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## Membrane process modelling for higher alcohol synthesis

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### Abstract

Mixed alcohol fuels are mixtures of methanol, ethanol, propanol, butanol and higher alcohols. A mixed alcohol fuel has advantages over pure methanol or ethanol fuels. The higher alcohols have higher energy content and also increase compatibility of gasoline and ethanol in a blend, which increases water tolerance and decreases emissions by evaporation. Higher alcohols have also lower heat of vaporization than ethanol, which is important for cold starts. Mixed alcohols can be produced from synthesis gas in a very similar process to the methanol synthesis process, albeit with a slightly different catalyst. However, a problem is that the catalysts still mostly produce methanol and ethanol (i.e. lower alcohols) and not the more wanted higher alcohols (propanol, butanol and higher). This process can be improved significantly by applying a membrane reactor system rather than a conventional reactor for synthesis of mixed alcohols. The purpose of this work was to evaluate and compare a process for higher alcohol synthesis (HAS) using a membrane module against an existing process. Membrane module works better than the typical process with high values of CO conversion and a better production of high alcohols (55% more than the typical process). The pressure of the system is very important for the good working of the membrane module (over 60 bar in a fixed temperature of 598 K).

**Keywords:** High alcohol, membrane process, CO conversion

### 1. Introduction

It has been known for many decades that mixtures of methanol and higher alcohols (i.e. long chain alcohols) could be used directly as fuel, as fuel additives for octane or cetane enhancement, or as oxygenate fuel additives for environmental reasons [1,2]. The term “mixed alcohols” refers to a mixture of C1 – C8 alcohols, with preference towards the higher alcohols (C2-C6), whereas mixed alcohols are a more attractive gasoline blending stock for octane enhancement compared to methanol; compared to methanol mixed alcohols have a lower vapor pressure, better solubility with hydrocarbon components, improved water tolerance, and higher overall heating value [3].

Mixed alcohols can be produced from synthesis gas in a very similar process to the methanol synthesis process, albeit with a slightly different catalyst. However, a problem is that the catalysts still mostly produce methanol and ethanol (i.e. lower alcohols) and not the more wanted higher alcohols (propanol, butanol and higher). This process could be improved significantly by applying a membrane reactor system rather than a conventional reactor for synthesis of mixed alcohols.

In the present work a novel process was evaluated and compared with a traditional process for higher alcohol synthesis (HAS) using membrane module. A membrane module act like a heat exchanger, although instead of exchanging heat it exchanges chemical species selectively. If a membrane that selectively separates higher alcohols is integrated in the process, the yield of higher alcohols should increase significantly, improving the whole process and being more attractive to implement the membrane instead of the typical process to produce high alcohols.

Catalysts used for the production of higher alcohols from synthesis gas (mixtures of CO and H<sub>2</sub>) can be divided into four categories [4, 5]. The first one is based on a soluble Ru complex used as a homogeneous catalyst. The second one can be described as modified methanol

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catalysts (e.g. alkali-doped ZnO/chromia or Cu-based catalysts). The third category of catalysts comprises mixed-metal Fischer-Tropsch (FT) catalysts (e.g. Co and Fe on a support). Finally, the last category includes alkali-promoted MoS<sub>2</sub> catalysts. HAS catalysts are essentially bifunctional base-hydrogenation catalysts and are typically categorized into several groups based on their composition. Common to all HAS catalysts is the addition of alkali metals to the formulation. The activating character of alkali metal promoters is a function of their basicity. Alkali metals provide a basic site to catalyze the aldol condensation reaction by activating surface adsorbed CO and enhancing the formation of the intermediate. [3]  
 One of the major hurdles to overcome before HAS

becomes an economic commercial process is improved catalysts that increase the productivity and selectivity to higher alcohols.  
 Currently there are no commercial plants that produce mixed alcohols in the C<sub>2</sub> to C<sub>6</sub> range. From a commercial viewpoint, the selectivity of HAS catalysts has not advanced to the point of commercial feasibility. However, the main process steps include synthesis gas production followed by gas clean up and conditioning, alcohol synthesis, and product purification [6]  
 Based on the mechanistic studies, kinetic models (Figures 1 and 2) have been developed to describe the alcohol production [6]. The Figures 1 and 2 represent the reaction over two different catalysts and all the reactions occurred.

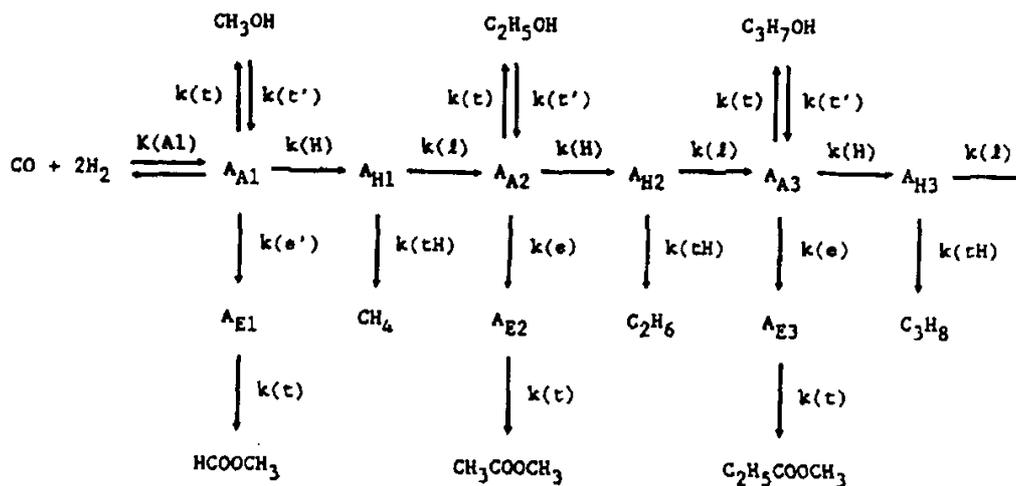


Fig. 1: The kinetic reaction network for the synthesis of alcohols, esters, and hydrocarbons over the alkali/MoS<sub>2</sub> catalyst.

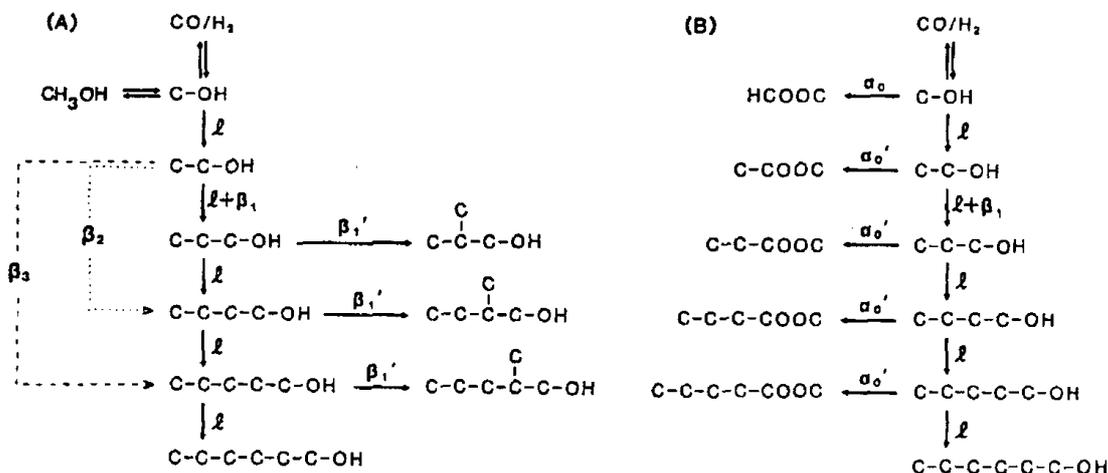


Fig. 2: The kinetic reaction network for the synthesis of oxygenates over the Cs/Cu/ZnO catalyst

Zeolites are crystalline aluminosilicates with a three-dimensional structure and open channels within the network. They have four major areas of application: catalysis, ion exchange, gas separation and adsorption. The zeolites most important properties as catalysts are the high activity and selectivity. The selectivity is a result of the microporous framework, which either prevents larger reactants to enter the porous structure or prevents larger products to either form or to leave the pores [7].  
 Membrane process is characterized by the use of a membrane to achieve a specific separation. A membrane is a permeable material that acts as a selective barrier between

two phases. The separation over a zeolite membrane can occur in different ways (Figure 3). Molecular sieving is when larger molecules are inhibited to permeate over the zeolite membrane due to their size, while smaller can diffuse through the zeolite pores. Adsorption is when high concentration of strongly adsorbing molecules inhibiting other molecules from permeating, while the adsorbed molecules diffuse through. The third way is when molecules with the high diffusivity are separated from molecules with lower diffusivity [7].

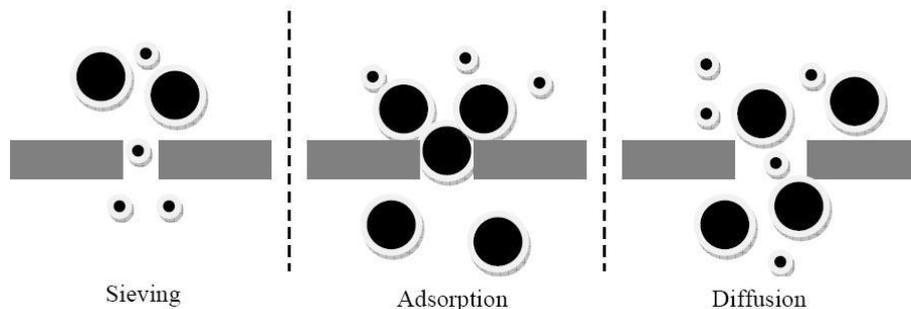


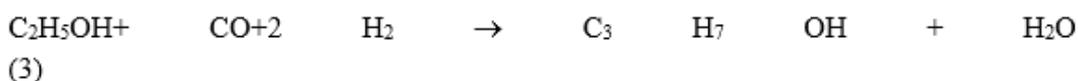
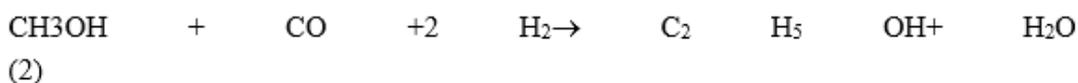
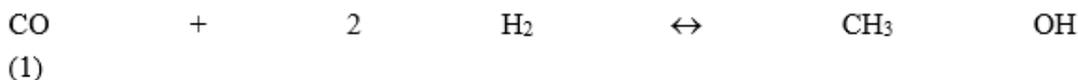
Fig. 3: Types of separation in a zeolite membrane

2. Materials And Methods

The mathematical model for simulating the processes considered in the present work is based on an existing model developed for methanol synthesis [7]. The model uses the following assumptions: one dimensional plug flow in the reactors and membrane modules, ideal gas, no radial diffusion resistance in the catalyst pellets, no axial dispersion of heat along the reactors. In the overall systems, the energy balances were neglected.

In a paper published by Gunturu et al. (1998) [8] a C-supported, K-promoted Co-Mo sulfide catalyst (Mo-Co-K/C) was used to study the kinetics of the synthesis of methanol and higher alcohols from syngas. The content of Mo in the catalyst was 18 wt. %, the molar ratio of K/Mo was equal to 1.3 and the ratio of Co/Mo was 0.34. The catalyst was tested in a gradientless Berty reactor, which was used as an internal recycle reactor. The kinetic runs were performed in the temperature range of 573-623 K, at the total pressure of 40-80 atm with a H<sub>2</sub>/CO feed ratio 2.

The adopted simplified reaction scheme for the synthesis of higher alcohols is shown below:



In this lumped reaction scheme, the production of methanol from CO and H<sub>2</sub>, reaction (1), is regarded as reversible, and limited by chemical equilibrium. The formation of ethanol, reaction (2), and the formation of propanol, reaction (3), proceeds by reaction of CO/H<sub>2</sub> with methanol and with ethanol, respectively, according to a consecutive scheme. Alcohols of carbon number higher than three (C<sub>4</sub>+ alcohols) are formed in quantities small enough to be

neglected for present purposes (C<sub>4</sub>+ carbon selectivity < 4% [9]). In addition, all the formed ethers (dimethyl ether, diethyl ether) and other oxygenates not explicitly identified as alcohols were lumped into the methane (hydrocarbon) fraction. The equation for the calculation of the gross rate of formation of methanol was published in Guruntu et al. (1998) [8] and modified by Larson et al. [9]:

$$r_{CH_3OH}^{gross} = \frac{A_m e^{-(E_m/R)(1/T-1/T_{cp})} \left( \left[ \frac{P_{CO}}{P_{CO}^{cp}} \right] \left[ \frac{P_{H_2}}{P_{H_2}^{cp}} \right]^2 - \frac{1}{K_{eq}} \left[ \frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right] \right)}{\left( 1 + K_1 \left[ \frac{P_{CO}}{P_{CO}^{cp}} \right] + K_2 \left[ \frac{P_{H_2}}{P_{H_2}^{cp}} \right] + K_3 \left[ \frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right] \right)^{nm}} \quad (5)$$

$$K_{eq} = \frac{K_a}{K_z K^{CP}} \quad (6)$$

$$K^{CP} = \frac{P_{CH_3OH}^{CP}}{P_{CO}^{CP} (P_{H_2}^{CP})^2} \quad (7)$$

Where  $r_i$  gross is the rate of formation of species  $i$  in kmol/h/kgcat and  $p$  are the partial pressures of the reactants measured in atm.  $T_{cp}$  is the temperature and  $p_{cp}$  is the partial pressure of the center-point experiment ( $T_{cp}=598$  K,  $p_{cp}=47.6$  atm),  $E_m$  is activation energy for methanol formation,  $R$  is the ideal gas constant, the parameters  $K_1$ ,  $K_2$  and  $K_3$  are adsorption coefficients,  $K_{eq}$  is nondimensional equilibrium constant and  $K_a$  is equilibrium constant in  $kPa^{-2}$ .  $K^{CP}$  is the nondimensionalizing term represented by the ratio of the partial pressures at the central point (equation 6). The expressions used for the calculation of ethanol, propanol and methane gross rates of formation were used exactly as reported in [8]:

$$r_{C_2H_5OH}^{gross} = \frac{A_e e^{-(E_e/R)(1/T-1/T_{cp})} \left[ \frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right]}{(1 + K_e \left[ \frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right])^{ne}} \quad (8)$$

$$r_{C_3H_7OH}^{gross} = \frac{A_p e^{-(E_p/R)(1/T-1/T_{cp})} \left[ \frac{P_{C_2H_5OH}}{P_{C_2H_5OH}^{cp}} \right]}{(1 + K_p \left[ \frac{P_{C_2H_5OH}}{P_{C_2H_5OH}^{cp}} \right])^{np}} \quad (9)$$

**Table 1.** Parameters published in [8] for Methanol, Ethanol, Propanol Synthesis Model<sup>a</sup>

Am=4.90 47	Em=117. 733	K1=0.06 96	K2=0.64 00	K3=0.69 40	nm= 2
Kz = 0.3359	Ka=8.686 x 10 <sup>-5</sup>				
Ae=1.52 59	Ee=24.98 6	Ke=0.73 67	ne=1		
Ap=0.11 01	Ep=89.94 3	Kp=0.25 02	np=1		

<sup>a</sup>Am, Ae, Ap, Ah [mol/h/kgcat], Em, Ee, Ep, Eh [kJ/mol], all other parameters are dimensionless.

The simulation program used subroutines to integrate numerically a system of ordinary differential equations (reactor model for PFR case):

$$\left\{ \begin{aligned} \frac{dF_{CO}}{dz} &= (-2.r_{CH_3OH}^{gross} - 2.r_{C_2H_5OH}^{gross} - 2.r_{C_3H_7OH}^{gross}) a_m \rho_B (1 - \phi) \end{aligned} \right. \quad (10)$$

$$\left\{ \begin{aligned} \frac{dF_{H_2}}{dz} &= (-r_{CH_3OH}^{gross} - r_{C_2H_5OH}^{gross} - r_{C_3H_7OH}^{gross}) a_m \rho_B (1 - \phi) \end{aligned} \right. \quad (11)$$

$$\left\{ \begin{aligned} \frac{dF_{H_2O}}{dz} &= (r_{C_2H_5OH}^{gross} + r_{C_3H_7OH}^{gross}) a_m \rho_B (1 - \phi) \end{aligned} \right. \quad (12)$$

$$\left\{ \begin{aligned} \frac{dF_{CH_3OH}}{dz} &= (r_{CH_3OH}^{gross} - r_{C_2H_5OH}^{gross}) a_m \rho_B (1 - \phi) \end{aligned} \right. \quad (13)$$

$$\left\{ \begin{aligned} \frac{dF_{C_2H_5OH}}{dz} &= (r_{C_2H_5OH}^{gross} - r_{C_3H_7OH}^{gross}) a_m \rho_B (1 - \phi) \end{aligned} \right. \quad (14)$$

$$\left\{ \begin{aligned} \frac{dF_{C_3H_7OH}}{dz} &= (r_{C_3H_7OH}^{gross}) a_m \rho_B (1 - \phi) \end{aligned} \right. \quad (15)$$

$$\left\{ \begin{aligned} \frac{dF_{N_2}}{dz} &= 0 \end{aligned} \right.$$

With the initial conditions:

$$\left\{ \begin{aligned} F_{CO}(z=0) &= F_{CO}^{IN} \end{aligned} \right. \quad (16)$$

$$\left\{ \begin{aligned} F_{H_2}(z=0) &= F_{H_2}^{IN} \end{aligned} \right. \quad (17)$$

$$\left\{ \begin{aligned} F_{H_2O}(z=0) &= F_{H_2O}^{IN} \end{aligned} \right. \quad (18)$$

$$\left\{ \begin{aligned} F_{CH_3OH}(z=0) &= F_{CH_3OH}^{IN} \end{aligned} \right. \quad (19)$$

$$\left\{ \begin{aligned} F_{C_2H_5OH}(z=0) &= F_{C_2H_5OH}^{IN} \end{aligned} \right. \quad (20)$$

$$\left\{ \begin{aligned} F_{C_3H_7OH}(z=0) &= F_{C_3H_7OH}^{IN} \end{aligned} \right. \quad (21)$$

$$\left\{ \begin{aligned} F_{N_2}(z=0) &= F_{N_2}^{IN} \end{aligned} \right. \quad (22)$$

$$\left\{ \begin{aligned} F_{N_2}(z=0) &= F_{N_2}^{IN} \end{aligned} \right. \quad (23)$$

Where  $F_i^{IN}$  is the feed flow of the  $i$ -species [kmol/h] and  $z$  is the length of the reactor [m]. To solve all the ordinary differential equations above an implicit Runge-Kutta was used. Permeation rates depend on the partial pressures and the composition of the feed to reactor depends on the recycled flow. An iterative method was used to determine these variables and MATLAB R2008b (MathWorks, Inc) was used for numerical solution.

The traditional reactor process (TRP), represented here by the Octamix process [5], see Figure 4a, consists of a water-cooled tubular reactor in which the feed-effluent heat exchanger preheats the recycled synthesis gas to the reactor inlet. Alcohols are condensed from the reactor effluent while unreacted synthesis gas is recycled using a compressor. The traditional reactor consists of steel tubes, which are filled with catalyst pellets. The tubes are cooled with boiling water generating medium pressure steam.

The membrane module process (MMP) evaluated in the

present work, see Figure 4b, consist of four 4 meter long water-cooled tubular reactors placed in series with membrane modules after each reactor. In each reactor, the cooling water temperature is set independently. The membrane modules consist of several membrane tubes that separate methanol and water from the synthesis gas at reaction temperature. High alcohols are condensed from the membrane permeate streams and the retentive from the last membrane module is purged. Synthesis gas from the condenser is used as sweep gas in the membrane modules. The membrane module consists of a steel housing that contains zeolite membrane tubes. The sweep gas is fed co-currently in the module while the synthesis gas from the reactor is fed to the centre of each membrane tube. The module tubes consist of 6 equally large sections in which the sweep gas is fresh for each section, while the retentive from each section is sent to the next section. The permeate from each module is sent to the condenser.

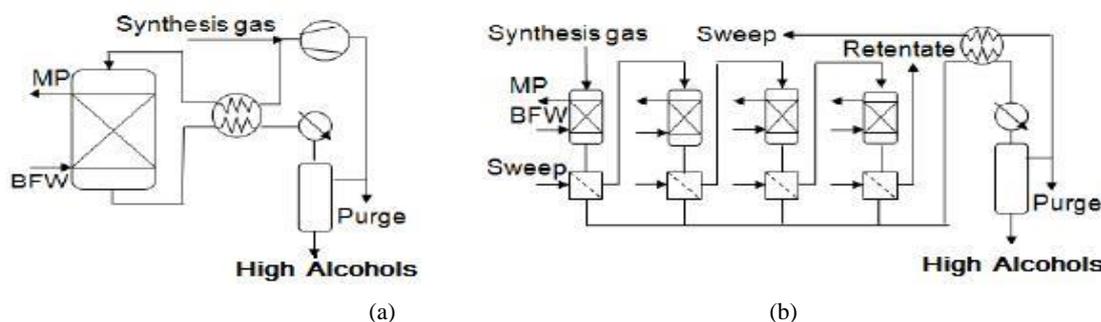


Fig. 4: Traditional reactor process (a), and membrane module process (b) for higher alcohol synthesis

All the specifications about the typical process and the membrane module process are listed in the table 2:

Table 2. Catalyst, feed, reactor and membrane specifications.

Parameter	Value	Parameter	Value
<b>Catalyst</b>		<b>Reactor</b>	
Catalyst density	1775 kg/m <sup>3</sup>	Tot. reactor length	16 m
Catalyst pellet diameter	0.0042 m	Reactor tube I.D.	0.0254 m
Porosity of bed	0.4	<b>Membrane</b>	
<b>Feed</b>		Membrane module length	4 m
H <sub>2</sub> /CO ratio in feed	2	<b>Sweep gas &amp; Cooling</b>	
Concentration of inert in feed	2 %	Sweep gas per MMP tube	0.000833 mol/s
Inlet temperature of feed	598 K	Sweep gas pressure	70 bar
Inlet pressure of feed	80 bar	C.W. temp. TRP	598 K
Fresh feed to each TRP tube	0.02 mol/s	C.W. temp. MMP	598 K
Feed to each MMP tube	0.03 mol/s		

### 3. Results and Discussion

In the Figure 5, we see the CO conversion versus reactor length. We note that in MMP, in Figure 5, the CO conversion is more efficient than the typical process.

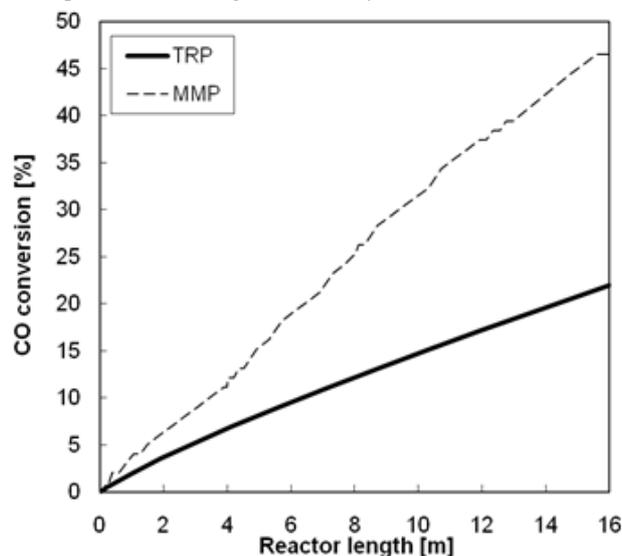


Fig. 5: CO conversion for TR and MM process

In the figures 6 and 7 are showed the graphics of alcohols concentration, ROH (methanol, ethanol and propanol) versus reactor length in, respectively, the MMP process and TRP process. In the figure 6, we see that methanol concentration increase until eight meters of the reactor, after the concentration is decreasing. So, it follows that the methanol reaction (Equation 1) is limited by chemical equilibrium. The concentration of methanol and propanol is always increasing along the reactor.

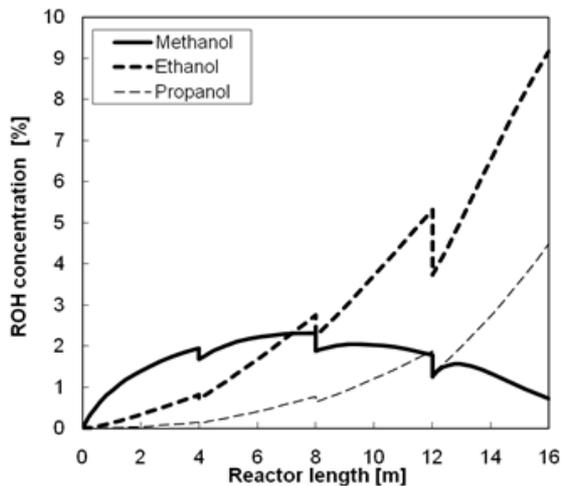


Fig. 6: ROH concentration in the MM process

In Figure 7 we note that methanol concentration is going to a steady state, instead of the concentration of ethanol and propanol that is growing. MMP is more interesting process because ethanol and propanol concentration is getting higher than the TR process.

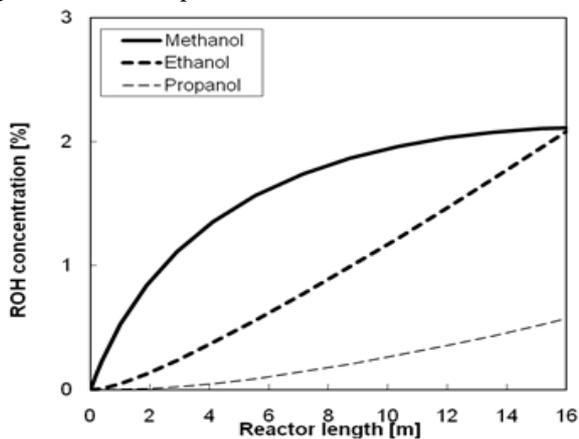


Fig. 7: ROH concentration in the TR process

Figures 8, 9 10 show the comparative between both process for each alcohol. The Fig. 8 shows the profile of concentration of methanol along the reactor, and we can note that methanol reaction is equilibrium limited, because, in TRP is getting steady state and in MMP is decreasing.

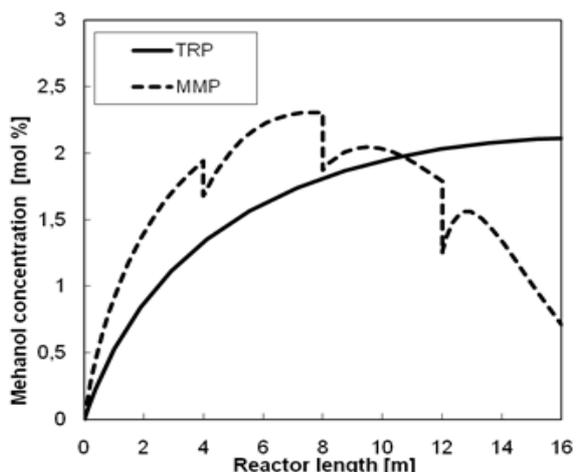


Fig. 8: Methanol concentration as a function of reactor length

The Fig. 9 shows the profile of concentration of ethanol along the reactor; ethanol formation is not the reaction limited, because the profile of concentration is always increasing. Similar to the Fig. 10.

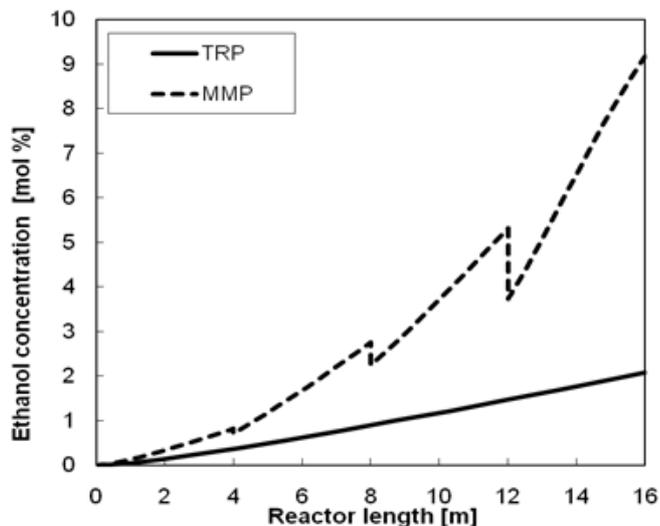


Fig. 9: Ethanol concentration as a function of reactor length

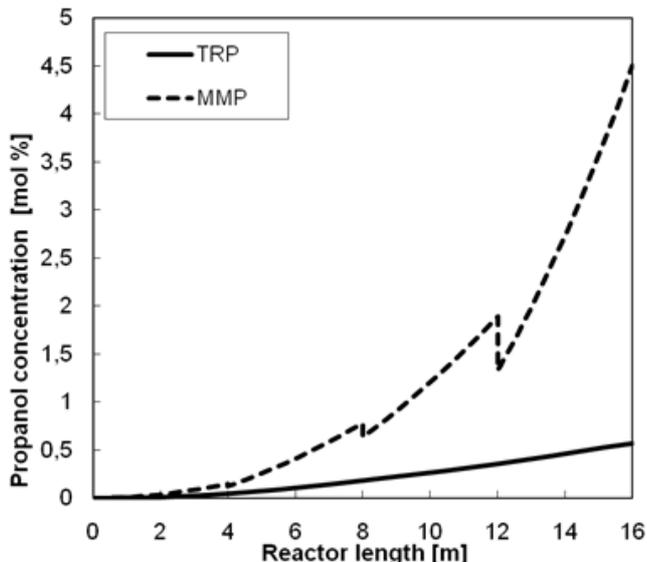


Fig. 10: Propanol concentration as a function of reactor length

The following graphics show the dependence of temperature (Figure 11) and pressure (Figure 12) over the CO conversion in both processes. We can note the high influence of the temperature in CO conversion in both processes; MMP is always the process that can convert more CO than TRP decreasing the temperature (over same pressure 80 bar, Table 2).

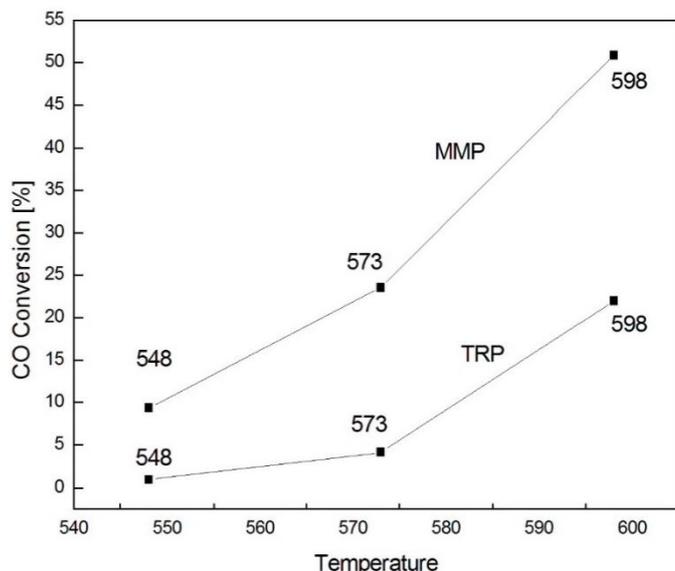


Fig. 11: Conversion of CO over different temperatures and different processes

About the pressure, we can note that MMP is more sensitive to variance the pressure, because over a 60 bar of pressure, the conversion of MMP is less than TRP (over same temperature 598K, Table 2). So, the pressure is an important factor in Membrane Module Process.

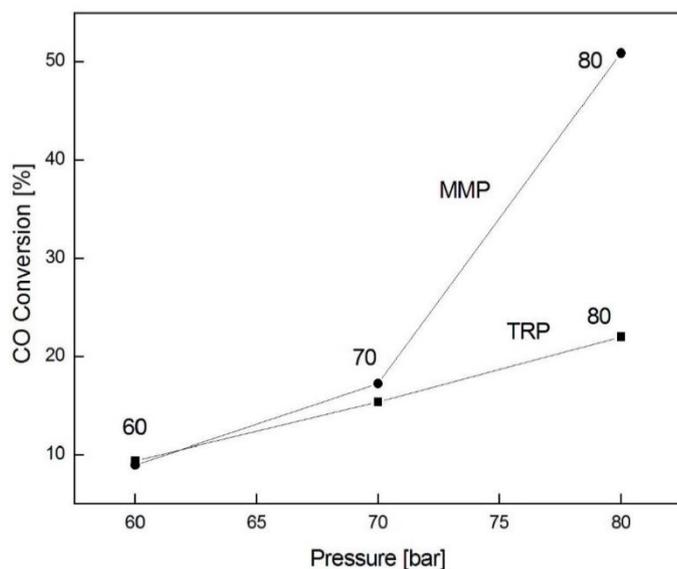


Fig. 12: Conversion of CO over different temperatures and different processes

In the follow table, there's the ROH produced per kg catalyst for each process and each alcohol. The amount of catalyst is 8.6343 kg.

Table 3: ROH produced per kg of catalyst for each processes

TRP [kg/h/kg cat]	MMP [kg/h/kg cat]
Methanol: 0.33 kg MeOH/h/kg cat	Methanol: 0.29 kg MeOH/h/kg cat
Ethanol: 0.48 kg EtOH/h/kg cat	Ethanol: 0.72 kg EtOH/h/kg cat
Propanol: 0.17 kg PrOH/h/kg cat	Propanol: 0.51 kg PrOH/h/kg cat
Total ROH: 0.98 kg ROH/h/kgcat	Total ROH: 1.52 kg ROH/h/kgcat
Onepass conversion: 21 %	
Overall conversion (%)	

So, with the values of Table 3, we got that Membrane Module reactor is the best process, because it can produce 55% more high alcohols than the typical process.

4. Conclusions

The process of synthesis of high alcohols can be improved significantly by applying a membrane reactor system rather than a conventional reactor for synthesis of mixed alcohols. With membrane module process, we got good values instead of a typical process of production of high alcohols: more conversion of CO, high values for the ROH concentration and the best production per kg of catalyst. MMP works better in high pressure (more than 60 bar, over a fixed temperature of 598 K) and Membrane module works better than the typical process with high values of CO conversion and a better production of high alcohols (55% more than the typical process).

5. Acknowledgment

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