

Simulating Trambouze reaction for a series reactor

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Abstract

Simulating the existing data on Trambouze reaction is compiled in this article. The objective of the work is to present the change of volumetric flow rate and the inlet concentration of key reactant A in a series continuous stirred tank reactor-plug flow reactor (CSTR-PFR) configurations. The volumetric flow rate does not affect selectivity and conversion for a constant volumetric flow rate operating condition, entering CSTR and PFR, at a specific concentration of reactant. The CSTR-PFR series reactor configuration is proposed for the aim of maximizing the selectivity of the desired product B in comparison to the undesired products X and Y. CSTR as the first reactor is capable to achieve the maximum conversion at the highest selectivity of A. PFR is then proposed after CSTR in a configuration of CSTR-PFR, to allow higher conversion value to be achieved for the resulted outlet stream conditions coming out of the first reactor, CSTR. Both reactors commonly encounter a decrease in the initial concentration of A and an increase to the formation of other products. The CSTR entering volumetric flow rate influence the volume sizes needed in achieving the maximum selectivity and conversion.

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1.0 Introduction

Conversion and selectivity of any reactants in a reactor, are crucial in order to maximise production of certain products. Selectivity in a chemical reactor with multiple reactions, informs on how one product is favoured over other products relating to desired and undesired products, needing certain control strategies (Luyben, 2007; Fogler, 2014). Alternatively, this can also be achieved by choosing the right reactor scheme for any reaction systems like either batch, continuous, fed batch, or packed bed system in a single or multiple set of systems. Multiple systems are described by either series or parallel arrangements.

In any chemical reactor, the chemical reaction produces desired and undesired products (Fogler, 2014 and Levenspiel, 1999). Therefore, selectivity and conversion are considered to minimise the unwanted or the undesired products, with proper choice of reactor operating conditions and reactor selection in a transient and steady state conditions (Varma & DeVera, 1979). The selectivity (Ghashghaei et al., 2019) in multicomponent reactions system and conversion other than the initial concentrations of the reactants are

crucial parameters to determine the best reactor design involving volumetric flow rate, specific rate of reactions and space time (da Silva et al., 2008). For instance, the volumes of CSTR and PFR for CSTR-PFR system vary depending on the initial concentration of reactants with various values of specific rate of reactions, initial concentration of reactants, and also volumetric flow rate as reported by the study of the reactor network synthesis in isothermal conditions varying from 600 to 900 L for continuous stirred tank reactor (CSTR) and 9 to 150 L for plug flow reactor (PFR) (da Silva et al., 2008; Achenie & Biegler, 1986; Kokossis & Floudas, 1990; Paynter & Haskins).

Trambouze reaction (Trambouze, 1959) is an example of a multiple reactions, best to illustrate simultaneous ordinary differential equations (ODE) solutions in a reactor from specific mole balance equations. In this article, the reactor arrangement scheme is selected based on maximising selectivity of the desired product against the undesired products, Whilst, the justification in operating at the highest conversion is described based on simulation of results from the multiple reaction equations.

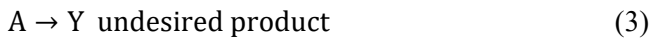
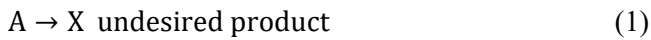
Simulations are supported to predict the conversion and selectivity of reactants and products in a chemical reactor system, validating the optimisation of reactor designs (Bandyopadhyay et al., 1993)

Therefore, in this article, the investigations on CSTR-PFR system together with the change of volume, conversion, and concentration of species with the effect of volumetric flow rate and space time are conducted.

2.0 Methodology

2.1 Trambouze reaction model

Trambouze reaction with three multiples reactions containing zero order (undesired product, Eq. (1)), first order (desired product, Eq. (2)), and second order (undesired product, Eq. (3)), are simulated based on the reported parallel chemical reactions equations in Fogler (2014). Trambouze reaction is composed of three parallel reactions that involves four species (one reactant, one desired product and two undesired products).



The multiple reaction rates with specific reaction rates of r_A , r_B , r_X , r_Y with specific rate constants of k_1 (in Eq. (3)), k_2 (in Eq. (4)), and k_3 (in Eq. (5)) at the operating temperature of $T=300\text{K}$ and activation energy of E_1 , E_2 , and E_3 of 10,000, 15,000, and 20,000 kcal/mole, for each equation, respectively (Fogler, 2014). C_A is defined as the concentration of reactant A in $\frac{\text{mol}}{\text{dm}^3}$.

$$-r_{1A} = r_X = k_1 = 0.0001 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}} \quad (4)$$

$$-r_{2A} = r_B = k_2 C_A = 0.0015 \frac{1}{\text{s}} C_A \quad (5)$$

$$-r_{3A} = r_Y = k_3 C_A^2 = 0.008 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} C_A^2 \quad (6)$$

The selectivity $S_{B/XY}$ and conversion X for the multiple reactions are expressed by the ratio of all specific rate of reactions and the dependence of concentration of reactants, respectively. Conversion X is expressed as a factor of initial concentration of A C_{A_0} and maximum concentration of A achieved $C_{A_{max}}$. The

equations of $S_{B/XY}$ and X are expressed by these equations, Eq. (7) and (8), respectively:

$$S_{B/XY} = \frac{r_B}{r_X+r_Y} = \frac{k_2 C_A}{k_1+k_3 C_A^2} \quad (7)$$

$$X = \frac{C_{A_0}-C_{A_{max}}}{C_{A_0}} \quad (8)$$

In maximising the desired products, based on Eq. (7) and (8), the selectivity and conversion are closely considered with an additional aspect of cost based on the efficiency of the selected reactor system. The reactor with high efficiency needs higher cost, and efficiency depends on selectivity and conversion from the multiple reactions and reactor arrangement scheme. Therefore, the investigation on the highest selectivity with the change of concentration of A C_A is conducted.

2.2 Reactor arrangement scheme

The choice of any reactor scheme influences the strategy to maximise selectivity and conversions. The chosen chemical reactor series arrangement with the first reactor as the continuous stirred tank reactor (CSTR) and later followed by a plug flow reactor (PFR). According to Trambouze (1959), simple kinetics equation, is defined as the rate depending only on one chemical component for instance Trambouze reaction. It is applicable that in designing a CSTR reactor with a specific calculated volume which can allow specific volumetric flow rate of the inlet stream for the reactor to be operated with the highest selectivity of the desired product.

2.3 Simulation of multiple reactions

The CSTR and PFR apply the design equations based on the mole balances and are expressed as the following equations in Eq. (9), (9a), (10), (10a), and (11). V , F_{A_0} , F_A , X , C_{A_0} , C_A^* , C_A , τ , and v_0 are defined as volume, initial flow rate of A, flow of A, initial concentration of A, maximum concentration of A, concentration of A, space time, and volumetric flow rate, respectively. The derivative expression of any parameters for instance for the concentration of A (C_A) towards space time τ is expressed as $\frac{dC_A}{d\tau}$.

$$V_{CSTR} = \frac{F_{A_0} X}{(-r_A)_{exit}} \quad (9)$$

$$V_{CSTR} = \frac{v_0(C_{A_0}-C_A^*)}{k_1+k_2 C_A^*+k_3 C_A^{*2}} \text{ (regardless of X)} \quad (9a)$$

$$dV_{PFR} = \frac{dF_A}{r_A} \quad (10)$$

$$\frac{dC_A}{d\tau} = -r_A \text{ (regardless of X)} \quad (10a)$$

$$\tau = \frac{V}{v_o} \quad (11)$$

The ordinary differential equations (ODEs) for plug flow (PFR) reactor system which are expressed as by Eq. (12), (13), (14), and (15) can be simulated in Polymath 6.1, Educational version, (trial version) and Excel software using numerical analytical (Runge-Kutta) method. The results were then plotted in Origin Pro 8 software.

$$\frac{dC_A}{d\tau} = -r_A = k_1 + k_2 C_A + k_3 C_A^2 \quad (12)$$

$$\frac{dC_X}{d\tau} = k_1 \quad (13)$$

$$\frac{dC_B}{d\tau} = k_2 C_A \quad (14)$$

$$\frac{dC_A}{d\tau} = k_3 C_A^2 \quad (15)$$

The assumptions for the simulations are tabulated in Table 1. Range of the initial concentrations of A of the reactant (C_{A_o}) for Trambouze reactions were investigated at a constant variable of the volumetric flow rate v_o . It is assumed that the volumetric flow rate is constant throughout the reaction (same as the initial volumetric flow rate); $v = v_o$ in a constant density system. The change of volume with this effect is investigated accordingly.

3.0 Results and discussion

3.1 Selectivity in continuous stirred tank reactor (CSTR)

According to Eq. (7), the simulated selectivity is shown as in Fig. 1, which shows that as the initial concentration of reactant A, C_{A_o} decreases, the selectivity $S_{B/XY}$ increases to a certain maximum peak indicating a certain concentration of A, before it starts to decrease. The peak can be interpreted as the maximum value of the selectivity. Due to this, the first chemical reactor design is chosen to be CSTR, so as the multiple reactions can be operated at the highest selectivity value, achieving certain conversion X, using Eq. (8). The maximum value of $S_{B/XY}$ is calculated by differentiating Eq. (7) over C_A and equalize it to zero (peak), as shown by Eq. (16). The solved C_A is now the C_A^* ($C_{A,max}$), which is the maximum concentration of A, found to be at $0.112 \frac{mol}{dm^3}$. The selectivity value as

calculated from Eq. (7) is proposed to be at 0.84 in CSTR with a maximum conversion X of 0.72, as calculated by Eq. (8).

$$\frac{dS_{B/XY}}{dC_A} = 0 \quad (16)$$

CSTR is proposed since maximum selectivity and conversion (at maximum values) with certain volume V and space time τ , can be operated. PFR operates as such that the concentration changes down the length of PFR with increasing V and X. Comparing either CSTR-PFR or PFR-CSTR configuration arrangements, only with the former option, would allow the highest

Table 1: Basic simulation input data based on assumptions

Input Name	Symbol	Data	Unit
Specific rate constant Eq. (1) & (4)	k_1	0.0001	$\frac{mol}{dm^3 \cdot s}$
Specific rate constant Eq. (2) & (5)	k_2	0.0015	$\frac{1}{s}$
Specific rate constant Eq. (3) & (6)	k_3	0.008	$\frac{dm^3}{mol \cdot s}$
Initial concentration of A	C_{A_o}	0.2–0.8	$\frac{mol}{dm^3}$
Volumetric flow rate $v = v_o$	v_o	2	$\frac{dm^3}{s}$

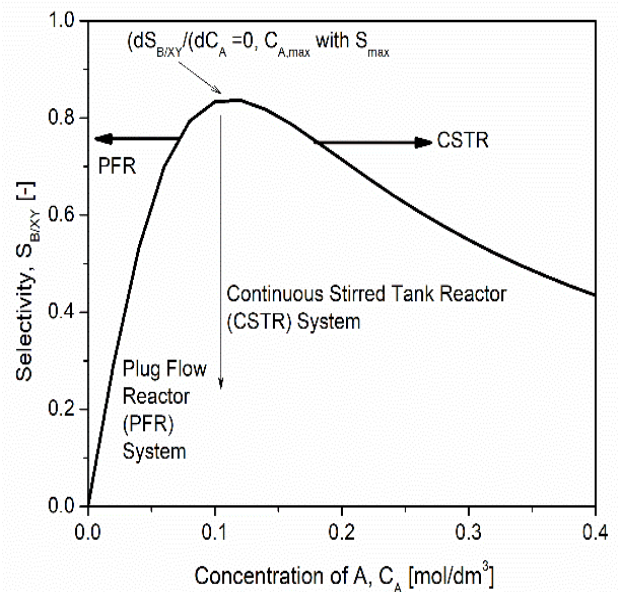


Fig. 1: Selectivity $S_{B/XY}$ versus concentration of A (C_A) at the temperature of 300 K, specific rate constants of k_1 , k_2 and k_3 of $0.0001 \frac{mol}{dm^3 \cdot s}$, $0.0015 \frac{1}{s}$ and $0.008 \frac{dm^3}{mol \cdot s}$, respectively

achievable selectivity and conversion to be targeted even from the beginning of the series operation.

3.2 Change of volume by volumetric flow rate

As the volumetric flow rate v_o entering the reactor system increases, from the range of $v_o = 1$ to $8 \frac{dm^3}{s}$ (with an increment of $1 \frac{dm^3}{s}$), the calculated volume for CSTR may also increase linearly, as shown as in Fig. 2, for a constant initial concentration of reactant A, $C_{A_o,CSTR}$ of $0.2 \frac{mol}{dm^3}$. It is also indicated that the selectivity and conversion are not influenced by the increasing volumetric flow rate, with a value of 0.84 and 0.44, respectively, for this case. This is shown as

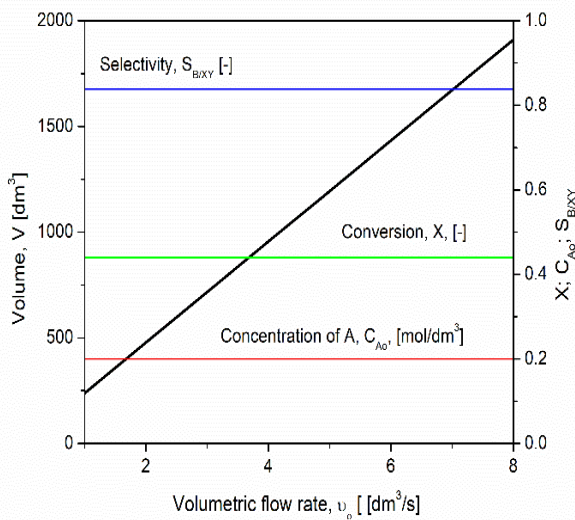


Fig. 2: Change of volume V by different volumetric flow rate v_o in a CSTR system of a series of CSTR-PFR reactor system, with v_o from 1 to $8 \frac{dm^3}{s}$ and with $C_A = C_{A_o,CSTR} = 0.2 \frac{mol}{dm^3}$.

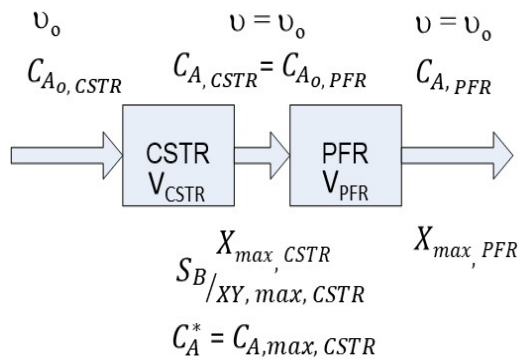


Fig. 3: Block diagram indicating the CSTR-PFR series configurations at the operation of having $S_{B/XY,max,CSTR}$, $C_A^* = C_{A,max,CSTR}$ and $X_{max,CSTR}$, as the outlet from CSTR (first reactor) entering PFR (second reactor) at $C_{A_o,PFR}$, in the target to maximise the product selectivity.

in Fig. 2, for a CSTR input values and the calculated volume based on Eq. (9), (9a), and (11). From here, it can be assumed that in a chemical reactor design, the volume of a reactor increases with the increase of volumetric flow rate entering the CSTR, but does not necessarily mean that the conversion and selectivity also would increase. Thus, it is crucial to choose the right parameters in order to operate CSTR at its highest value of selectivity of the desired product and conversion value.

3.3 Change of concentration of reactant and products in PFR for CSTR-PFR series reactor system

As shown earlier in Fig. 1., the CSTR as the first reactor in CSTR-PFR series of reactor configuration, being operated with a specific inlet concentration of A and to be achieving the maximum selectivity of having for instance $C_{A_o,CSTR} = 0.112 \frac{mol}{dm^3}$, a direct correlation can be made for conversion value. It is calculated that, as the initial concentration of A increases, the conversion increases, when the CSTR is operated at the maximum selectivity of 0.84 and at a constant volumetric flow rate of v_o . For instance, at $v_o = 2 \frac{dm^3}{s}$, with varying $C_{A_o} = 0.2$ to 0.8 (with an increment of $0.1 \frac{dm^3}{s}$), the conversion increases from 0.44 to 0.86, respectively (not plotted). This achievable conversion (outlet of CSTR) can later be improved with its introduction to a second reactor system which is PFR (as mentioned earlier). Refer to Fig. 3.

Fig. 4 shows that the simulated results of a PFR having the maximum selectivity and conversion values of inlet streams, originating from the outlet of the first reactor which is CSTR. If for instance, the operating parameters for PFR inlet is from having the volumetric flow rate of $v_{CSTR-PFR} = v_o = 2.0 \frac{dm^3}{s}$, and at the initial concentration of reactant A, $C_{A_o,in,CSTR}$ of $0.2 \frac{mol}{dm^3}$, now entering PFR, it is shown that the concentration of the reactant A, C_A decreases whilst other products increase for instance for products X, Y and B (Refer to Fig. 3 and 4).

It is also shown that along the length of PFR, the conversion X , increases with the increase of space time τ (s). This proves the claim that in PFR, the concentration of A C_A decreases with the increase of conversion. The selectivity in PFR decreases with the increases of conversion and volume are also observed (illustrated result is not shown). Thus, with the reactor arrangement of CSTR-PFR, the increasing conversion

from the earlier achieved conversion of 0.44, may now increase the conversion of remaining reactants to desired products in PFR. Thus, instead of using this operating parameters as instance to indicate this trend, the maximum achievable selectivity and conversion should therefore be targeted even from the first reactor scheme, in this case, the CSTR, then only continue to improve in the second reactor scheme which is PFR.

Fig. 5 illustrates sets of results from the simulation of the ODEs in PFR, illustrating the increasing trend of the concentrations of the desired product which is product B in Trambouze reaction, as shown as in Fig. 5B, C, D, and E, for an initial concentration of the reactant A, $C_{A_0,CSTR}$, ranging from 0.2 to 0.8 $\frac{mol}{dm^3}$, with an increment of 0.2 $\frac{mol}{dm^3}$, respectively. At the initial space time of τ (s) when $\tau = 0$ s, the C_{A_0} increases from 40.1, 131.4, 222.6 and 318.8 $\times 10^{-3} \frac{mol}{dm^3}$, respectively, at different ν_0 . Take note for instance that $C_{A_0} = 0.2 \frac{mol}{dm^3}$ is equivalent to $C_{A_0} \times 10^3 = 200 \frac{mol}{dm^3}$ (for reference in Table 2).

Fig. 5A shows the increasing values of conversion, X as the $C_{A_0,CSTR}$ increasing from 0.2 to 0.8 $\frac{mol}{dm^3}$, with an initial X, entering PFR at 0.44, 0.72, 0.81, and 0.86 $\frac{mol}{dm^3}$, respectively, from the outlet stream of CSTR (the first reactor). For instance, if the CSTR as in the first reactor is operated at $S_{B/XY}$ and X of 0.84 and 0.72, respectively, for $C_{A_0,CSTR} = 0.4 \frac{mol}{dm^3}$ and $\nu_0 = 2 \frac{dm^3}{s}$, the outlet stream which is fed to the PFR is now the inlet stream, will undergo higher conversion with the decreasing of the reactant A, thus, increasing the conversion of A to products, even though the $S_{B/XY}$ decreases. The instances of additional simulation data are as tabulated in Table 2 below.

Therefore, the best strategy is to first operate the multiple reactions in CSTR and later to PFR, targeting to increase the maximum selectivity and conversion, as the final outcome. Economically, with the best volume

calculated having the maximum selectivity and conversion, need to be well balanced with cost and production of the desired product in any chemical reactor design.

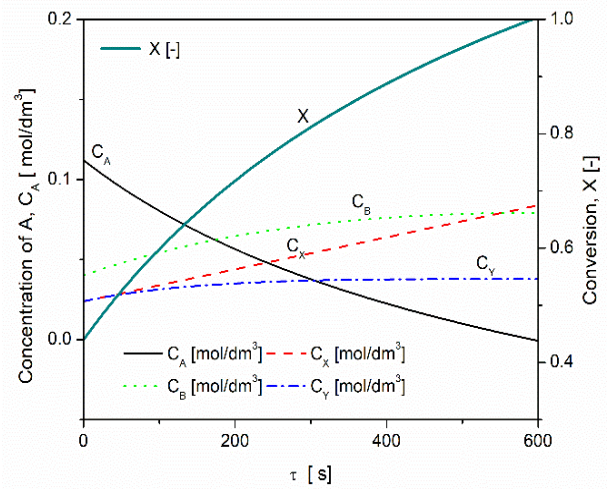


Fig. 4: Change of concentrations of reactant and products in Trambouze reaction in a plug flow reactor (PFR) system in a series of CSTR-PFR.

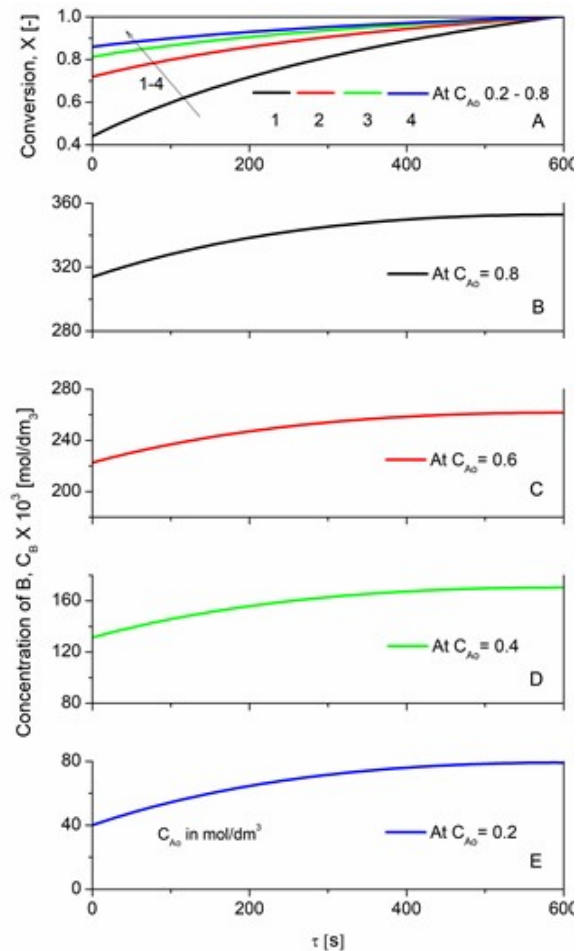


Fig. 5: The conversion and change of concentrations of reactant and products in Trambouze reaction in a plug flow the reactor (PFR) system in a series of CSTR-PFR at constant ν_0 . 5A indicates the X versus τ with varying $C_A = C_{A_0,CSTR}$. 5B-E indicate the change C_B at varying τ .

Table 2: Additional simulation input data for PFR ODEs

C_{A_0} $\times 10^3$ to CSTR	$C_{A, \text{exit}}$ $\times 10^3$ From CSTR to PFR	C_X $\times 10^3$ to PFR	C_B $\times 10^3$ to PFR	C_Y $\times 10^3$ to PFR	ν_0 $\frac{dm^3}{s}$
200	112	23.9	40.1	24.0	2.0
400	112	78.2	131.4	78.5	2.0
600	112	132.5	222.6	132.9	2.0
800	112	186.8	313.8	187.4	2.0

*Units for all C is $\frac{mol}{dm^3}$

4.0 Conclusions

In any chemical reactor design, selectivity and conversion are for instance the most crucial parameters to be considered in overall decisions of to whether to have only a single reactor system or with an additional reactor after the first reactor. In an isothermal, isobaric and constant volumetric flow rate conditions as discussed, the decision may also depend on the need of the product for the market, whether it is adequately fit for commercial supply or is it more worthwhile to

increase the investment a little more on chemical reactor design but giving significant profit as in overall.

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