 2,3-butanediol (**1**) with acetic acid (**5**) (Scheme 3). The esterification products resulted in the formation of the corresponding acetic acid 2-hydroxy-1-methyl-propyl ester (**6**) and acetic acid 2-acetoxy-1-methyl-propyl ester (**7**); the chemical structures of which were confirmed from ^{1}H-NMR and ^{13}C NMR data (Fig. S10 and S11, ESI†). Also, the m/z estimated for the acetic acid 2-acetoxy-1-methyl-propyl ester (**7**) was 175.0970 and the measured value was 175.0971. An evaluation of esterification using 2,3-butandeiol with acetic acid time-on-stream (Fig. 2) indicates that the optimum time required for the reaction is 10 h where the selectivity of acetic acid 2-acetoxy-1-methyl-propyl ester (**7**) is enhanced at the expense of acetic acid 2-hydroxy-1-methyl-propyl ester (**6**) as the reaction proceeded. After 10 h, reaction mixture turned dark brown which can be attributed to the production of acetic acid 2-acetoxy-1-methyl-propyl ester (**7**) (Fig. S13, ESI†). Unlike the esterification of 2,3-butanediol with formic acid, the formed acetic acid 2-acetoxy-1-methyl-propyl ester (**7**) was not degraded into other products. The esterification of 2,3-butanediol with acetic acid required an extended reaction time to achieve the maximum production of acetic acid 2-acetoxy-1-methyl-propyl ester (**7**) compared to the esterification of 2,3-butanediol with formic acid; this can be attributed to the steric effect conferred by the longer alkyl chain.[9] It should be noted, however, that the selectivity at the equilibrium state for acetic acid 2-acetoxy-1-methyl-propyl ester (**7**) (selectivity: 85 %) is higher than formic acid 2-formyloxy-1-methyl-propyl ester (**4**) (selectivity: 70 %), indicating that the selectivity in the reaction is influenced more by thermodynamics than the steric hindrance caused by length of the alkyl chain. In this experiment, no loss of acetic acid was observed. The esterification mixture production after a reaction time of 10 h was used in the subsequent pyrolysis step.

Pyrolysis of product 4 and 7

Considering the proposed mechanism shown in Scheme 1, the pyrolysis of formic acid 2-formyloxy-1-methyl-propyl ester (**4**) and acetic acid 2-acetoxy-1-methyl-propyl ester (**7**) would sequentially occur following the esterification reaction to produce 1,3-butadien. In this step, the pyrolysis of formic acid 2-formyloxy-1-methyl-propyl ester (**4**) and acetic acid 2-acetoxy-1-methyl-propyl ester (**7**) would proceed in the absence of a catalyst at a relatively high temperature.

Electrostatic potential maps for the formic acid 2-hydroxy-1-methyl-propyl ester (**3**) and formic acid 2-formyloxy-1-methyl-propyl ester (**4**) show that the electron densities are highly localized on ester groups, which can function as a good leaving group because the anion produced in the reaction is stable (Fig. 3, we only discuss product **3** and **4** as a similar explanation can be valid for product **6** and **7**). In the case of product **3**, since the –OH in 2,3-butanediol is a much poorer leaving group; it is typically aided by protonation, the electrophilic ester functional group leaves first via cleavage of the C-O bond to give a secondary carbocation.[10] Consistent with the E1 mechanism in organic chemistry, the ester anion would attack the β-hydrogen in the carbocation intermediate with the regeneration of formic acid and the production of a carbon-carbon double bond in the carbocation intermediate.[11] This step is repeated in another ester functional group in product **4** with 1,3-butadiene being produced as a final product. When the elimination of the ester functional group occurs in the mono-ester (product **3** and **6**), 3-buten-2-ol and methyl ethyl ketone are readily produced. The formation of the carbocation intermediate crosses the high energy barrier which is the rate-determining step in the reaction, and, because of this, a high temperature is required for the pyrolysis of formic acid 2-formyloxy-1-methyl-propyl ester (**4**) and acetic acid 2-acetoxy-1-methyl-propyl ester (**7**).[11]

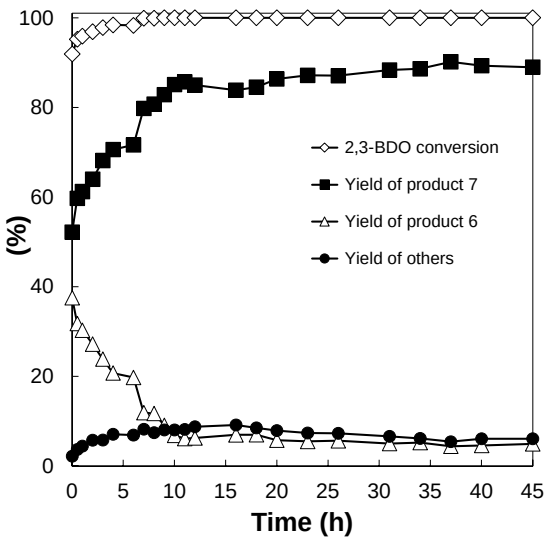


Fig. 2 Time-on-stream of esterification of 2,3-butanediol with acetic acid. Reaction conditions: **1** (0.22 mol), **5** (0.55 mol) and 0.2 mL of H_2SO_4. The temperature of the reaction mixture gradually increased during the course of the run from about 110 ºC to 140 ºC. The conversion of 2,3-butanediol and selectivity was determined by GC-FID.

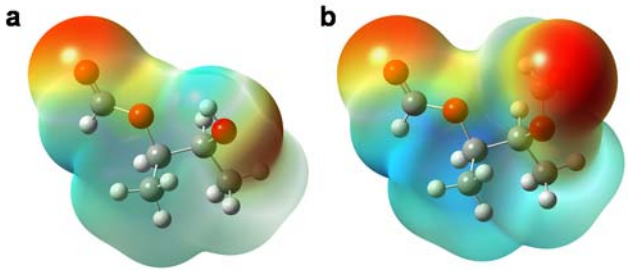


Fig. 3 Electrostatic potential map for (a) formic acid 2-hydroxy-1-methyl-propyl ester (**3**) and (b) formic acid 2-formyloxy-1-methyl-propyl ester (**4**).

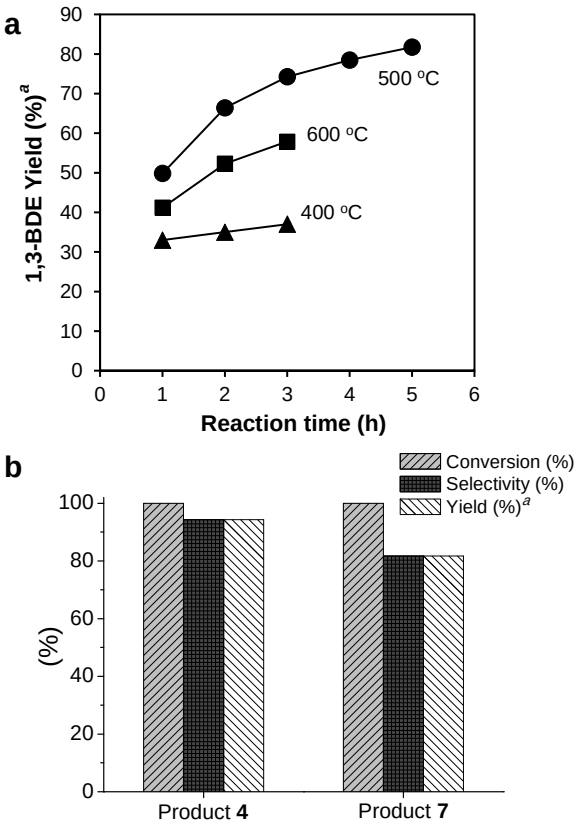


Fig. 4 (a) Pyrolysis results for product **7** at 400 °C, 500 °C, and 600 °C; (b) Pyrolysis result of product **4** and **7** after 5 h at 500 °C in the absence of catalyst. Reaction conditions: 0.3 mLh^{-1} of feed flow rate, 30 $mLmin^{-1}$ of N_2, LHSV = 0.028 h^{-1}. The final liquid products were trapped in methanol. [a] Yield (%) = produced 1,3-butadiene (mol) compared to introduced product **4** (mol) and **7** (mol).

The reaction temperature in the pyrolysis was optimized in the range of 400-600 °C (Fig. 4a). In the early of pyrolysis, the yield of 1,3-butadiene was lowered due to the slightly soluble property of 1,3-butadiene in the methanol.[12] The constant yield of 1,3-butadiene could be obtained after 5 h. When the reaction occurred at 400 °C, the conversion of acetic acid 2-acetoxy-1-methyl-propyl ester (**7**) was lowered. An increase in the reaction temperature to 600 °C, however, promoted the decomposition of the products, resulting in the formation of C1-C3 hydrocarbons (methane, ethylene, and propylene). Based on the above results, the reaction temperature for the pyrolysis was set at 500 °C for the conversion of all of the esterification products with high selectivity for 1,3-butadiene. In the pyrolysis of formic acid 2-formyloxy-1-methyl-propyl ester (**4**), the selectivity was about 94 % whereas it was 82 % for acetic acid 2-acetoxy-1-methyl-propyl ester (**7**) (Fig. 4b). The high selectivity for 1,3-butadiene in the pyrolysis can be attributed to the selective elimination of the ester functional group as explained in Fig. 3. It is noteworthy that coke formation after the pyrolysis step is negligible (0.5 % for the pyrolysis of product **7**). In addition, an analysis of the output gas phase stream shows that highly pure 1,3-butadiene is produced. The high purity of 1,3-butadiene (the peak at 51 min in the GC chromatogram) above 93 % for both the pyrolysis of formic acid 2-formyloxy-1-methyl-propyl ester (**4**) and acetic acid 2-acetoxy-1-methyl-propyl ester (**7**) were analyzed by on-line GC-FID (Fig. S14 and S15, ESI†). The small peak in the GC chromatogram at 27 min corresponds to trans-2-butene which is the main side reaction product in gas phase along with the minor decomposition to C1-C3 hydrocarbons (methane, ethylene, and propylene). Building upon these results, this approach would be potentially useful for extracting pure 1,3-butadiene in the form of a gas phase from the glucose-derived fermentation products.

Sustainable production of 1,3-butadiene from glucose fermentation liquor

The attractive point of this process is that the original C1-C2 acids in the final liquid products can be recovered. If a recycling process were possible; the C1-C2 acids produced in the reaction could be transferred to the esterification process, which would permit the C1-C2 acids to accumulate where excessive amounts are needed to adjust the stoichiometric molar ratio. Given the fact that the C1-C2 acids are collected at the final stage, they could be trapped in methanol and the results were as expected. In the GC-MS chromatogram of the trapped liquid phase, formic acid and acetic acid were regenerated with methyl ethyl ketone (Fig. 5). The recovery rate of C1-C2 acids after pyrolysis was also quantified. Interestingly, the recovery of acetic acid was 100 % whereas the formic acid show the much lower recovery rate (20 %) which could be related with the low stability of formic acid at high temperature.[13] Some unknown products were present in the resulting liquid phase after the pyrolysis of the esterification product using 2,3-butanediol with acetic acid. This is in agreement with the observed decreased selectivity for 1,3-butadiene in the output gas phase stream at these conditions (Fig. 4b).

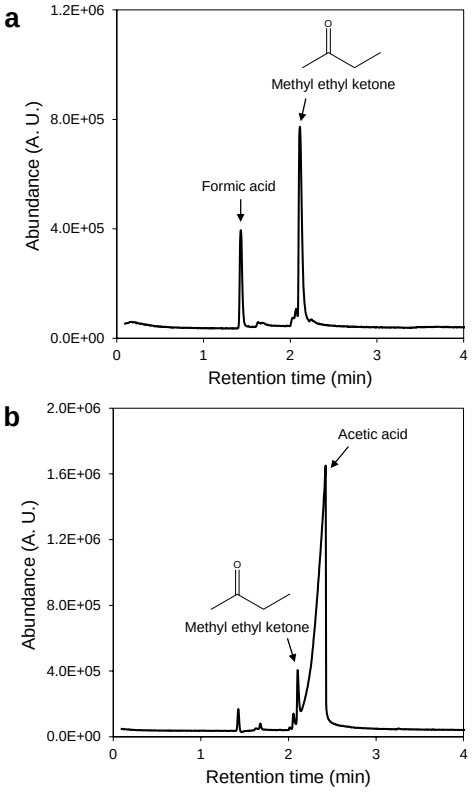


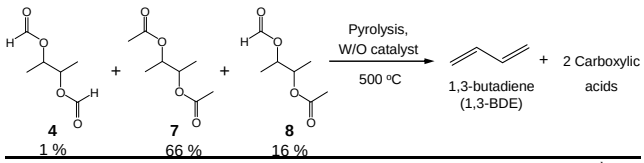
Fig. 5 GC-MS chromatogram of the liquid products obtained after the pyrolysis of (a) product **4** and (b) **7** (500 °C, 5 h, the final liquid products were trapped in methanol).

Based on these results, we attempted to apply the model mixture to the esterification followed by pyrolysis reaction. The model mixture is proposed where it is comprised of 2,3-butanediol : formic acid : acetic acid = 1 : 0.5 : 2.5 molar ratio with considering the recovery rate of C1-C2 acids throughout the two sequential reactions and low boiling point of C1-C2 acids. This model mixture proportion allows the process to be recycled if an additional 2.4 mol of acetic acid is added to the glucose fermentation liquor (2,3-butanediol : formic acid : acetic acid = 1 : 0.5 : 0.1). The reaction temperature was increased to 140 °C in the light of dominant composition of acetic acid in the model mixture. In Table 2, conversion of 2,3-butanediol showed 100 % after 3h which can be attributed to enough amounts of C1-C2 acids for the esterification reaction step. In accordance with the previous esterification results, the composition of mono-esters (product **3** and **6**) decreased as the reaction proceeded by the self-destruction to the di-esters (product **4** and **7**). The produced product **4** and **7** are also confirmed. Interestingly, entirely new peak in the GC-FID chromatogram was generated and it is confirmed as acetic acid 2-formyloxy-1-methyl-propyl ester (**8**) where each formic acid and acetic acid comprise two ester functional group to one 2,3-butanediol molecule (^{1}H NMR and ^{13}C NMR, Fig. S16 and S17, ESI†). The product **8** also has capability of producing 1,3-butadiene with a high selectivity of 92 % (data not shown here). It should be noted that the yield of di-esters (product **4**, **7**, and **8**) remained essentially unchanged after a reaction time of 10 h. Thus, the optimum reaction time is considered to be 10 h for the following pyrolysis. Concerning the origin of 1,3-butadiene, one can predict the yield of 1,3-butadiene from the glucose fermentation is maximized at 83 %. Finally, 70 % of the 1,3-butadiene was obtained via the pyrolysis reaction after 5 h (Table 3). This is probably the highest yield ever reported.[14] Along with the obtained high yield of 1,3-butadiene from glucose fermentation liquor, the recycling of recovered C1-C2 acids after pyrolysis as reactants has considerable merit from the environmental and economic point of view.

Conclusions

An integrated route consisting of esterification followed by pyrolysis for the conversion of glucose fermentation products into 1,3-butadiene is demonstrated. This biomass-based process appears to be quite efficient, sustainable, and reusable compared with typical petrochemical processes. The catalytic esterification of 2,3-butanediol with the excess C1-C2 acids that are produced from glucose fermentation was achieved, with a 70 % and 85 % selectivity for the di-ester (product **4** and **7**, respectively) in an organic phase at a 100 % conversion of 2,3-butanediol. The subsequent elimination of ester functional group in the pyrolysis process enables C-O bond cleavage to occur, via E1 mechanism resulting in the formation of 1,3-butadiene and the regeneration of the C1-C2 acids. Furthermore, this combined process proceeded in the when a model mixture of glucose fermentation products were used. The present methodology provides an example of producing a diene product (1,3-butadiene) from a diol compound (2,3-butanediol) from biomass products via fermentation. Finally, as the controlled C-O cleavage is a very general issue in the conversion of biomass-derived substrate, the procedure reported herein would be expected to have broad applicability for the production of dienes from corresponding diol compounds.

Table 3 1,3-butadiene production from the model mixture of glucose fermentation liquor[a]



Temperature (°C)	Time (h)	Conversion (%)	Yield (%)[b]
500	5	100	70

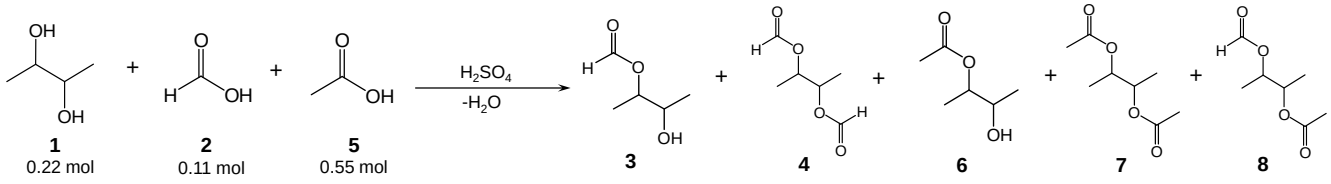
[a] Reaction conditions: The feed (Table 2, entry 3) flow rate was set to 0.3 mLh^{-1} with 30 mLmin^{-1}of N_2 gas. LHSV = 0.028 h^{-1}. [b] Yield (%) = produced 1,3-butadiene relative to the initial 2,3-butanediol.

Experimental

General procedure for the esterification process

A mixture of 2,3-butanediol with formic acid or acetic acid and 0.2 ml of sulfuric acid were placed in a round-bottomed flask fitted with a Dean-Stark trap and a condenser. The solution was stirred and the reaction temperature was gradually increased from 110 °C to 130 °C and 110 °C to 140 °C for the esterification of 2,3-butanediol with formic acid and acetic acid, respectively (Direct increasing of reaction temperature results in the higher yield of methyl ethyl ketone and loss of C1-C2 acids used for the

Table 2 Esterification of model mixture glucose fermentation liquor[a]



Entry	Temperature (°C)	Time (h)	Conversion (%)[b]	Selectivity in organic phase (%)[b]					
				3	**4**	**6**	**7**	**8**	others
1	140	3	99	3	2	17	54	18	6
2	140	7	100	2	1	11	60	18	8
3	**140**	**10**	**100**	**1**	**1**	**7**	**66**	**16**	**9**
4	140	12	100	1	1	7	68	15	8

[a] Reaction conditions: **1** (0.22 mol), **2** (0.11 mol), **5** (0.55 mol) and 0.2 mL of H_2SO_4. The temperature of the reaction mixture gradually increased during the course of the run from about 110 °C to 140 °C. [b] The conversion and selectivity was determined by GC-FID.

esterification). The resulting mixture was then extracted with dichloromethane and the organic layer was dried over anhydrous esterification). The resulting mixture was then extracted with dichloromethane and the organic layer was dried over anhydrous magnesium sulfate, filtered, and flash evaporated. The liquid products were analyzed by GC using a Younglin YL 6100 gas chromatograph equipped with a FID. The amount of loss of C1-C2 acids during the esterification was analyzed by HPLC using Younglin YL 9100.

General procedure for the pyrolysis process

The pyrolysis in the absence of catalyst was carried out in a flow-type quartz reactor, which was then placed in an electric furnace. The temperature was monitored by means of a K-type thermocouple controlled by a PID controller in the range of 400-600 °C. The feed was preheated to 250 °C in a stream of dry N_2 (30 cm^3min^{-1}). The feed consisted of a mixture of organic phase and the flow rate was set as 0.3 mLh^{-1}. The liquid hourly space velocity (LHSV) was calculated from the volumetric feed rate and volume of reactor. The liquid phase after pyrolysis was trapped in 30 mL of methanol cooled at -15 °C and analyzed using Agilent 7890 gas chromatograph coupled with a model 5975 mass spectrometer. The output gas phase stream was analyzed using an on-line gas chromatograph Donam DS 6200. For the quantification of loss of C1-C2 acids during the pyrolysis, D. I. water was used for the trapping agent produced C1-C2 acidsand analyzed by HPLC using Younglin YL 9100. The coke formation was analysed by CHNS-932 elemental analyser using SiO_2 (Degussa, Aerosil 200) as an inert material.

Characterization of products

New compounds were characterized by ^{1}H NMR, ^{13}C NMR and high resolution mass spectra (HRMS). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer. Chemical shifts (δ) are qouted in parts per million relative to acetone-d_6 2.05 ppm for ^{1}H and 29.92 ppm for ^{13}C as the internal standard. HRMS were measured with a JEOL JMS-700 instrument and accurate masses were reported for the molecular ion (M^+).

Formic acid 2-hydroxy-1-methyl-propyl ester (3): ^{1}H NMR (500 MHz, Acetone-d6): δ=8.116 (d, *J*=11.5 Hz, 1H), 4.854-4.807 (m, 1H), 3.843 (d, *J*=31 Hz, 1H), 1.267-1.190 (m, 3H), 1.116 (d, *J*=6.5 Hz, 3H); ^{13}C NMR (125 MHz, Acetone-d6): 161.78, 161.39, 75.02, 69.38, 19.01, 18.87, 15.48, 15.23.

Formic acid 2-formyloxy-1-methyl-propyl ester (4): ^{1}H NMR (500 MHz, Acetone-d_6): δ=8.116 (d, *J*=11.5 Hz, 2H), 5.124-5.059 (m, 2H), 1.267-1.190 (m, 6H); ^{13}C NMR (125 MHz, Acetone-d_6): 161.78, 161.39, 71.62, 71.57, 16.39, 16.09. HRMS (CI): $[M+H]^+$ ($C_6H_{11}O_4$) m/z calculated: 147.0657; Found 147.0659.

Acetic acid 2-hydroxy-1-methyl-propyl ester (6): ^{1}H NMR (500 MHz, Acetone-d_6): δ=4.727-4.678 (m, 1H), 3.758-3.696 (m, 1H), 1.997-1.954 (m, 4H), 1.192-1.133 (m, 3H), 1.093 (dd, *J*1=6.5 Hz *J*2=4 Hz, 3H); ^{13}C NMR (125 MHz, Acetone-d_6): 170.63, 170.47, 170.44, 74.99, 74.90, 69.53, 69.42, 21.23, 21.05, 20.98, 19.17, 18.95, 15.36, 15.26.

Acetic acid 2-acetoxy-1-mehtyl-propyl ester (7): ^{1}H NMR (500 MHz, Acetone-d_6): δ=4.957-4.900 (m, 2H), 1.997-1.954 (m, 6H), 1.192-1.133 (m, 6H); ^{13}C NMR (125 MHz, Acetone-d_6): 170.63, 170.47, 170.44, 71.85, 71.75, 21.23, 21.05, 20.98, 16.20, 15.91. HRMS (CI): $[M+H]^+$ ($C_8H_{15}O_4$) m/z calculated: 175.0970; Found 175.0971.

Acetic acid 2-formyloxy-1-methyl-propyl ester (8): ^{1}H NMR (500 MHz, Acetone-d_6): δ=8.158-8.134 (m, 1H), 5.079-5.053 (m, 1H), 4.979-4.881 (m, 1H), 2.021-2.000 (m, 3H), 1.236-1.087 (m, 6H); ^{13}C NMR (125 MHz, Acetone-d_6): 170.38, 161.62, 161.42, 76.62, 76.51, 76.25, 76.16, 76.12, 76.00, 75.96, 73.62, 73.57, 73.44, 73.05, 72.91, 72.56, 21.20, 21.05, 20.99, 16.21, 15.29.

Electrostatic potential map of products

The electrostatic potential map was produced using the GaussView 5.0 program based on the DFT (density functional theory) calculation results. All structures were fully optimized at the DFT level using B3LYP hybrid functional and 6-311 basis set by Gaussian 03W program package. The reported optimized structure of (R,S)-2,3-butanediol was used to construct the initial structure of the formic acid 2-hydroxy-1-methyl-propyl ester (**3**) and the formic acid 2-formyloxy-1-methyl-propyl ester (**4**).[15]

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Notes and references

[a] *World Class University (WCU) program of Chemical Convergence for Energy & Environment (C2E2), Institute of Chemical Processes, School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea*
E-mail: jyi@snu.ac.kr
[b] *Chemical & Polymer Lab. R&D Center, GS-Caltex Corporation, Daejeon 305-380, Republic of Korea*

† Electronic Supplementary Information (ESI) available: ^{1}H NMR & ^{13}C NMR spectra, photographs of esterification products, and GC chromatograms are provided. See DOI: 10.1039/b000000x/

‡ These authors contributed equally to this work.

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