

## Abstract

Recent research on the biological conversion of carbon monoxide (CO) and hydrogen (H<sub>2</sub>) into multi-carbon compounds have revealed that syngas fermentation is one of the potential alternatives for the production of more sustainable fuels and chemicals. However, poor mass transfer of the sparingly soluble gaseous substrates (CO and H<sub>2</sub>) and low cell density in the fermentation media are the big hurdles in the commercialization of the technology. These issues can be resolved by using the membrane based reactors (MBR) instead of most widely employed stirred tank reactors (STR) and less common bubble column reactors (BCR). This study has successfully utilized a hydrophobic polyvinylidene fluoride (PVDF) membrane to achieve high CO volumetric mass transfer coefficient ( $k_L a$ ) in submerged HFMBR. We have found a  $k_L a$  of 135.72 h<sup>-1</sup> under transmembrane pressure of 93.76 kPa and  $A_s/V_L$  (membrane surface area/working volume of the liquid) of 27.5 m<sup>-1</sup>. High  $k_L a$  of 155.16 h<sup>-1</sup> was achieved by increasing  $A_s/V_L$  to 62.5 m<sup>-1</sup> under lower transmembrane pressure of 37.23 kPa. Finally, *Eubacterium limosum* KIST612 was grown in the proposed HFMBR system and organic product formation has been monitored for three days.

## Introduction

Synthesis gas (syngas), a mixture of principally carbon monoxide (CO) and hydrogen (H<sub>2</sub>), can be produced by gasification of many types of organic matter from both fossil and renewable resources, such as coal and biomass (Latif et al., 2014). The versatility in the feedstocks for syngas fermentation enables a gradual changeover to more sustainable energy and bio-chemicals production (Henstra et al., 2007). However, challenges still exist in the microbial conversion process, including low achievable cell density and an insufficient gas-liquid mass transfer rate for microbial utilization (Bredwell et al., 1999). It was reported that the gas-liquid mass transfer was the most limiting factor in the syngas fermentation reaction, leading to reduced productivity (Abubakar et al., 2011; Munasinghe & Khanal, 2010a). Various strategies have been adopted to increase the gas-liquid mass transfer rate, including larger gas to liquid interfacial areas, high gas and liquid flow rates, high pressure, reactor schemes, novel impeller designs, improved flow patterns for gas-liquid mixing, variation in mixing times and agitation speeds, use of nanoparticles and applying microbubble dispersions. Most of these methods cause an increase in the interfacial surface area available for the mass transfer and increase bubble breakup. These approaches, however, should be evaluated for whether they can be scaled-up for commercial systems.

The use of an HFMBR could make it possible to achieve the higher mass transfer efficiency with the lowest gas supply rate, representing a feasible industrial process for the biological conversion of syngas (Lee et al., 2012). An increase in the CO mass transfer rate above the maintenance requirement by increasing the CO partial pressure has resulted in an increased cell concentration (Chang et al., 2001). Therefore, an HFMBR is likely to achieve high cell concentrations and rapid gas-liquid mass transfer, thus resolving the issues of kinetic and mass transfer limitations simultaneously. The main aim of this study was to develop an HFMBR with high gas-liquid mass transfer rates using the internal pressure (P) and the external surface area of the hollow fibre membrane per unit working volume of the liquid ( $A_s/V_L$ ) as controllable parameters.

## Experimental Section

### Experimental Setup

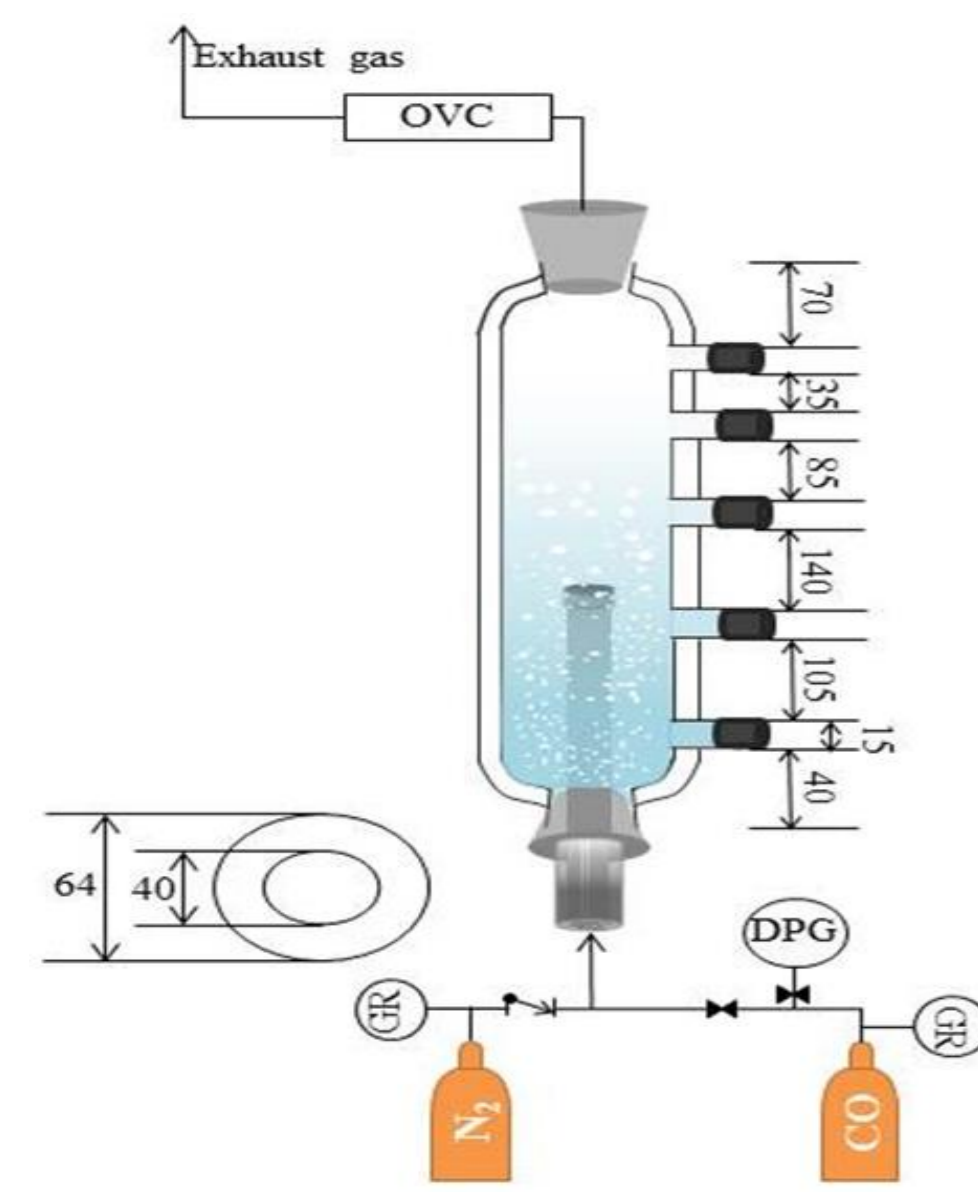


Fig. 1. Schematic of reactor setup

### Hollow fibre membrane module (HFMM) fabrication

A microporous PVDF membrane fibre (0.1 μm pore size, 1.2 mm OD, 0.7 mm ID, ECONITY, Yongin, Korea) was used in this study.

### $k_L a$ measurement

The method for measurement of dissolved CO ( $C_L$ ) and  $k_L a$  was adopted from Park et al. (2013), with slight modification. Equation 1 was used (under fully homogenised conditions).

$$\ln\left(1 - \frac{C_L}{C^*}\right) = -(k_L a)t \quad (1)$$

### Experimental conditions and variables for abiotic test

All experiments were conducted at 35°C and pH 7.0.  $P$  and  $A_s/V_L$  were used as key control experimental variables.

### Bacterial strain

A CO-utilizing acetogen, *Eubacterium limosum* KIST612 was used in this study.

### Media composition and strain cultivation

Carbonate-buffered basal medium (CBBM) adopted from (Chang et al., 1999)

### HFMM for biotic operation

A hollow fibre membrane module with the lowest  $A_s/V_L$  (27.5 m<sup>-1</sup>) was chosen as CO diffuser for biotic test.

### Statistical analysis

The precision and accuracy of data were evaluated using the standard error of estimate (SE), standard deviation (SD) and coefficient of determination (R<sup>2</sup>).

### Analyses of cell concentration and organic product

- **UV-VIS spectrophotometer:** OD measurement at 600nm
- **Cell concentration (g L<sup>-1</sup>):** 1 unit of OD = 0.27 g dry cell weight L<sup>-1</sup>
- **Organic products:** Gas chromatograph equipped with a flame ionization detector (FID) and capillary column was used to find the concentration of acetate.

## Results

### 1. $k_L a$ changes by two controllable factors

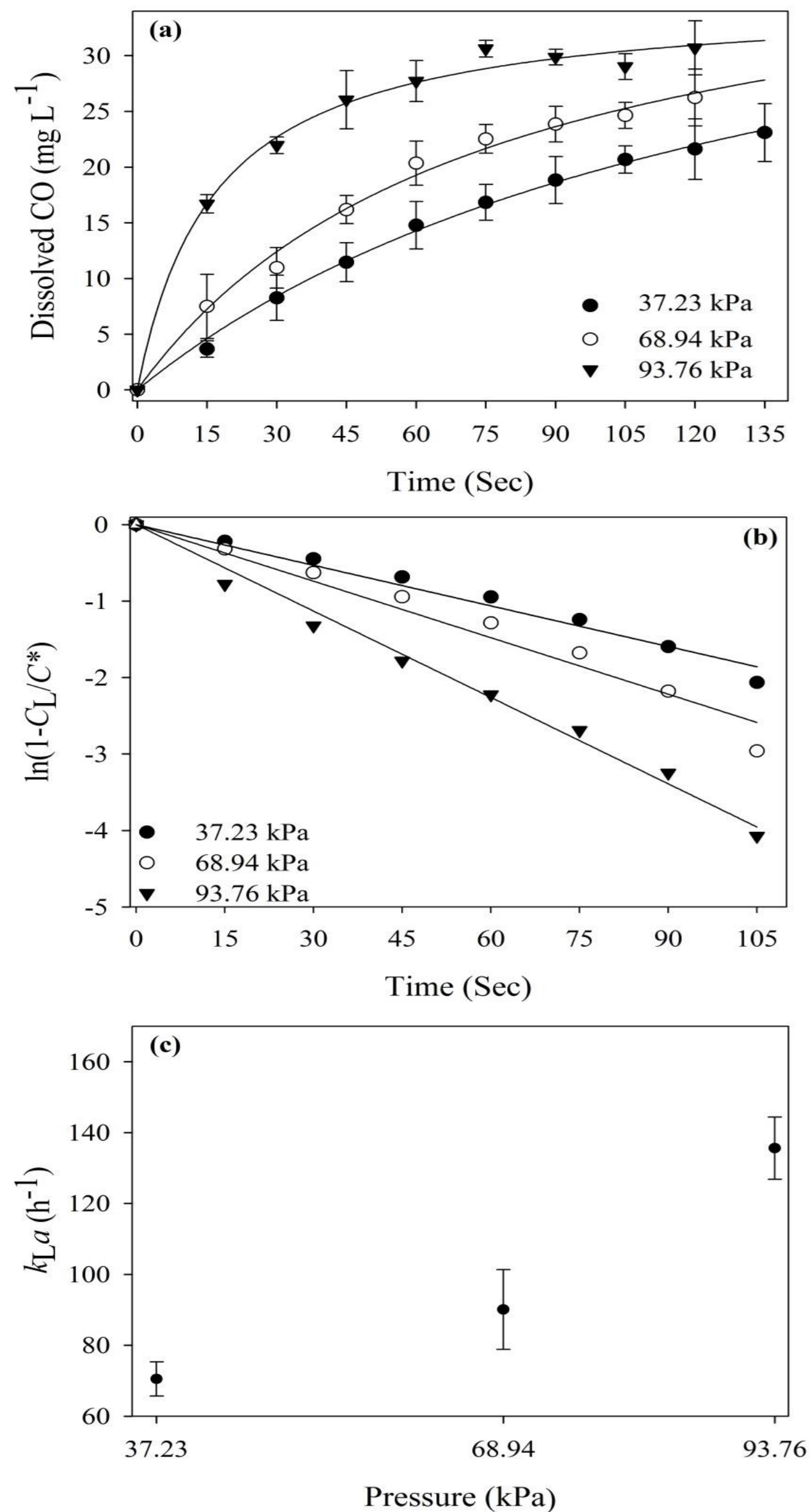


Fig. 2. (a) Dissolved CO at varying pressure using fixed  $A_s/V_L$ . Each point for dissolved CO ( $C_L$ ) is the mean of multiple (minimum triplicate) measurements. (b)  $k_L a$  at varying pressure using fixed  $A_s/V_L$ , obtained as the slope of the eq. (1) using a linear fit. (c) Summary of  $k_L a$  using data for the individual measurements in Fig. 2a.

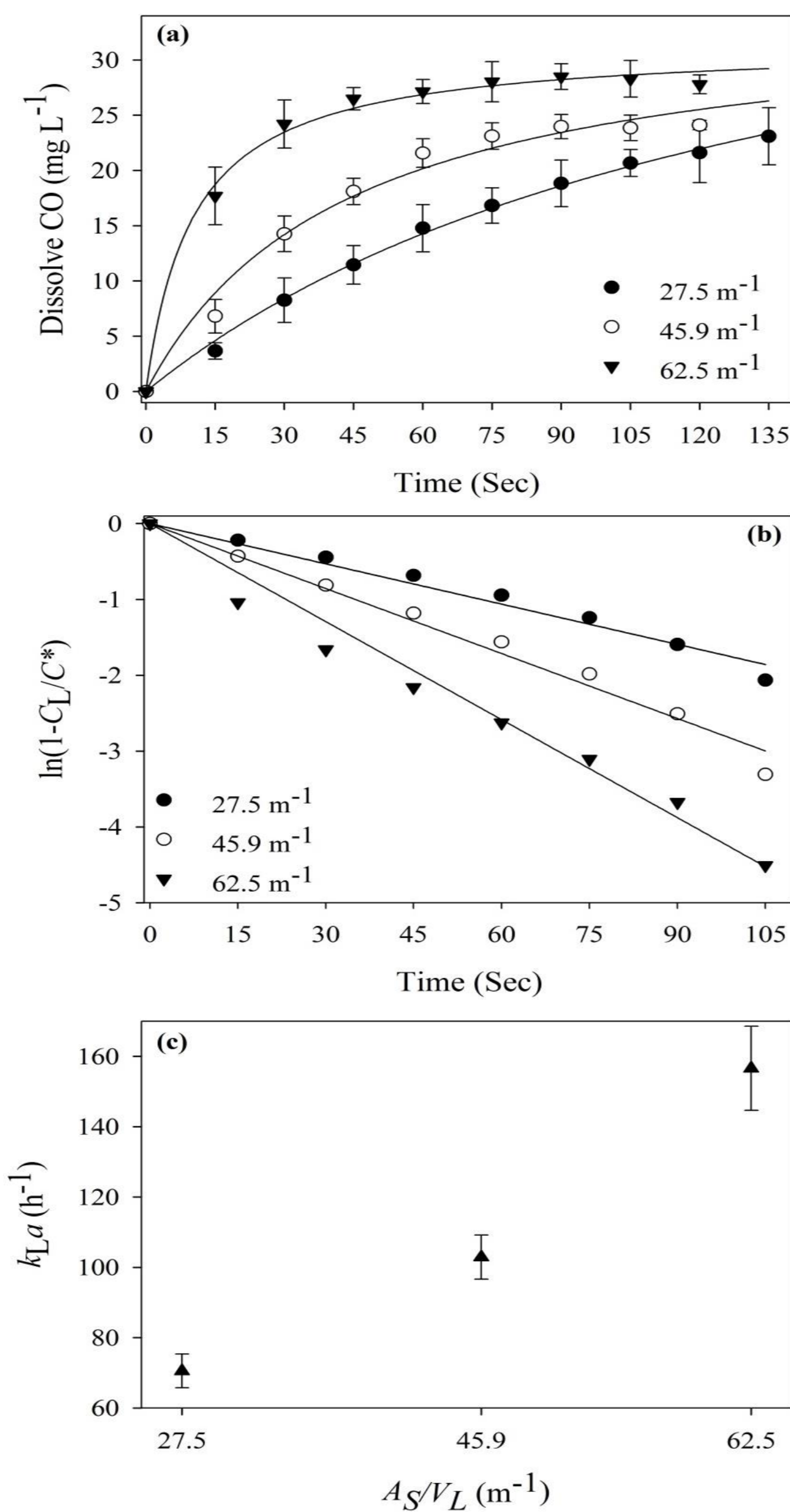


Fig. 3. (a) Dissolved CO at fixed pressure using varying  $A_s/V_L$ . Each point for dissolved CO ( $C_L$ ) is the mean of multiple (minimum four) measurements. (b)  $k_L a$  at a fixed pressure of 37.23 kPa using varying  $A_s/V_L$ , obtained as the slope of the eq. (1) using a linear fit. (c) Summary of  $k_L a$  using data for the individual measurements in Fig. 3a.

### 2. Biotic test in HFMBR and comparison with serum vial culture

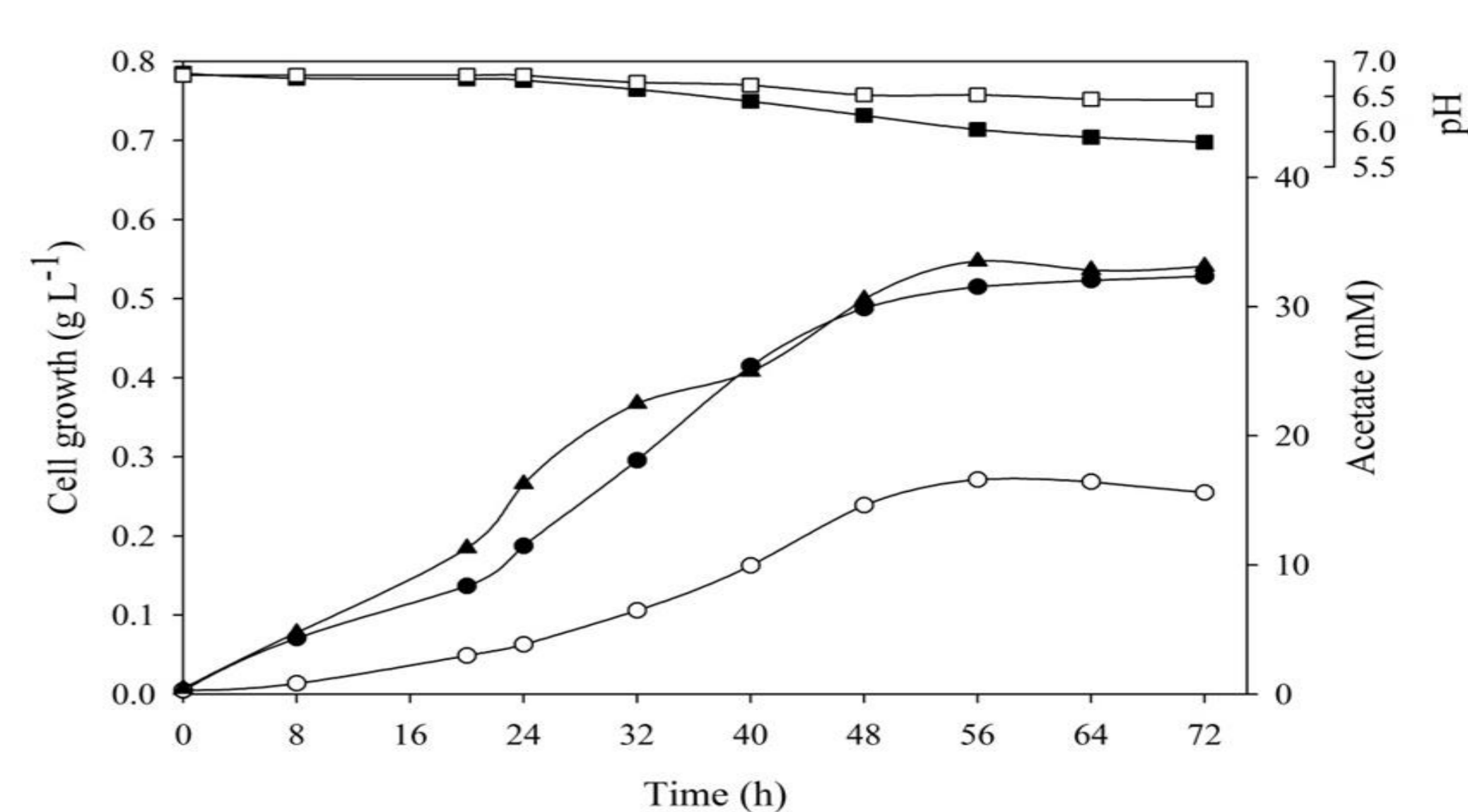


Fig. 4. Cell growth and product formation in HFMBR and serum vial from CO/CO<sub>2</sub> fermentation using *Eubacterium limosum* KIST612 (●: Cell conc. in HFMBR, ○: Cell conc. in vial, ▲: Acetate conc. in HFMBR, ■: pH in HFMBR, □: pH in vial)

## Conclusions

1. Simple HFMBR configuration able to support microbial growth and product formation
2. High gas-liquid mass transfer system
3.  $k_L a$  achieved in this study using PVDF hollow fibre membrane is the highest one
4. Highest  $k_L a$  in submerged type HFMBR configuration

(This work has been accepted for publication in *Bioresource Technology*)

## References

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