

MODELLING OF A THREE-PHASE MEMBRANE REACTOR FOR THE PARTIAL OXIDATION OF PROPANE

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ABSTRACT

A mathematical model describing the performance of a three phase catalytic membrane reactor for the partial oxidation of propane has been developed. The theoretical study pointed out that the recovery of products in the gas phase is strongly related to the membrane hydrophobicity.

INTRODUCTION

The catalytic partial oxidation of light alkanes is an interesting way for producing value-added products from natural gas. In order to carry out the reactions under mild conditions, several studies have been attempted, mainly related to the development of catalytic systems suitable for the process. Among them, the liquid phase oxidation in superacid media resulted to be selective for the desired products¹⁻⁵. This system present, as main drawbacks, the separation of the catalyst from the reaction media and the recovery of products. To overcome these limits, a three phase catalytic membrane reactor has been developed with the active species immobilised on the surface of a membrane that separates the liquid media and the gaseous stream. Once formed, the reaction products permeate the membrane and are recovered in the gas phase by condensation⁵. The aim of this work is to model the three phase membrane reactor in order to describe the behaviour of the system and to provide some useful information on the characteristics that the membrane has to offer for efficiently carrying out the process. The partial oxidation of propane is considered as “model reaction”.

EXPERIMENTAL SECTION

The three phase catalytic membrane reactor is depicted in figure 1. It consists of a flat membrane interposed between two teflon plates. The catalytic side of the membrane is in direct contact with the liquid phase while the gaseous phase is fed at the other side and reaches the catalytic sites by permeating through the membrane pores.

The experimental apparatus is shown in figure 2. Both liquid and gaseous streams are recirculated by means of pumps and the products present in the gaseous phase are recovered by condensation downstream the reactor. More details about the system are furnished elsewhere.⁵ The membrane used for the reaction tests is a disk of PEEK-WC (diameter, 5 cm). It presents an asymmetric structure with a dense layer of 5 μm .⁶ The catalyst (Nafion) has been loaded in the membrane by ultrafiltration.⁶

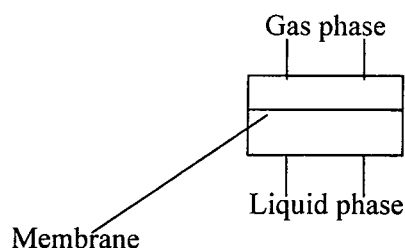


Figure 1. The three phase catalytic membrane reactor

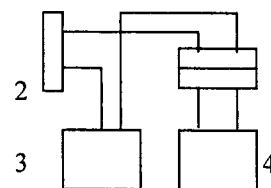


Figure 2. Simplified flow sheet of the experimental apparatus.
(1) membrane reactor; (2) condenser;
(3) gas tank(4) liquid tank

The experiments have been carried out by feeding H_2O_2 (liquid phase) and C_3H_8 at 80°C and 150 kPa absolute pressure. The reaction products are isopropanol and n-propanol; acetone and propionic aldehyde are also found as result of the further oxidation of isopropanol and n-propanol, respectively. The output of the system is obtained in terms of cumulative amount of oxygenated products in the two phases. ⁷

THEORETICAL SECTION

The experimental system above described has been modelled by writing mass balances for the reactants and products. The balances for the membrane reactor are:

Liquid phase

$$Q_l \cdot C_{\text{H}_2\text{O}_2\text{in}} - Q_l \cdot C_{\text{H}_2\text{O}_2\text{out}} - r = 0 \quad (1)$$

$$Q_l \cdot C_{p\text{in}} - Q_l \cdot C_{p\text{out}} + \text{Flu}_{\text{liq}} \cdot A_m = 0 \quad (2)$$

with:

Q_l , liquid flow rate, m^3/s

$C_{\text{H}_2\text{O}_2\text{in}}/ C_{\text{H}_2\text{O}_2\text{out}}$, inlet and outlet H_2O_2 concentration, mmol/m^3

r , reaction rate, mmol/s

$C_{p\text{in}}/ C_{p\text{out}}$, inlet and outlet products concentration/liquid phase, mmol/m^3

Flu_{liq} , flux of products towards the liquid phase, $\text{mmol}/(\text{s} \cdot \text{m}^2)$

A_m , membrane area, m^2

Gas phase

$$Q_g \cdot C_{\text{C}_3\text{H}_8\text{in}} - Q_g \cdot C_{\text{C}_3\text{H}_8\text{out}} - r = 0 \quad (3)$$

$$- Q_g \cdot C_{p\text{gout}} + \text{Flu}_{\text{gas}} \cdot A_m = 0 \quad (4)$$

with:

Q_g , gas flow rate, m^3/s

$C_{C_3H_8in}/C_{C_3H_8out}$, inlet and outlet C_3H_8 concentration, $mmol/m^3$

C_{pgout} , outlet products concentration/gas phase, $mmol/m^3$

Flu_{gas} , flux of products towards the gas phase, $mmol/(s \cdot m^2)$

In the gas phase there is no feed of products to the membrane reactor because they are recovered in the condenser downstream the reactor.

The membrane is not selective for products⁸, then a simple diffusion of species through pores has been considered. Fluxes have been calculated by the following expressions:

$$Flu_{gas} = kt \cdot C_{pint} \quad (5)$$

$$Flu_{liq} = kl \cdot (C_{plint} - C_{pjin}) \quad (6)$$

with:

kt , total mass transfer coefficient, m/s

kl , liquid mass transfer coefficient, m/s

C_{pint} , concentration of products at the interface, $mmol/m^3$

C_{plint} , concentration of products left at the interface after the permeation towards the gas phase, $mmol/m^3$

The mass transfer coefficients have been calculated by:

$$kt = 1/Res \quad (7)$$

$$Res = 1/km + 1/km_{wetted} + 1/kg \quad (8)$$

$$km = D_{pC_3H_8}/\delta_{dry} \quad (9)$$

$$km_{wetted} = D_{pH_2O_2}/\delta_{wetted} \quad (10)$$

with:

kg , gas mass transfer coefficient, m/s

km , membrane mass transfer coefficient for dry pores, m/s

km_{wetted} , membrane mass transfer coefficient for wetted pores, m/s

$D_{pC_3H_8}$, diffusion coefficient of products in the gas stream, m^2/s

$D_{pH_2O_2}$, diffusion coefficient of products in the liquid stream, m^2/s

δ_{dry} , thickness of the dry membrane pores, m

δ_{wetted} , thickness of the wetted membrane pores, m

The liquid and gas mass transfer coefficients have been calculated by using an expression proposed by Bird et al.⁹ for tangential flow along flat sheets:

$$k_g = v_{\text{gas}} / (\mu_{\text{C}_3\text{H}_8} / (\rho_{\text{C}_3\text{H}_8} \cdot D_{\text{pC}_3\text{H}_8}))^{0.67} \cdot 0.333 / (v_{\text{gas}} \cdot \rho_{\text{C}_3\text{H}_8} \cdot \phi / \mu_{\text{C}_3\text{H}_8})^{0.50} \quad (11)$$

$$k_l = v_{\text{liq}} / (\mu_{\text{H}_2\text{O}_2} / (\rho_{\text{H}_2\text{O}_2} \cdot D_{\text{pH}_2\text{O}_2}))^{0.67} \cdot 0.333 / (v_{\text{liq}} \cdot \rho_{\text{H}_2\text{O}_2} \cdot \phi / \mu_{\text{H}_2\text{O}_2})^{0.50} \quad (12)$$

with:

v_{gas} , gas velocity, m/s
 $\mu_{\text{C}_3\text{H}_8}$, gas viscosity, $\text{g} \cdot \text{m}^{-1} \text{s}^{-1}$
 $\rho_{\text{C}_3\text{H}_8}$, gas density, $\text{g} \cdot \text{m}^{-3}$
 ϕ , membrane disk diameter, m
 v_{liq} , liquid velocity, m/s
 $\mu_{\text{H}_2\text{O}_2}$, liquid viscosity, $\text{g} \cdot \text{m}^{-1} \text{s}^{-1}$
 $\rho_{\text{H}_2\text{O}_2}$, liquid density, $\text{g} \cdot \text{m}^{-3}$

The reaction rate is:¹⁰

$$r = k \cdot P_{\text{C}_3\text{H}_8}^{0.96} \cdot C_{\text{H}_2\text{O}_2}^{1.02} \quad (13)$$

with:

$P_{\text{C}_3\text{H}_8}$, C_3H_8 pressure, atm
 $C_{\text{H}_2\text{O}_2}$, H_2O_2 concentration, mol/l

The concentrations entering the membrane module were considered equal to the concentrations in the tanks (hypothesis of perfect mix). The equations set has been solved as function of time by repeating the calculations until the time of the experimental runs was reached.

RESULTS AND DISCUSSION

The mathematical model has been solved on the basis of the experimental operating conditions. A comparison between the experimental and theoretical results, achieved by considering completely dry membrane pores, is reported in figure 3. As it can be seen, from the calculations made products are completely located in the gas phase, due to the lower mass transfer resistance offered by the membrane and the gas phase with respect to the liquid phase. This result is in contrast with the experimental one that presents a distribution of products in the two phases. A possible explanation of the discrepancy can be the presence of liquid in the membrane pores which increases the mass resistance of the membrane and, then, reduces the flux of products to the gaseous phase.

Figure 4 shows the comparison between the experimental and theoretical results when taking into account a higher mass transfer resistance for the membrane. The theoretical data fit now quite well the experimental points, indicating that the membrane hydrophobicity is the key factor for recovering all products in the gas phase. This result has been confirmed also by

analysing the influence of the operating conditions on the performance of the process.

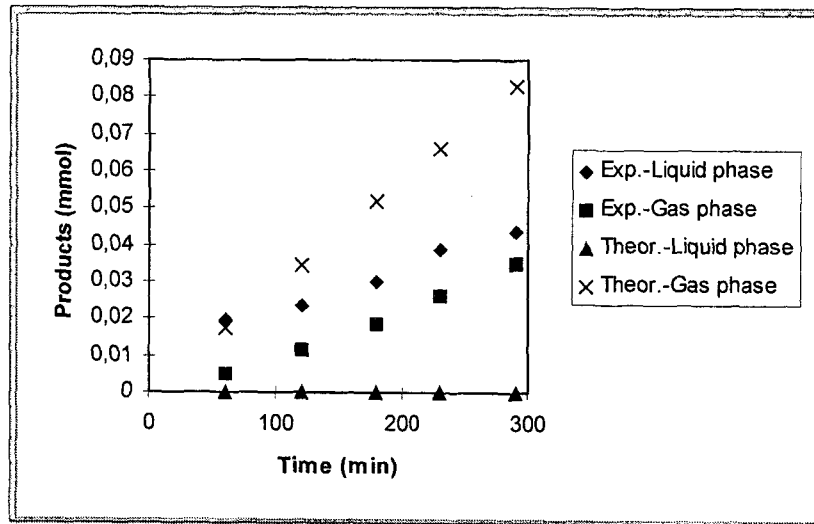


Figure 3. Comparison between experimental and theoretical results. *Completely dry membrane pores; $kl, 2.24 \cdot 10^{-6} \text{ m/s}$; $kt, 1.75 \cdot 10^{-3} \text{ m/s}$.*

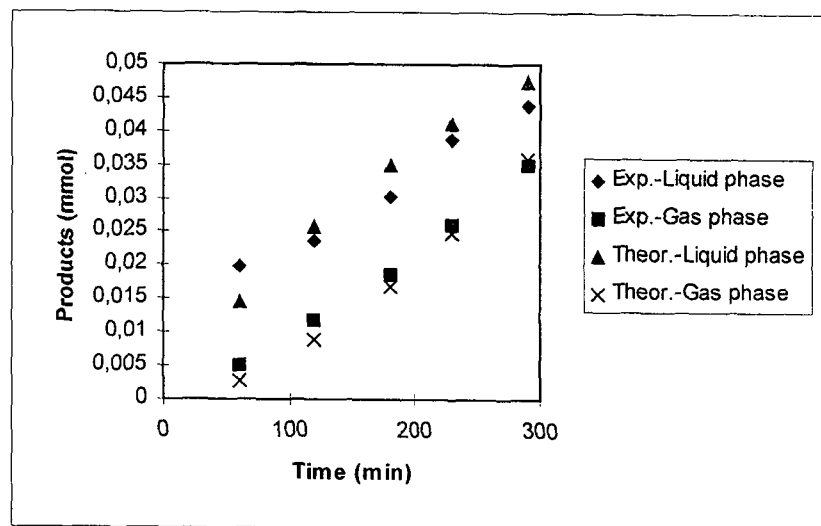


Figure 4. Comparison between experimental and theoretical results. *$kl, 2.24 \cdot 10^{-6} \text{ m/s}$; $kt, 4.4 \cdot 10^{-7} \text{ m/s}$.*

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