# Conversion, selectivity, yield and specific energy in DBD reactors: are they well measured?

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**Abstract:** Many results found in literature for conversion, selectivity, yield and specific energy in DBD plug-flow reactors neglect the gas expansion due to chemical reactions. We discuss the errors introduced by this approximation and propose a simple method to obtain correct values. The method is applied to study methane conversion in He/$CH_4$/$CO_2$ mixtures.

**Keywords:** conversion, selectivity, specific energy, methane conversion

## 1. Introduction

Although conversion, selectivity and yield are base concepts in chemical reaction engineering, we find different, and sometimes conflicting, definitions in literature for batch or continuous processes. In this paper, we focus on continuous processes as characteristics of DBD plug-flow reactors and assume isobaric and isothermal conditions. For continuous processes, the definitions for the above three concepts (1-3) are based on the time rate of amounts fed into or exiting the reactor. A fourth important definition is of the specific input energy (SIE) as the energy per unit volume supplied to the gas (4). Finally, we assume that the composition of gases fed into or exiting the reactor is determined by gas chromatography, GC.

## 2. Effect of gas expansion on measurements

The reactions on a DBD reactor change the number of molecules and, under isobaric and isothermal conditions, this implies a change in the volumetric flux of gases, $\Phi_V$. Let us assume, without loss of generality, that the number of molecules and volumetric flux increases along the reactor. The concentration of any species changes with $\Phi_V$, even if it does not take part in reactions. If $\Phi_{V,in}$ and $\Phi_{V,out}$ are the fluxes entering and exiting the reactor, respectively, and writing the time rate of amount *i*, through surface $S$ as $\dot{N}_i = c_i n \Phi_V$ where $c_i$ is the concentration of *i* and *n* the gas density, for a species that does not react, the concentrations entering and exiting the reactor (for constant *S*), are written as $c_{j,in} = \alpha c_{j,out}$ where $\alpha = \Phi_{V,out}/\Phi_{V,in}$ is the gas expansion ratio [1].

In gas chromatography, a small volume of the gas stream is sampled and the species concentration obtained from a calibration curve. The calibration curve, however, is obtained for a constant gas flux and does not take into account the effect of gas expansion. In order to compensate for this, the GC results should be corrected by the gas expansion ratio. With this correction, equations (1-3) can be written as (5-7).

The measurement of $\Phi_{V,out}$, however, is not commonly done and many authors fail to include the gas expansion factor α in the computation of conversion, yield and selectivity or in numerical model [2]. This omission introduces a non-negligible systematic error in their results as shown in section 3.

As for the SIE, the energy deposition also decreases with gas expansion and this needs to be considered. Assuming uniform power deposition along the reactor and a linear dependency of α with the reactor length, we obtain for SIE the corrected value (8). In the limit $\alpha \rightarrow 1$ we obtain the $P/\Phi_{V,in}$ value commonly found.

## 3. Errors in neglecting the gas expansion ratio

To estimate the errors introduced neglecting α we use the ideal *Syngas* production reaction from methane and carbon dioxide,

$$CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2$$

and assume the same conversion value for $CH_4$ and $CO_2$, $X$. In this case $\alpha = 1 + X$, and the percent errors (9) can be estimated as a function of X (Fig. 1). Neglecting the gas expansion overestimates the conversion and SIE values and underestimates the selectivity and yield. In this case, the error in selectivity is independent of X.

For other mixtures and reactions, the qualitative trend is the same as in this simple case: for $\alpha > 1$, neglecting α leads to a large overestimation of conversion, with the percent error decreasing with conversion; an underestimation of selectivity, independent or weakly dependent on conversion; yield and SIE errors increasing with conversion. For $\alpha < 1$, the percent errors change sign.

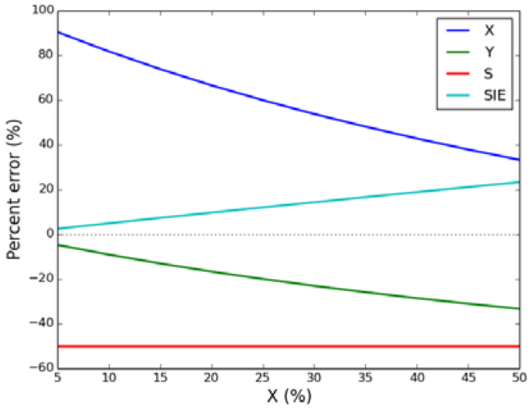

Fig. 1. Percent error on conversion, X, yield, Y, selectivity, S, and SIE, as a function of conversion for the test case, when the gas expansion is neglected.

## 4. Measurement of the gas expansion ratio, α

The measurement or estimation of α, however, is not straightforward. Only for the simplest reaction schemes can α be estimated. The measurement of the exhaust gas flux by thermal mass flow meters is not reliable as the exact gas composition is unknown and depends on the experimental conditions.

We have devised a simple method to measure α mixing a small, fixed, flux $\Phi_r$ of a reference gas *r*, to the flux exiting the reactor. Measuring the areas obtained by GC for this gas with, $A_r$, and without, $A_{r,0}$, discharge, the gas expansion ratio is obtained from (10). If $\beta \ll 1$, $\alpha \approx A_{r,0}/A_r$. Note that the method does not require any calibration of the MFC or GC for the reference gas.

## 5. Experimental set-up

We applied this method to study the influence of temperature on the conversion of methane in mixtures of $He/CH_4/CO_2$ with $c_{CH4/}c_{CO2} = 1$. The gas expansion was measured using a flux of $N_2O$ of 1 ml/min as internal standard. $N_2O$ was chosen because it does not overlap with other gases in the chromatogram. The experimental system, indicated in Fig 2, includes a cylindrical DBD reactor having a central Stainless Steel electrode, supported by MACOR fittings, inside a quartz tube. The ground electrode is a thin metal foil stretched around the quartz.

The gas temperature is measured by a thermocouple and by optical emission spectroscopy of the rotational bands of CH ($^2\Delta \rightarrow {}^2\Pi$). The output gas composition was analysed in a Shimadzu 9A GC equipped with a thermal conductivity detector. The discharge power was obtained from V-Q diagrams. The value of the power supply voltage was controlled using the thermocouple signal in order to keep the ratio of the peak voltage to the gas density constant. The experiment and data acquisition are controlled by a Linux based USB-DUX board.

In these mixtures, the rare gas is responsible for a spread of the electron energy distribution to higher energies and a large increase in conversion as discussed in [3].

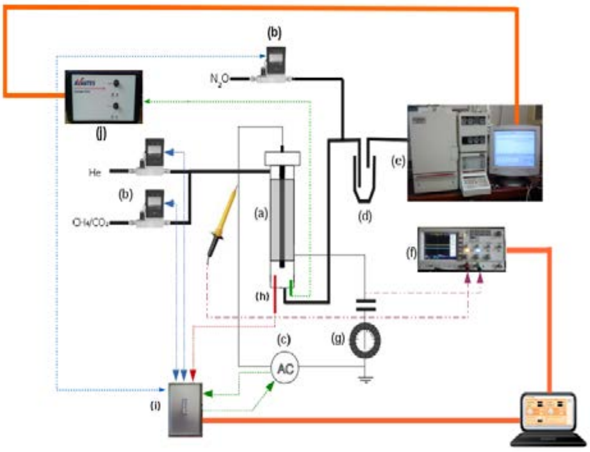

Fig. 2. Experimental set-up. (a) Reactor; (b) MFC; (c) HV power supply; (d) trap; (e) GC; (f) oscilloscope; (g) Rogowski coil; (h) thermocouple; (i) ADC; (j) UV-Vis spectrometer.

## 6. Experimental results

We only report here results relevant to the discussion of the influence of gas expansion. In this case the reactor was kept at room temperature. The gas expansion factor can be estimated from the reaction in section 3, including the helium concentration, $c_{He}$, as $\alpha = 1 + X(1 - c_{He})$. In the mixtures studied, with large $c_{He}$, the gas expansion is small as the experimental values in Fig 3 show. The relative uncertainty on α depends only on the GC areas and, in this case, is below 1.5%. The method is precise enough to measure variations of a few percents.

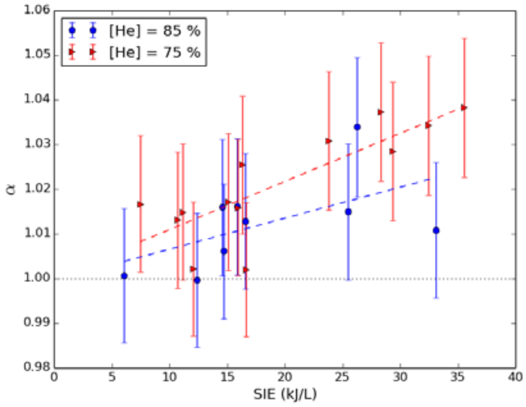

Fig. 3. Gas expansion ratio, α, measured using $N_2O$ as reference gas, in $He/CH_4/CO_2$ mixtures with $c_{CH4/}c_{CO2} = 1$, as a function of SIE for two values of helium concentration.

The measurement of α also provides an indirect estimate of a mixture average conversion value $\langle X \rangle$.

Fig 4 shows the conversion values for $CH_4$ and $CO_2$, respectively for three values of $c_{He}$. The results were fitted to a function defined by equation (11). The dashed lines correspond to fits neglecting the gas expansion while the solid lines are the fits to the correct values.

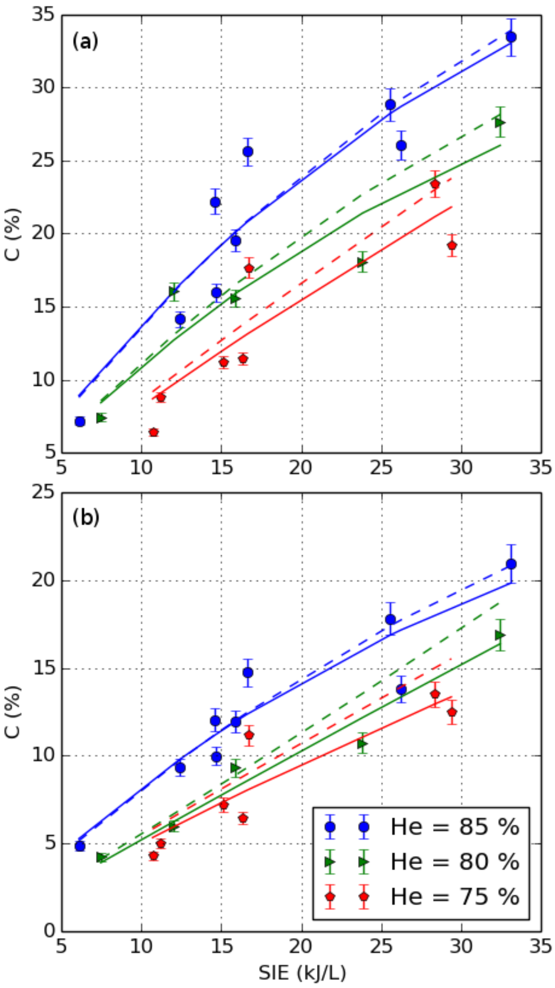

Fig. 4. Values of conversion as a function of the specific input energy for (a) $CH_4$ and (b) $CO_2$, in mixtures of $He/CH_4/CO_2$ with $c_{CH4}/c_{CO2} = 1$, for three values of helium concentration. The solid and dashed lines are the fitted results to eq. (11) with or without α, respectively.

The non-corrected values of selectivity were between -5% and -10% of those computed from (7).

## 7. Conclusions

The reactions on a DBD reactor change the number of molecules and, under isobaric conditions, lead to the expansion (or contraction) of the gases and increase (decrease) the volumetric flux of gases. The gas expansion ratio intervenes in the computation of conversion, yield, selectivity and the specific input energy. The failure to consider the expansion ratio leads to significant systematic errors in these quantities. A simple method to measure the gas expansion was proposed and tested on $He/CH_4/CO_2$ mixtures. Even for mixtures with high helium concentrations and a small gas expansion, the method is sufficiently sensitive and the corrections significant.

## 8. Equations

(1) Conversion: $X_i = 1 - \frac{\dot{N}_{i,out}}{\dot{N}_{i,in}}$, where $\dot{N}_i$ are the time rates of input or output, respectively, of amount *i*;

(2) Yield: $Y_m = \frac{\mu_m \dot{N}_{m,out}}{\sum_k \nu_k \dot{N}_{k,in}}$, where μ and ν are stoichiometric coefficients and the sum is on all reactants producing *m*;

(3) Selectivity: $S_{m,a} = \frac{\mu_{m,a} \dot{N}_{m,out}}{\sum_k \nu_{k,a} (\dot{N}_{k,in} - \dot{N}_{k,out})}$, in this case the selectivity for product *m* is based on the number of *a* atoms and the stoichiometric coefficients account the number of *a* atoms;

(4) Specific input energy: $SIE = \frac{P}{\Phi_V}$, with P the power supplied to the reactor and $\Phi_V$ the volumetric gas flux.

(5) $X_i = 1 - \frac{\alpha c_{i,p}}{c_{i,0}}$, where the index *p* and *o* indicate the values with plasma and initial, respectively;

(6) $Y_m = \frac{\mu_m \alpha c_{m,p}}{\sum_k \nu_k c_{k,0}}$

(7) $S_{m,a} = \frac{\mu_{m,a} \alpha c_{m,p}}{\sum_k \nu_{k,a} (c_{k,0} - \alpha c_{k,p})}$

(8) $SIE = \frac{P}{\Phi_{V,in}} \frac{\log(\alpha)}{\alpha - 1}$

(9) Percent error: $(y_0 - y(\alpha))/y(\alpha) \times 100$, where $y_0$ is the value neglecting α.

(10) $\alpha = \frac{A_{r,0}}{A_r}(1 + \beta) - \beta$, where $\beta = \frac{\Phi_r}{\Phi_{V,0}}$ is the ratio between the reference gas flux and the gas flux without discharge.

(11) $X_i = [1 + \alpha(SIE)\exp(-k_i \cdot SIE)] \times 100$.

## 9. Acknowledgements

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