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# Fermentation–pervaporation–catalysis integration process for bio-butadiene production using sweet sorghum juice as feedstock

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## ABSTRACT

Fermentation–pervaporation–catalysis (FPC) integration process was employed to produce bio-butadiene using sweet sorghum juice as feedstock. After *in situ* ethanol removal from fermentation broth, permeate of pervaporation membrane (478.6 g/L bio-ethanol) was directly converted into butadiene by an Ag/Mg–Si catalyst. A butadiene yield of 64.1% with a butadiene selectivity of 75.8% was achieved within 6 h of operation. The integration process showed a great potential on high final product yield in a long-term operation. Following this protocol, about 16 g of bio-butadiene was produced from 1 kg sweet sorghum stalk. The integration process showed a potential in further application for bio-butadiene and materials production.

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## 1. Introduction

In the milieu of sustainable and environmental concern, renewable biochemical productions from biomass resources have been recognized as a potential way to reduce the usage of petrochemical resources and decrease the emission of greenhouse gases [1,2]. Butadiene is an important platform chemical for synthetic rubber, elastomers and resins production [3]. Recently, over 95% of butadiene (1,3-butadiene) is produced based on petro-chem routes, which was unsustainable [4]. To produce renewable butadiene, an esterification-pyrolysis integration process was suggested to convert bio-2,3-butanediol form glucose into butadiene. Typically, the route was complex and environmental unfriendly since organic sol-

vents assisted in this process [5]. In addition, the feedstocks in previous research were not based on biomass resources. Hence, there is an opportunity in technical improvement in order to use abundant biomass resource for the butadiene production [3,6].

Compared with the above method, butadiene production from ethanol by one step catalysis process is attractive since ethanol can be easily produced via fermentation from biomass resources [1,7]. However, although numerous researches have been done for preparing different types of catalysts to covert ethanol into butadiene, its application is limited not only because of the high energy demand for ethanol distillation and dehydration, but also due to the poor performances in butadiene catalyzing process [8]. Generally, the conversion of ethanol into butadiene was extensively studied over different types of catalyst, especially using MgO–SiO<sub>2</sub> based materials [9,10]. The formation of magnesia-silicate plays a significant role in butadiene production. Moreover, the MgO–SiO<sub>2</sub> catalysts with dehydrogenation promoters (such as Ag, Cu and Zn) with ethanol dehydrogenating potential provide a high catalytic performance [7,11]. Among these catalysts, MgO–SiO<sub>2</sub> materials containing Cu and Ag modifiers provided a relatively high butadiene yield of 55% with full ethanol conversion. However, improvement of the catalytic performance is still encouraged.

Cu<sup>2+</sup>, the only species initially present, is extensively reduced to a mixture of Cu<sup>0</sup> and Cu<sup>+</sup>, leaving only a limited amount of unreduced Cu<sup>2+</sup> in the conversion of ethanol to butadiene over CuO–MgO–SiO<sub>2</sub> catalyst [9]. This formation of Cu<sup>0</sup> is thought to be mainly responsible for the improved performance of the Cu-promoted catalyst. Therefore, the comparison of the MgO–SiO<sub>2</sub> catalysts modified dehydrogenation promoters (such as Ag, Cu

**Abbreviations:** FPC, fermentation–pervaporation–catalysis; VLE, vapor liquid equilibrium; NREL, non-random two-liquid; PVDF, polyvinylidene fluoride; PDMS, polydimethylsiloxane; DBTDL, dibutyltindilaurate; TEOS, tetraethyl orthosilicate; DBSA, dodecylbenzene sulfonic acid; ICP-MS, inductively coupled plasma mass spectrometry; HPLC, high performance liquid chromatography; XRD, X-ray diffraction; XPS, X ray-photoelectron spectroscopy; FID, flame ionization detector; GC, gas chromatograph; Si, selectivity toward i-product; *n*, amount of C moles;  $\beta$ , separation factor of ethanol;  $x_p$ , mass fractions of ethanol in the permeate;  $x_f$ , mass fractions of ethanol in the feed; *J*, mass of the permeate; *Q*, mass of the permeate collected; *A*, effective area of the membrane; *t*, operation time;  $Q_{norm}^{evap}$ , evaporation energy for ethanol pervaporation;  $\Delta H_e$ , enthalpies of vaporization of ethanol;  $\Delta H_w$ , enthalpies of vaporization of water;  $J_w$ , partial fluxes of water;  $J_e$ , partial fluxes of ethanol;  $X_e$ , ethanol concentration in the vapor of permeate.

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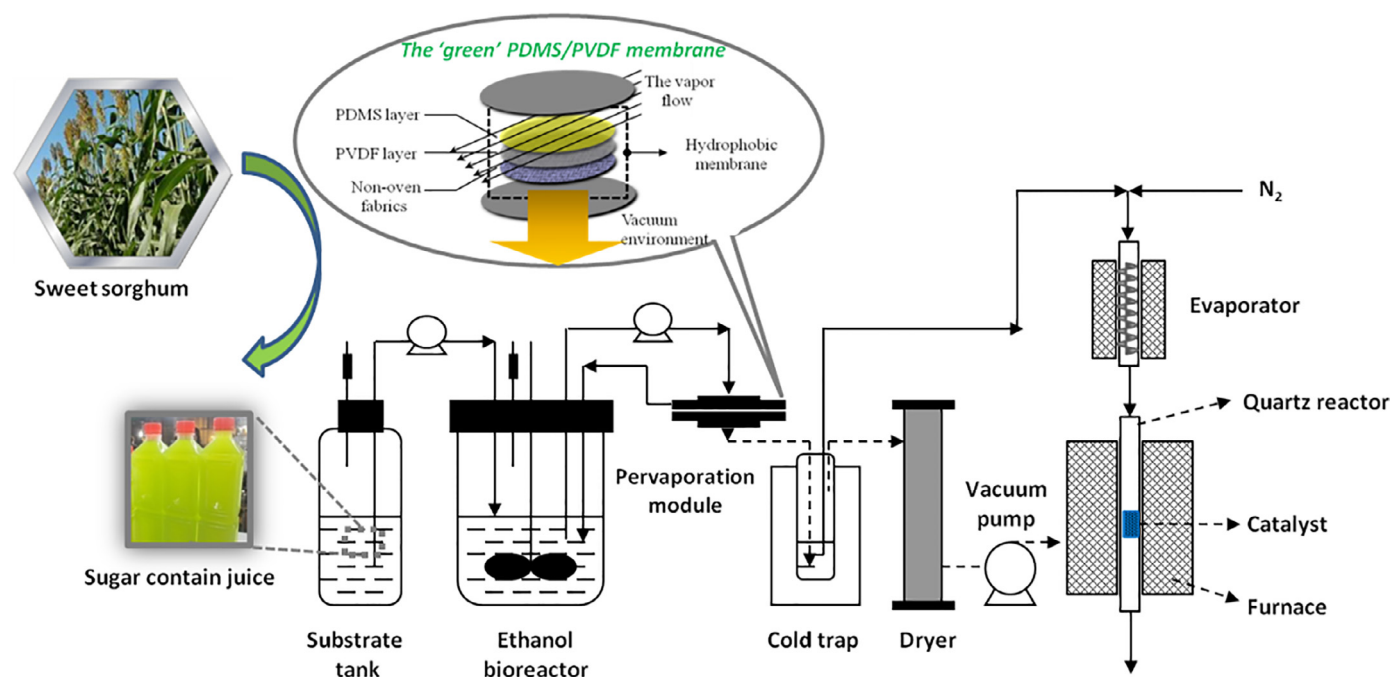


Fig. 1. Flowchart of the FPC process for the production of bio-butadiene.

and Zn) with different oxide state is required in this reaction. Besides, water-resistance of catalysts is an important parameter in industry application. Recently, research indicated that the presence of water (10 wt%) led to a considerable decrease in ethanol conversion and butadiene selectivity when MgO–SiO<sub>2</sub> catalyst was used to convert ethanol to butadiene [12]. For the MgO–SiO<sub>2</sub> catalysts modified dehydrogenation promoters, the effect of water content on catalytic performance is little investigated, especially high water content of 50%. The improvements of water-resistance for catalysts are valuable in ethanol conversion into butadiene. Metal-containing MgO–SiO<sub>2</sub> based catalysts were investigated in butadiene production from ethanol obtained by fermentation.

Except for developing reliable catalyst that has excellent activity and stability in long-term butadiene production, ethanol fermentation process also calls for improvements in order to reduce ethanol recovery cost and enhance ethanol productivity [13,14]. Pervaporation, the membrane based separation technique, has been used for *in situ* ethanol separation from fermentation broth [15,16]. Coupling with pervaporation separation, the high titer of bio-ethanol product is continually obtained in the permeate condensate. Correspondingly, the energy requirement is reduced, while the fermentative productivity of ethanol might be also facilitated by the removal of toxic ethanol product [13,17].

In the current work, using the fermentation–pervaporation–catalysis (FPC) integration process shown in Fig. 1, we verified the feasibility in bio-butadiene produce production from mixing sugars solutions. Sweet sorghum juice, the inexpensive sugar-based bioresource from agriculture residual, was used as the raw material [18,19]. There are five highlights in bio-butadiene production via the integrated FPC process.

- (1) The integration process is environmental friendly. It is because the pervaporation membrane was prepared using “green” method, with no toxic volatility compounds formation during its production. In addition, the lignocellulosic bagasse could be used for heat so that reducing the green house gas emission [20,21].
- (2) The fermentable juice from biomass resource was used for bio-butadiene production for the first time.

- (3) The highest ethanol concentration and separation factor ever reported were achieved in the fermentation–pervaporation integrated unit.
- (4) Wet ethanol was used for butadiene production, and the Ag/Mg–Si catalyst exhibited high water-resistance. In the FPC process, ethanol obtained in the permeate side of pervaporation membrane (<50%) was directly used for butadiene production. At the same time, high butadiene selectivity of 75.8% was still obtained. The results show that the Ag/Mg–Si catalyst has an obvious improvement in water-resistance compared the MgO–SiO<sub>2</sub> catalyst [12]. Therefore, huge energy would be saved by practicing the FPC process since less water needs to be removed from the broth. By rough calculation, the theoretical evaporation energy demand for ethanol recovery in the FPC process was only 1.8–1.9 MJ/kg (based on VLE data and NRTL model based on Aspen Plus 8.0, calculated by Eq. (6), similar with the method described in [22]), which was only 33–43% of the energy cost for the conventional process (4.4–5.4 MJ/kg, by conventional distillation system for a 10 wt% ethanol feed [23]).
- (5) The FPC process showed a long-term stability.

## 2. Materials and methods

### 2.1. Raw material

The sweet sorghum stem was kindly provided by Chinese Academy of Agricultural Sciences and was collected in Beijing, China. The nutrients and carbon sources constituents of the fermentable juice were analyzed by ICP-MS and HPLC, respectively. The main composition of the sweet sorghum juice was listed in Table 1.

### 2.2. Preparation of PDMS/PVDF membrane

The polydimethylsiloxane (PDMS) membrane used in this work was laboratory prepared applying water as solvent [20]. A solution with dibutyltindilaurate (DBTDL), tetraethyl orthosilicate (TEOS), as well as PDMS was mixed well at 25 °C for 2 h using 3% of DBSA as

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