

# Commande d'un procédé de déshydrogénisation de propane par catalyse

Weijun Zhou

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**Commande d'un procédé de déshydrogénisation de propane par catalyse**

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## 2 Introduction

This work is part of a new project between the SNLEP team at the LAGEP (UMR CNRS 5007 UCBL1) and SKLOCHE (State Key Laboratory of Chemical Engineering) from ECUST (East China University of Science and Technology), Shanghai, China. As a result, the report is in English because of the convenience of the communication.

A dynamic model was developed by ECUST for the dehydrogenation of propane and the regeneration of the catalyst Pt-Sn/Al<sub>2</sub>O<sub>3</sub>. It is a dynamic process considering the internal and external mass transfer and the heat transfer during the process. An ECUST simulator (open loop) exists in Matlab, which can simulate the 2 phases of operation (dehydrogenation and regeneration).

We are interested in the synthesis of the model and using the optimal control (which does not seem to have been studied so far) possibly predictive control, to control the reactor during the two phases operations to maximize overall performance.

Compared to what was originally planned, we have met many problems. The existing documents (We have a report from ECUST not yet published and some chemical reports) and programs are difficult to use for analysis and control: for example, data and equations may differ between the ECUST report and the ECUST matlab files (for the activity equation e.g.). Sometimes, if the ECUST matlab files, we have codes like: compute activity (which should be mathematically >0)if activity<0 ,activity=0 ; end

Firstly, we had to write the full model form of PDE dynamic system, which is exploitable from an automatical viewpoint. All the numerical values of all model parameters have to be found and are now listed here in the Annex. Unfortunately, we have some numerical problems .So our work is stopped in the open-loop dehydrogenation model numerical study.

### 3 Synthesis of the model

#### 3.1 Introduction

The increasing demand for propylene derivatives such as polypropylene, acrylonitrile, propylene oxide, cumene, phenol, isopropyl alcohol and many others has produced a correspondingly heavy increase in propylene demand during the last 20 years. It is expected that the propylene extracted from steam crackers or cat cracking does not satisfy the growing demand. Consequently, there is a great interest in alternative routes to propylene. Propane dehydrogenation is believed to have a great potential as a propylene booster in the future.

For model based optimization control of this propylene production process, dynamic models studied at ECUST are reminded here:

- an adiabatic fixed bed for propane dehydrogenation with continuously deactivating
- a dynamic heterogeneous model for the coke burning process (to regenerate the catalyst)

The operation of the process consists of four repeating sequential modes (Fig. 1):

- propane dehydrogenation (DH)
- purge
- catalyst regeneration (RG, coke burning)
- and evacuation

DH and RG feature dynamics to be controlled. Purge and evacuation are the preparative modes that are instantaneous.

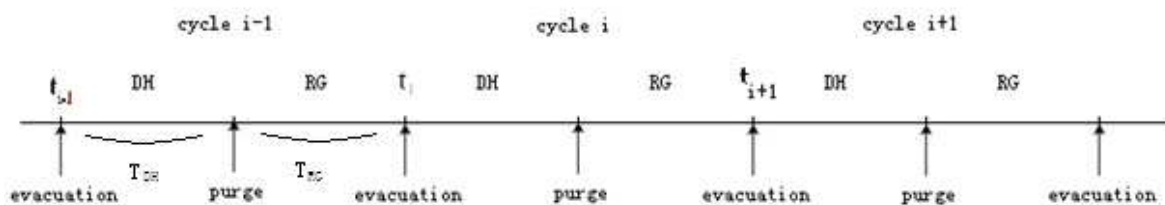


Figure 1: Production cycle.

The Fig. 2 shows a simplified view of the process used. The industrial reactor is usually a radial-flow reactor, where there is no axial flow in the reactor. The inlet is at the inner surface, and outlet is at the outer surface. It consists of multiple parallel adiabatic fixed bed reactors that contain catalyst, where the DH of propane and RG of catalyst are carried out alternatively after instantaneous periods of purging and evacuation.

Many molecules are involved in several chemical reactions, where the coefficients signification is given in the table 1 (in the annex)



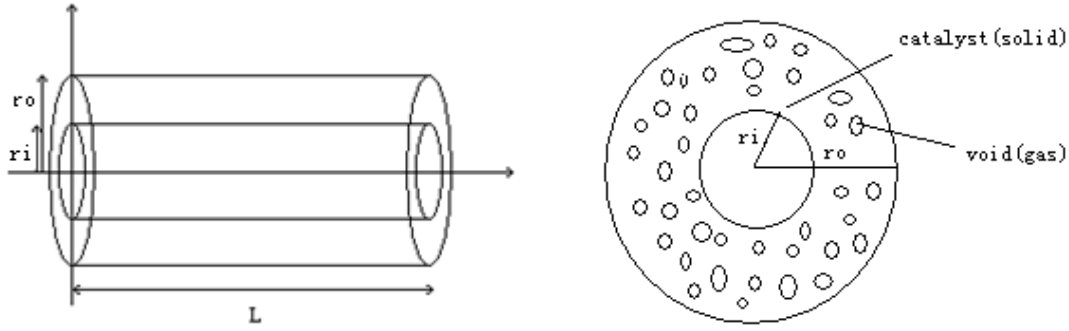


Figure 2: Simplified view of the process.

### 3.2 Model for dehydrogenation

Propane dehydrogenation is equilibrium limited and a highly endothermic reaction that is generally carried out at 525–625C and atmospheric pressure using platinum or chromium catalysts; those catalysts are not full selective, and the catalyst is continuously deactivating owing to coke formation, which needs to be burnt off periodically to regenerate the catalyst.

At the inlet, propane is mixed with argon, which is the inert gas (since using pure propane would decrease the propane conversion and the selectivity, which is not good for the production). Though the productivity will be increased if pure propane is used, but the yield to propene would be low.

#### 3.2.1 Definition of the state and input vectors

We consider dynamic model states  $\underline{x}$  as follows with 11 components:

$$\forall r_i \leq r \leq r_o, t_i < t < t_i + T_{DH}$$

- $C_M(r, t)$  multilayer coke content
- $C_m(r, t)$  monolayer coke content
- $n_T(r, t)$  transient total flow rate
- $P(r, t)$  pressure inside the reactor
- $T(r, t)$  temperature inside the reactor
- $x_{Ar}(r, t)$  mole fraction of Argon inside the reactor
- $x_{CH_4}(r, t)$  mole fraction of methane inside the reactor
- $x_{C_2H_4}(r, t)$  mole fraction of ethylene inside the reactor
- $x_{C_2H_6}(r, t)$  mole fraction of ethane inside the reactor
- $x_{C_3H_6}(r, t)$  mole fraction of propylene inside the reactor
- $x_{C_3H_8}(r, t)$  mole fraction of propane inside the reactor
- $x_{H_2}(r, t)$  mole fraction of hydrogen inside the reactor

We consider the candidate manipulated variables (MV)  $u$  as follows, with a maximum of 3 components:

- input flow rate of mixture (propane argon)  $n_T^0(t)$ , at  $r=ri, t>0$
- hydrogen concentration in the feed  $x_{H_2}^0(t)$  [3], at  $r=ri, t>0$
- duration of dehydration phase  $T_{DH}(t)$ ,  $t>0$

After some discussions with ECUST:

- If only 1 MV should be used for online control, we would choose  $n_T^0$  as  $u1$ .
- If 2 MVs should be used for online control, we would choose  $n_T^0$  and  $x_{H_2}^0$  as  $u2$ .
- If 3 MVs should be used for online control, we add  $T_{DH}$  as a new MV  $u3$ .
- If one of the previous candidates MV is not a reel MV, it is turn to a constant value.

### 3.2.2 Reaction kinetics

The kinetics expression comes initially from the work of J.Gascón and C.Télliez [5]. The kinetics of propane dehydrogenation to produce propylene over a Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst has been investigated over the temperature range of 525–575°C at atmospheric pressure.

Propane dehydrogenation [7]:

$$\left\{ \begin{array}{l}
 C_3H_8 \rightleftharpoons C_3H_6 + H_2 \\
 r_1(P, T, x_{C_3H_6}, x_{C_3H_8}, x_{H_2}) = \frac{-k_1(T)(P \cdot x_{C_3H_8} - \frac{P \cdot x_{C_3H_6} \cdot P \cdot x_{H_2}}{K_{eq}(T)})}{1 + P \cdot \frac{x_{C_3H_6}}{K_1(T)}} \\
 k_1(T) = k_{01} \cdot \exp\left(\frac{-E_{a1}}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \\
 K_1(T) = K_{01} \cdot \exp\left(\frac{-\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \\
 K_{eq}(T) = \exp\left(16.858 - \frac{15934}{T} + \frac{148728}{T^2}\right)
 \end{array} \right. \quad (1)$$

Cracking [7]:

$$\left\{ \begin{array}{l} C_3H_8 \rightarrow CH_4 + C_2H_4 \\ r_2(P, T, x_{C_3H_8}) = -k_2(T) \cdot P \cdot x_{C_3H_8} \\ k_2(T) = k_{02} \cdot \exp\left(\frac{-E_{a2}}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \end{array} \right. \quad (2)$$

Ethylene hydrogenation [2]:

$$\left\{ \begin{array}{l} C_2H_4 + H_2 \rightarrow C_2H_6 \\ r_3(P, T, x_{C_2H_4}, x_{H_2}) = -k_3(T) \cdot P \cdot x_{C_2H_4} \cdot P \cdot x_{H_2} \\ k_3(T) = k_{03} \cdot \exp\left(\frac{-E_{a3}}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \end{array} \right. \quad (3)$$

More details about constant and variables are in tables (in the annex).

### 3.2.3 Coke formation dynamic

The model used in this work to describe coke formation at the surface of the catalyst is called the monolayer–multilayer coke growth model. In this model, coke content in the catalyst versus time  $t$  and space  $r$  can be described taking into account a simultaneous formation of coke over the surface of the catalyst and a multi-layer coke deposition. Therefore, the total coke formation velocity must be described as the addition of monolayer and multilayer coke growth. Based on [2], we obtain by differentia of  $C_m$  and  $C_M$ :

$$\left\{ \begin{array}{l} C = C_M + C_m \\ \frac{\partial C_M}{\partial t} = k_{2C}(T) \left(1 + \frac{E_{a_2c}}{RT^2} \cdot t\right) \\ \frac{\partial C_m}{\partial t} = \frac{k_{1C}(T) C_{\max}^2 \left(1 + \frac{E_{a_1c}}{RT^2} \cdot t\right)}{(1 + C_{\max} k_{1C}(T) t)^2} \\ k_{1c}(T) = k_{01c} \exp\left(\frac{-E_{a1c}}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \end{array} \right. \Rightarrow \left\{ \begin{array}{l} C = C_M + C_m \\ \frac{\partial C_M}{\partial t} = k_{2C}(T) + \frac{C_M E_{a_2c}}{RT^2} \\ \frac{\partial C_m}{\partial t} = \frac{C_m k_{2C}^2(T) RT^2 + C_M E_{a_1c} k_{2C}(T) \frac{\partial T}{\partial t}}{C_M RT^2 (k_{2C}(T) + C_{\max} C_M k_{1C}(T))} \\ k_{1c}(T) = k_{01c} \exp\left(\frac{-E_{a1c}}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \end{array} \right. \quad (4)$$

As  $\frac{\partial T}{\partial t}$  is negligible, we have:

$$\begin{cases} C = C_M + C_m \\ \frac{\partial C_M}{\partial t} = k_{2C}(T) \\ \frac{\partial C_m}{\partial t} = \frac{C_m k_{2C}^2(T) RT^2}{C_M RT^2 (k_{2C}(T) + C_{\max} C_M k_{1C}(T))} \\ k_{ic}(T) = k_{0ic} \exp\left(\frac{-E_{aic}}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \end{cases} \quad (5)$$

More details about constant and variables are in tables (in the annex).

### 3.2.4 Catalyst activity

The catalyst activity  $a$  is a simple and empirical activity–time relationship deactivation model [7]:

$$\begin{cases} a(C_M, C_m, T) = (1 - \alpha_1(T) C_m) + \alpha_2 C_m e^{-\alpha_3 \frac{C_M}{C_m}} \\ \alpha_1(T) = r_{01} e^{\frac{-E_{ar1}}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)} \end{cases} \quad (6)$$

More details about constant and variables are in tables (in the annex).

Some remarks about the activity  $a$ :

- According to (6),  $0 < a < 1$ .
- If  $a \rightarrow 1$ , the catalyst is in perfect condition for its use.
- If  $a \rightarrow 0$ , the catalyst does not work.
- When it is too low, the process must be switched from dehydrogenation to regeneration (in the same reactor).
- During DH,  $a$  will be decrease.

The particular value of  $a$  when the process must be switched from DH to RG is not defined but will be controlled by the closed loop controller.

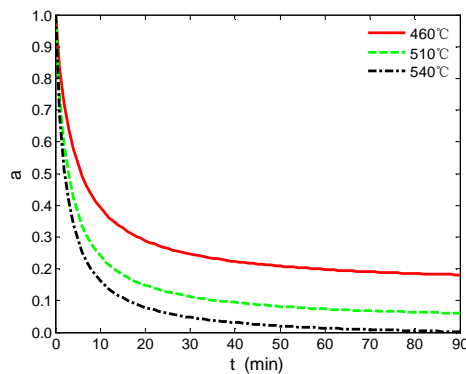


Figure 3: Catalyst activity at some temperatures [7]

Indeed, Fig. 3 shows that at the beginning, catalyst activity decrease rapidly. Sometime later, the decline rate slows, corresponding to the monolayer and multilayer coke growth. Moreover, the higher the temperature  $T$  is, the faster  $a$  decrease.

### 3.2.5 Stoichiometric analysis

Assuming initial mole fraction of each component in feed, according to stoichiometry analysis, mole fraction of each component at time  $t$  is as follows [9]:

$$\left\{ \begin{array}{l} n_T(n_T^0, x_{CH_4}, x_{C_2H_6}, x_{C_3H_6}, x_{H_2}^0) = \frac{x_{C_3H_8}^0 + x_{H_2}^0 + x_{CH_4}^0 + 2x_{C_2H_6}^0 + x_{Ar}^0}{(1 - x_{C_3H_6} - x_{CH_4} + x_{C_2H_6})} n_T^0 \\ x_{Ar}(x_{CH_4}, x_{C_2H_6}, x_{C_3H_6}, x_{H_2}^0) = \frac{x_{Ar}^0}{x_{C_3H_8}^0 + x_{H_2}^0 + 2x_{C_2H_6}^0 + x_{C_2H_4}^0 + x_{Ar}^0} (1 - x_{C_3H_6} - x_{CH_4} + x_{C_2H_6}) \\ x_{C_2H_4}(x_{CH_4}, x_{C_2H_6}, x_{C_3H_6}, x_{H_2}^0) = \frac{x_{C_2H_4}^0 - x_{CH_4}^0 + x_{C_2H_6}^0}{x_{C_3H_8}^0 + x_{H_2}^0 + 2x_{C_2H_6}^0 + x_{C_2H_4}^0 + x_{Ar}^0} (1 - x_{C_3H_6} - x_{CH_4} + x_{C_2H_6}) + x_{CH_4} - x_{C_2H_6} \\ x_{C_3H_8}(x_{CH_4}, x_{C_2H_6}, x_{C_3H_6}, x_{H_2}^0) = \frac{x_{C_3H_8}^0 + x_{C_3H_6}^0 + x_{CH_4}^0}{x_{C_3H_8}^0 + x_{H_2}^0 + 2x_{C_2H_6}^0 + x_{C_2H_4}^0 + x_{Ar}^0} (1 - x_{C_3H_6} - x_{CH_4} + x_{C_2H_6}) - x_{C_3H_6} - x_{CH_4} \\ x_{H_2}(x_{CH_4}, x_{C_2H_6}, x_{C_3H_6}, x_{H_2}^0) = \frac{x_{H_2}^0 - x_{C_3H_6}^0 + x_{C_2H_6}^0}{x_{C_3H_8}^0 + x_{H_2}^0 + 2x_{C_2H_6}^0 + x_{C_2H_4}^0 + x_{Ar}^0} (1 - x_{C_3H_6} - x_{CH_4} + x_{C_2H_6}) + x_{C_3H_6} - x_{C_2H_6} \end{array} \right. \quad (7)$$

More details about constant and variables are in tables (in the annex).

### 3.2.6 Balances

The model is as follows [9]:

- Mass balance:

$$\left\{ \begin{array}{l} \frac{\partial x_{CH_4}}{\partial r} = \frac{A(r) \cdot \rho_B}{n_T} \cdot [-x_{CH_4} \cdot a(C_M, C_m, T) \cdot r_1(P, T, x_{C_3H_6}, x_{C_3H_8}, x_{H_2}) + (1 - x_{CH_4}) \cdot r_2(P, T, x_{C_2H_8}) - x_{CH_4} \cdot r_3(P, T, x_{CH_4}, x_{C_2H_6}, x_{C_3H_6})] \\ \frac{\partial x_{C_2H_6}}{\partial r} = \frac{A(r) \cdot \rho_B}{n_T} \cdot [-x_{C_2H_6} \cdot a(C_M, C_m, T) \cdot r_1(P, T, x_{C_3H_6}, x_{C_3H_8}, x_{H_2}) - x_{C_2H_6} \cdot r_2(P, T, x_{C_2H_8}) + (1 - x_{C_2H_6}) \cdot r_3(P, T, x_{CH_4}, x_{C_2H_6}, x_{C_3H_6})] \\ \frac{\partial x_{C_3H_6}}{\partial r} = \frac{A(r) \cdot \rho_B}{n_T} \cdot [(1 - x_{C_3H_6}) \cdot a(C_M, C_m, T) \cdot r_1(P, T, x_{C_3H_6}, x_{C_3H_8}, x_{H_2}) - x_{C_3H_6} \cdot r_2(P, T, x_{C_2H_8}) + (2 - x_{C_3H_6}) \cdot r_3(P, T, x_{CH_4}, x_{C_2H_6}, x_{C_3H_6})] \end{array} \right. \quad (8)$$

where  $A(r) = 2\pi Lr$

- Energy balance:

$$\begin{aligned} \frac{\partial T}{\partial r} = & \frac{A(r) \cdot \rho_B \cdot}{n_T(n_T^0, x_{CH_4}, x_{C_2H_6}, x_{C_3H_8}) \cdot C_{pm}(T, x_{Ar}, x_{CH_4}, x_{C_2H_4}, x_{C_2H_6}, x_{C_3H_6}, x_{C_3H_8}, x_{H_2})} \cdot \\ & (... \\ & (-H_1(T)) \cdot a(C_M, C_m, T) \cdot r_1(P, T, x_{C_3H_6}, x_{C_3H_8}, x_{H_2}) + ... \\ & (-H_2(T)) \cdot r_2(P, T, x_{C_3H_8}) + ... \\ & (-H_3(T)) \cdot r_3(P, T, x_{C_2H_4}, x_{H_2}) ... \\ & ) \end{aligned} \quad (9)$$

- Pressure drop of bed:

$$\frac{\partial P}{\partial r} = -f_r(n_T, r, T, x_i) \frac{\rho_g(P, T, x_i) u^2(n_T, P, r, T, x_i, x_{H_2}^0)}{d_s} \cdot \frac{1 - \varepsilon}{\varepsilon^3} \quad (10)$$

where :

$$\left\{ \begin{aligned} f_r(n_T, r, T, x_i) &= \frac{150}{\text{Re}(n_T, r, T, x_i)} + 1.75 \\ \text{Re}(n_T, r, T, x_i) &= \frac{d_s G(n_T, r, x_i)}{\mu(T, x_i)} \cdot \frac{1}{1 - \varepsilon} \\ u(n_T, P, r, T, x_i) &= \frac{G(n_T, r, x_i)}{\rho_g(P, T, x_i)} \\ G(n_T, r, x_i) &= \frac{n_T M g(x_i)}{60(2\pi r l)} \\ \rho_g(P, T, x_i) &= \frac{P \cdot M_g(x_i)}{RT} \\ M_g(x_i) &= \sum x_i M_i \quad i \in \{Ar, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, H_2\} \end{aligned} \right. \quad (11)$$

### 3.2.7 Synthesis of this mathematical model

According to the above equations and previous state (12 components) and input (3 possible components) definitions, we have the following model structure for the DH model based on PDE, with some equations  $f$  inside the spatial domain (D) and some others at the boundary (B):

$$\begin{cases} \frac{\partial x}{\partial t} = f_{DH.D}(\frac{\partial x}{\partial r}, x, u) \\ f_{DH.B}(\frac{\partial x}{\partial r}, x, u) = 0 \end{cases} \quad (12)$$

- The equations inside the spatial domain D:

$$\begin{cases} \frac{\partial C_m}{\partial t} = f_{DH.D.C_m}(C_m, C_M, T, \frac{\partial T}{\partial t}) \\ \frac{\partial C_M}{\partial t} = f_{DH.D.C_M}(C_M, T, \frac{\partial T}{\partial t}) \\ n_T = f_{DH.D.n_T}(x_{CH_4}, x_{C_2H_6}, x_{C_3H_6}, u_1, u_2) \\ \frac{\partial P}{\partial r} = f_{DH.D.P}(n_T, P, r, T, x_{Ar}, x_{CH_4}, x_{C_2H_4}, x_{C_2H_6}, x_{C_3H_6}, x_{C_3H_8}, x_{H_2}) \\ \frac{\partial T}{\partial r} = f_{DH.D.T}(C_M, C_m, n_T, P, T, r, x_{C_2H_4}, x_{C_3H_6}, x_{C_3H_8}, x_{H_2}) \\ x_{Ar} = f_{DH.D.x_{Ar}}(x_{CH_4}, x_{C_2H_6}, x_{C_3H_6}, u_2) \\ \frac{\partial x_{CH_4}}{\partial r} = f_{DH.D.x_{CH_4}}(C_M, C_m, n_T, P, T, r, x_{CH_4}, x_{C_2H_6}, x_{C_3H_6}, x_{C_3H_8}, x_{H_2}) \\ x_{C_2H_4} = f_{DH.D.x_{C_2H_4}}(x_{CH_4}, x_{C_2H_6}, x_{C_3H_6}, u_2) \\ \frac{\partial x_{C_2H_6}}{\partial r} = f_{DH.D.x_{C_2H_6}}(C_M, C_m, n_T, P, T, r, x_{CH_4}, x_{C_2H_6}, x_{C_3H_6}, x_{C_3H_8}, x_{H_2}) \\ \frac{\partial x_{C_3H_6}}{\partial r} = f_{DH.D.x_{C_3H_6}}(C_M, C_m, n_T, P, T, r, x_{CH_4}, x_{C_2H_6}, x_{C_3H_6}, x_{C_3H_8}, x_{H_2}) \\ x_{C_3H_8} = f_{DH.D.x_{C_3H_8}}(x_{CH_4}, x_{C_2H_6}, x_{C_3H_6}, u_2) \\ x_{H_2} = f_{DH.D.x_{H_2}}(x_{CH_4}, x_{C_2H_6}, x_{C_3H_6}, u_2) \end{cases} \quad (13)$$

where  $t_i < t < t_i + u_3$ ,  $r_i < r < r_o$

- The initial conditions at the beginning of the DH phase at  $t=t_i$ ,  $r_o \leq r \leq r_i$  are :

$$\begin{cases} C_M(r, t) = C_M^0(r), C_m(r, t) = C_m^0(r), P(r, t) = P^0(r), T(r, t) = T^0(r), n_T(r, t) = n_T^0(r) \\ x_{Ar}(r, t) = \frac{2}{3}, x_{CH_4}(r, t) = 0, x_{C_2H_4}(r, t) = 0, x_{C_2H_6}(r, t) = 0, x_{C_3H_6}(r, t) = 0, x_{C_3H_8}(r, t) = \frac{1}{3}, x_{H_2}(r, t) = 0 \end{cases} \quad (14)$$

at  $t=0$ ,  $C_M^0(r) = C_m^0(r) = 0, P^0(r) = P_{inlet}, T^0(r) = T_{inlet}$  at first DH phase

- The boundary conditions  $t_i < t < t_i + u_3, r=r_i$

$$P(r_i, t) = P_{inlet}, T(r_i, t) = T_{inlet}, x_{CH_4}(r_i, t) = 0, x_{C_2H_6}(r_i, t) = 0, x_{C_3H_6}(r_i, t) = 0 \quad (15)$$

We consider the model outputs y as follows as the mol flow rates:

$$n_i(n_T, x_i) = n_T(n_T^0, x_{CH_4}^0, x_{C_2H_6}^0, x_{C_3H_6}^0, x_{H_2}^0) \cdot x_i \quad i \in \{CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8\} \quad (16)$$

These flow rates are all measured.

The temperature and pressure are measured online without any delays and the concentrations are measured with the delay which will be about a few minutes, or a few seconds for on-line mass spectrometry. All these are measured at the outlet.



### 3.3 Model for regeneration

During dehydrogenation, coking that deactivates the catalyst should be periodically burnt in oxygen-diluents mixture: this is regeneration of the catalyst, where no propylene production takes place.

The coke combustion involves both chemical reaction and transport processes, since oxygen must be transported by the external mass transfer and the pore diffusion to the internal coked surface where the combustion reaction takes place, and the heat of combustion must be transferred to the bulk fluid.

In this report, a dynamic model [9] for the coke combustion regeneration of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst regeneration studied at ECUST is reminded, which is capable of predicting the changes of the solid temperature and the coke load distribution with time  $t$  and space  $r$ .

#### 3.3.1 Definition of the state and input vectors

Our colleagues at ECUST gave us an effectiveness factor modified coke burning model [1]. In this model, the influence of gas reactants diffusion within particle describe by the effectiveness factor.

When heat effect is very large owing to the coke rapid burning rate and smaller gas flow rate or other factors, the effect of external diffusion will have to consider, In this case, respectively, the heterogeneous model that takes into consideration the mass balance and energy balance of gas phase and solid phase is necessary.

We define the dynamic model states  $x$  of the system as follows, with 6 components:

$$\forall r_i \leq r \leq r_0, t_{i+1} - T_{RG} < t < t_{i+1}$$

- $C_M(r, t)$  multilayer coke content
- $C_m(r, t)$  monolayer coke content
- $P_{as}(r, t)$  pressure inside the solid
- $P(r, t)$  pressure of the gas
- $T_{as}(r, t)$  temperature of the solid
- $T(r, t)$  temperature of the gas
- $x_{O_2}(r, t)$  mole fraction of oxygen inside reactor

We consider all our candidate manipulated variables  $u$  as follows:

- Inlet flow rate  $G(t)$ : at  $r=ri$   $t>0$
- Inlet pressure of the gas  $P^0(t)$ : It may be kept constant, but can be different than atmosphere. at  $r=ri$   $t>0$
- Inlet temperature  $T^0(t)$ : key factor (consider catalyst tolerance temperature and multi-steady state) at  $r=ri$   $t>0$

- Duration of dehydration phase  $T_{RG}(t) t > 0$
- Inlet O2 concentration  $x_{O_2}^0(t)$ : not economic to use a value higher than air at  $r=ri t > 0$

After some discussion with ECUST colleagues, for the online control:

- Except of course the duration of this phase  $u_3=T_{RG}$  that is always needed, we prefer the inlet temperature  $T^0$  as the first MV  $u_1$ .
- If needed the flow rate  $G$  is a possible second MV  $u_2$ .
- If one of the previous candidates MV is not a real MV, it is turned to a constant value.

### 3.3.2 Balances

The mass balance and energy balance equations are respectively given as follow [9]:

- Gas phase:

$$\left\{ \begin{array}{l}
 \frac{\partial C_M}{\partial t} = -\frac{1}{3}\eta(C_M, C_m, P, T_{as})r_m(C_M, C_m, P_{as}, T_{as}) \\
 \frac{\partial C_m}{\partial t} = -\frac{2}{3}\eta(C_M, C_m, P, T_{as})r_m(C_M, C_m, P_{as}, T_{as}) \\
 \frac{\partial P}{\partial r} = -f_r(G, T, x_{O_2})\frac{\rho_g(P, T, x_{O_2})u^2(G, P, T, x_{O_2})}{d_s} \cdot \frac{1-\varepsilon}{\varepsilon^3} \\
 (\varepsilon\rho_g(P, T, x_{O_2})c_p(T, x_{O_2}) + \rho_Bc_s(T))\frac{\partial T}{\partial t} = -Gc_p(T, x_{O_2})\frac{\partial T}{\partial r} + (-\Delta H_r)\rho_B\eta(C_M, C_m, P, T_{as})r_m(C_M, C_m, P_{as}, T_{as}) \\
 \varepsilon\frac{\rho_g(P, T, x_{O_2})}{M_g(x_{O_2})}\frac{\partial x_{O_2}}{\partial t} = -\frac{G}{M_g(x_{O_2})}\frac{\partial x_{O_2}}{\partial r} - \rho_B\eta(C_M, C_m, P, T_{as})r_m(C_M, C_m, P_{as}, T_{as})
 \end{array} \right. \quad (17)$$

where:

$$\begin{cases}
C = C_m + C_M \\
f_r(G, T, x_{O_2}) = \frac{150}{\text{Re}(G, T, x_{O_2})} + 1.75 \\
u(G, P, T, x_{O_2}) = \frac{G}{\rho_g(P, T, x_{O_2})} \\
r_m(C, P_{as}, T_{as}) = k_o e^{\left(\frac{-1000Ea}{R} \left(\frac{1}{T_{as}} - \frac{1}{T_0}\right)\right)} \cdot P_{as} \cdot C \\
c_p(T, x_{O_2}) = \frac{C_p(T, x_{O_2})}{Mg(x_{O_2})} \\
c_s(T) = (102.429 + 38.7498T - 15.9109T^2 + 2.628181T^3 - \frac{3.007551}{T^2}) / Ms \\
\rho_g(P, T, x_{O_2}) = \frac{101325PMg(x_{O_2})}{RT} \\
Mg(x_{O_2}) = M_{N_2}(1 - x_{O_2}) + M_{O_2}x_{O_2}
\end{cases} \quad (18)$$

- Solid phase:

$$\begin{cases}
P_{as} = Px_{O_2} - \frac{\eta(C_M, C_m, P, T_{as})r_m(C_M, C_m, P_{as}, T_{as})RT}{k_G(G, P, T, x_{O_2})a_m} \\
T_{as} = T + \frac{\eta(C_M, C_m, P, T_{as})r_m(C_M, C_m, P_{as}, T_{as})(-\Delta H_r)}{h_s(G, T, x_{O_2})a_m}
\end{cases} \quad (19)$$

- The initial conditions:

$$t = t_{i+1} - u_3, r_i < r < r_0, x_{O_2}(r, t) = 0, C_M(r, t) = C_M^0(r), C_m(r, t) = C_m^0(r), P(r, t) = P(r), T(r, t) = T(r) \\
x_{O_2}(r, t) = 0$$

(20)

For solid phase, no initial conditions are needed because we have only algebra equations.

- The boundary conditions:

$$r = r_i, t > 0, x_{O_2}(r, t) = x_{O_2}^0(t), T(r, t) = T^0(t), P(r, t) = P_a \quad (21)$$

### 3.3.3 Synthesis of this mathematical model

According to the above equations and previous state (5 components) and input (3 possible components) definitions, we have the following model structure for the RG model based on PDE, with some equations  $f$  inside the spatial domain (D) and some others at the boundary (B):

$$\begin{cases}
\frac{\partial x}{\partial t} = f_{RG,D} \left( \frac{\partial x}{\partial r}, x, u \right) \\
f_{RG,B} \left( \frac{\partial x}{\partial r}, x, u \right) = 0
\end{cases} \quad (22)$$

- With some equation inside the spatial domain D:

$$\left\{ \begin{array}{l} \frac{\partial C_M}{\partial t} = f_{RG.D.C_M}(C_M, C_m, P, P_{as}, T_{as}) \\ \frac{\partial C_m}{\partial t} = f_{RG.D.C_m}(C_M, C_m, P, P_{as}, T_{as}) \\ \frac{\partial P}{\partial r} = f_{RG.D.P}(P, T, x_{O_2}, u_2) \\ P_{as} = f_{RG.D.P_{as}}(C_M, C_m, P, P_{as}, T, T_{as}, x_{O_2}, u_2) \\ \frac{\partial T}{\partial t} = f_{RG.D.T}(C_M, C_m, P, P_{as}, \frac{\partial T}{\partial r}, T, T_{as}, x_{O_2}, u_2) \\ T_{as} = f_{RG.D.T_{as}}(C_M, C_m, P, P_{as}, T, T_{as}, x_{O_2}, u_2) \\ \frac{\partial x_{O_2}}{\partial t} = f_{RG.D.x_{O_2}}(C_M, C_m, P, P_{as}, T, T_{as}, \frac{\partial x_{O_2}}{\partial r}, x_{O_2}, u_2) \end{array} \right. \quad (23)$$

where  $t_{i+1} - u_3 < t < t_{i+1}, r_i < r < r_0$  ,

- with the initial conditions at the beginning of the RG phase at  $t=t_{i+1} - u_3, r_o \leq r \leq r_i$  :  
 $t = t_{i+1} - u_3(t), r_i < r < r_0, x_{O_2}(r, t) = 0, C_M(r, t) = C_M^0(r), C_m(r, t) = C_m^0(r), P(r, t) = P(r), T(r, t) = T(r)$   
 $x_{O_2}(r, t) = 0$

(24)

- with the boundary conditions  $t_{i+1} - u_3 < t < t_{i+1}, r=r_i$

$$r = r_i, t > 0, x_{O_2}(r, t) = x_{O_2}^0(t), T(r, t) = u_1, P(r, t) = P_{inlet} \quad (25)$$

We consider the bed temperature  $Ts(r_i < r < r_0, t)$  and outlet CO2 concentration are the model outputs y, where  $x_{CO_2} = x_{O_2}(r_i, t) - x_{O_2}(r_0, t)$

As the time for regeneration may not be very long, the coke content C may not be 0 at the end of regeneration. When it reaches at a low value, the process must be switched to the dehydrogenation phase. This must be decided by the controller.

The temperature and pressure are measured online without any delays and the concentration is measured with the delay which will be about a few minutes, or a few seconds for on-line mass spectrometry.

We measure the temperature at different locations from inlet to outlet including. We measure the pressure at inlet and the concentration at inlet and outlet.

### 3.4 Connection between process state when switching between the 2 models

The operation of the process consists of repetition of four sequential modes: propane dehydrogenation (DH), purge, catalyst regeneration (RG, coke burning), and evacuation. Purge and evacuation are the preparative modes. The purge and evacuation cannot be considered to reset the system because the coke deposit and the temperature are transferred from DH to RG and also RG to DH, respectively, and the process can be classified as a repetitive process instead of a batch process.[6] Purge and evacuation are the preparative modes, that are assumed instantaneous.

The following table sums up the condition for the states when switching at the end of DH (resp. RG) to the beginning of RG (resp. DH):

The final value of one state in DH (resp. RG) gives the initial value for the state in RG (resp. DH), if the states always exist ( $C_M$ ,  $C_m$ ,  $P$ ,  $T$ )

DH	previous final condition at $t = t_f^- =$ next initial conditions at $t = t_f^+$	RG
$C_M$	$\longleftrightarrow_{C_M}$	$C_M$
$C_m$	$\longleftrightarrow_{C_m}$	$C_m$
$n_t$		
$P$	possible to use different pressure	$P$
		$P_{as}$
$T$	$\longleftrightarrow_T$	$T$
		$T_{as}$
$x_{Ar} = \frac{2}{3}$		
$x_{CH_3} = 0$		
$x_{C_2H_4} = 0$		

---

$$x_{C_2H_6} = 0$$

---

$$x_{C_3H_6} = 0$$

---

$$x_{C_3H_8} = \frac{1}{3}$$

---

$$x_{H_2} = 0$$

---

$$x_{O_2} = x_{O_2}^0(t)$$

---

### 3.5 Control objective

The process can be classified as a repetitive process instead of a batch process because the coke deposit and the bed temperature are transferred from DH to RG and also from RG to DH.

During the DH phase, we consider

- the candidate manipulated variable: input flow rate  $n_i^0(t)$  and the hydrogen concentration in the feed  $x_{H_2}^0(t)$
- the model output: flow rate of propane  $n_{C_3H_8}(r = r_o, t)$ , propylene  $n_{C_3H_6}(r = r_o, t)$ , ethane  $n_{C_2H_6}(r = r_o, t)$ , ethylene  $n_{C_2H_4}(r = r_o, t)$ , and methane  $n_{CH_4}(r = r_o, t)$

During the RG phase, we consider

- the candidate manipulated variable: inlet temperature  $T^0(t)$  and flow rate  $G(t)$
- the model outputs: bed temperature  $T_s(r_i < r < r_o, t)$  and outlet CO2 concentration  $x_{CO_2}(r = r_o, t)$

For Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst, the difference between  $T_S$  and  $T_G$  is small.

We will have to pay attention to the gas temperature and gas flow rate in order to avoid the multiple steady state condition

We have some variables of strong interest, in order to assess the reactor efficiency:

- $C = C_M + C_m$  carbon (coke) content defined during DH and RG phases by the models (12) and (23)

- $a$ : activity of catalyst defined during the DH phase (given in (6) )
- $x_{C3H8}$  conversion defined during the DH phase (given by the DH model (12): because of catalyst deactivation, the conversion changes with time.
- Selectivity [9] defined during the DH phase, which is the amount of propylene produced divided by the sum of the amount propylene + the amount of by-products:

$$S(n_T, x_{C3H6}, x_{C3H8}) = \frac{x_{C3H6} n_T (n_T^0, x_{CH_4}, x_{C_2H_6}, x_{C_3H_6}, x_{H_2}^0)}{x_{C3H8} n_T^0 - n_{C3H8} (n_T, x_{C3H8})} \quad (26)$$

- And the Yield defined during the DH phase:

$$Yield(n_T, x_{C3H6}, x_{C3H8}) = S(n_T, x_{C3H6}, x_{C3H8}) * x_{C3H8} \quad (27)$$

In terms of process control, globally, we will have to tackle different problems at the same time:

1. optimize the averaged daily productivity of propylene, which is

$$\eta = \frac{\sum_{DH(i)} \int_{t_i}^{t_i+T_{DH}(i)} n_{C_3H_6}(t) dt}{\sum_{DH(i)} \int_{t_i}^{t_i+T_{DH}(i)} n_T^0 dt}$$

where  $i \in \{1, \dots, N_i\}$  with  $\sum_i (T_{DH}(i) + T_{RG}(i)) = 24H$

(28)

We can consider a yield = 100% as our target of optimization even if it is not possible. The maximum value has to be found.

2. maximize  $n_i^0(t)=u_1(t)$  during DH phase

3. some constraints must be satisfied during DH and RG phases

$T < T_{max}$  (catalyst must not be destroyed)

$u_{min} < u < u_{max}$

U	umin	umax
$n_T^0$	0	+inf
$x_{H_2}^0$	0	1
$T^0$	673.15K	893.15K
$G$	0	+inf

According to above equations and discussions, we are proposed to construct a predictive controller [8].

## 4 Numerical simulation of the open loop dehydrogenation model

### 4.1 Introduction

In the chapter 1, we have presented the model of the propylene production process, where we have 12 model states during the dehydrogenation and 7 model states during the regeneration. This chapter is dedicated to the study of the model for the predictive control of this process based on the system of ordinary differential equation and partial differential equations. We will here get into the discretization of dehydrogenation and its numerical simulation.

### 4.2 ECUST existing simulator

We have received two matlab files which describe the simulation of the system. However, after some synthesis, we find that though the programs return some data, the dynamic make no sense. Because by example for the dehydrogenation as we have a model of 12 states, in the file the dynamic is calculated by a function of model with 5 states and the other 7 states are calculated by the 5 states with mathematic expressions. However, the 5 states calculated are not independent. And we do not agree with the method how the discretization is calculated. Furthermore, some variables appear in many functions and are calculated several time which is not necessary. There is no connection between the switching of the 2 models.

### 4.3 Model used for our simulations

As we have study in chapter 1, we have obtained the equations as follows:

$$\begin{cases} \frac{\partial x}{\partial t} = f_{DH.D}(x, u) \\ f_{DH.B}(\frac{\partial x}{\partial r}, x, u) = 0 \end{cases} \quad (29)$$

We have 2 dynamic model states and 10 static model states. As a result, we can consider the system of differential-algebraic equations as follows, where the origin is defined in 3.7, page 10.



$$\left\{ \begin{array}{l}
\frac{\partial x_{dyn_1}}{\partial t} = f_{DH.D.C_m}(x_{dyn_1}, x_{dyn_2}, x_{dyn_5}) \\
\frac{\partial x_{dyn_2}}{\partial t} = f_{DH.D.C_M}(x_{dyn_2}, x_{stat_3}) \\
x_{stat_1} = f_{DH.D.n_r}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_1, u_2) \\
\frac{\partial x_{stat_2}}{\partial r} = f_{DH.D.P}(x_{stat_1}, x_{stat_2}, r, x_{stat_3}, x_{stat_4}, x_{stat_5}, x_{stat_6}, x_{stat_7}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \\
\frac{\partial x_{stat_3}}{\partial r} = f_{DH.D.T}(x_{dyn_1}, x_{dyn_2}, x_{stat_1}, x_{stat_2}, x_{stat_3}, r, x_{stat_6}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \\
x_{stat_4} = f_{DH.D.x_{Ar}}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_2) \\
\frac{\partial x_{stat_5}}{\partial r} = f_{DH.D.x_{CH_4}}(x_{dyn_1}, x_{dyn_2}, x_{stat_1}, x_{stat_2}, x_{stat_3}, r, x_{stat_5}, x_{stat_7}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \\
x_{stat_6} = f_{DH.D.x_{C_2H_4}}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_2) \\
\frac{\partial x_{stat_7}}{\partial r} = f_{DH.D.x_{C_2H_6}}(x_{dyn_1}, x_{dyn_2}, x_{stat_1}, x_{stat_2}, x_{stat_3}, r, x_{stat_5}, x_{stat_7}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \\
\frac{\partial x_{stat_8}}{\partial r} = f_{DH.D.x_{C_3H_6}}(x_{dyn_1}, x_{dyn_2}, x_{stat_1}, x_{stat_2}, x_{stat_3}, r, x_{stat_5}, x_{stat_7}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \\
x_{stat_9} = f_{DH.D.x_{C_3H_8}}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_2) \\
x_{stat_{10}} = f_{DH.D.x_{H_2}}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_2)
\end{array} \right. \quad (30)$$

- The initial conditions at the beginning of the DH phase at  $t=t_i$ , are :

$$\left\{ \begin{array}{l}
C_M(r, t) = C_M^0(r), C_m(r, t) = C_m^0(r), P(r, t) = P^0(r), T(r, t) = T^0(r), n_i(r, t) = n_i^0(r) \\
x_{AR}(r, t) = \frac{2}{3}, x_{CH_4}(r, t) = 0, x_{C_2H_4}(r, t) = 0, x_{C_2H_6}(r, t) = 0, x_{C_3H_6}(r, t) = 0, x_{C_3H_8}(r, t) = \frac{1}{3}, x_{H_2}(r, t) = 0
\end{array} \right. \quad (31)$$

at  $t=0$ ,  $C_M^0(r) = C_m^0(r) = 0$ ?,  $P^0(r) = P_{inlet}$ ,  $T^0(r) = T_{inlet}$  at first DH phase

Within the 10 static states, the expressions characterizing pressure, temperature, molar fraction of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>6</sub> have the differential equations where the states are derived by  $r$ . The boundary conditions are:

$$P(r_i, t) = P_{inlet}, T(r_i, t) = T_{inlet}, x_{CH_4}(r_i, t) = 0, x_{C_2H_6}(r_i, t) = 0, x_{C_3H_6}(r_i, t) = 0 \quad (32)$$

at  $t_i < t < t_i + u_3$ ,  $r=r_i$

Then the rest 6 static states have just the algebraic equations, which is not necessary to define the boundary condition.

For the resolution of the model, we will resolve numerically the system with the finite difference method.

## 4.4 Discretization of the dehydrogenation

The balances of the system are governed by differential equations of infinite dimension, involving many independent variables. The numerical resolution will be resolved by transforming the initial problem to differential-algebraic equations by a spatial discretization. Using ode15s, we can solve the problem with a mass matrix singular.

In the general case of the model defined, we consider the class of the distributed parameter system defined by the equation:

$$M[y(z; t)] + g(z; t) = 0 \quad (33)$$

The limit condition of type Dirichlet at the left extremity

$$y(z_{\min}; t) = v(t) \quad (34)$$

The initial condition :

$$y(z; 0) = y_0(z) \quad (35)$$

The problem is a function  $y$  defined for  $(z; t) \in [z_{\min}; z_{\max}] \times ]0; +\infty[$ ,  $M$  is a linear operator and  $g(z, t)$  a source term. The conditions (34) et (35) are compatible:  $y_0(z_{\min}) = v(0)$ .

### 4.4.1 The finite difference method

We consider the equation (33) associated to the limit condition (34) and the initial condition (35). The finite difference method is a numerical tool based on the local equation which is discretized and resolved gradually. The spatial field is divided on a finite number of intervals called step of discretization. These discretization points consist of a finite number of points  $z_i$  of field  $[z_{\min}; \dots; z_{\max}]$ . On the discretized axis to constant step  $\Delta z$ ,  $y$  is supposed derivable 2 times. The development of Taylor of second order in the vicinity of  $z_i$  is as follows:

$$\begin{aligned} y(z_i + \Delta z, t) &= y_{i+1}(t) = y_i(t) + \Delta z \left. \frac{\partial y(t)}{\partial z} \right|_{z=z_i} + \frac{\Delta z^2}{2} \left. \frac{\partial^2 y(t)}{\partial z^2} \right|_{z=z_i} + O(\Delta z^3) \\ y(z_i - \Delta z, t) &= y_{i-1}(t) = y_i(t) - \Delta z \left. \frac{\partial y(t)}{\partial z} \right|_{z=z_i} + \frac{\Delta z^2}{2} \left. \frac{\partial^2 y(t)}{\partial z^2} \right|_{z=z_i} + O(\Delta z^3) \end{aligned} \quad (36)$$

Limiting the development in the first order, the first derivative is written:

The schema of finite difference in the left or before:

$$\left. \frac{\partial y(t)}{\partial z} \right|_{z=z_i} = \frac{y_{i+1}(t) - y_i(t)}{\Delta z} + O(\Delta z) \quad (37)$$

The schema of finite difference in the right or after:

$$\left. \frac{\partial y(t)}{\partial z} \right|_{z=z_i} = \frac{y_i(t) - y_{i-1}(t)}{\Delta z} + O(\Delta z) \quad (38)$$

The schema of finite difference in the center:

$$\left. \frac{\partial y(t)}{\partial z} \right|_{z=z_i} = \frac{y_{i+1}(t) - y_{i-1}(t)}{2\Delta z} + O(\Delta z^2) \quad (39)$$

Considering the finite difference method described, we apply it to the equation (33) of our model of dehydrogenation. The function  $nlp$  is close to a finite number points of discretization  $r_i$  for  $i = \{0, 1, \dots, N\}$ . The field is divided to  $N$  elements of fixed length  $\Delta r$  (figure 4)



(figure 4)

The numerical resolution obtained at the points of discretization  $r_i$  is noted  $x_i(t) = x(r_i, t)$

With the approximation of the operator of finite difference in the left, the model becomes a system of  $N$  differential-algebraic equations (DAEs).

$$\left\{ \begin{array}{l} \frac{\partial x_{dyn_1}}{\partial t} = f_{DH.D.C_m}(x_{dyn_1}, x_{dyn_2}, x_{dyn_5}) \\ \frac{\partial x_{dyn_2}}{\partial t} = f_{DH.D.C_M}(x_{dyn_2}, x_{stat_3}) \\ x_{stat_1} = f_{DH.D.n_r}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_1, u_2) \\ \frac{x_{stat_2 i} - x_{stat_2 i-1}}{\Delta r} = f_{DH.D.P}(x_{stat_1}, x_{stat_2}, r, x_{stat_3}, x_{stat_4}, x_{stat_5}, x_{stat_6}, x_{stat_7}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \\ \frac{x_{stat_3 i} - x_{stat_3 i-1}}{\Delta r} = f_{DH.D.T}(x_{dyn_1}, x_{dyn_2}, x_{stat_1}, x_{stat_2}, x_{stat_3}, r, x_{stat_6}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \\ x_{stat_4} = f_{DH.D.x_{Ar}}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_2) \\ \frac{x_{stat_5 i} - x_{stat_5 i-1}}{\Delta r} = f_{DH.D.x_{CH_4}}(x_{dyn_1}, x_{dyn_2}, x_{stat_1}, x_{stat_2}, x_{stat_3}, r, x_{stat_5}, x_{stat_7}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \\ x_{stat_6} = f_{DH.D.x_{C_2H_4}}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_2) \\ \frac{x_{stat_7 i} - x_{stat_7 i-1}}{\Delta r} = f_{DH.D.x_{C_2H_6}}(x_{dyn_1}, x_{dyn_2}, x_{stat_1}, x_{stat_2}, x_{stat_3}, r, x_{stat_5}, x_{stat_7}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \\ \frac{x_{stat_8 i} - x_{stat_8 i-1}}{\Delta r} = f_{DH.D.x_{C_3H_6}}(x_{dyn_1}, x_{dyn_2}, x_{stat_1}, x_{stat_2}, x_{stat_3}, r, x_{stat_5}, x_{stat_7}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \\ x_{stat_9} = f_{DH.D.x_{C_3H_8}}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_2) \\ x_{stat_{10}} = f_{DH.D.x_{H_2}}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_2) \end{array} \right. \quad (40)$$

## 4.5 Calculation of the system with ode15s

The system of N differential-algebraic equations (DAEs) can be solved by applying the ode 15s.

We have to define the input argument 'odefun' to the solvers. The function evaluates the right side of the differential equations. All solvers solve systems of equations in the form  $y' = f(t, y)$  or problems that involve a mass matrix,  $M(t, y)y' = f(t, y)$ .

In order to realize ode15s, we have to transfer the equations as follows:

$$\begin{cases} y' = f_1(t, y) \\ 0 = f_2(t, y) \end{cases} \quad (41)$$

In our case, we obtain

$$\left\{ \begin{array}{l} \frac{\partial x_{dyn_1}}{\partial t} = f_{DH.D.C_m}(x_{dyn_1}, x_{dyn_2}, x_{dyn_5}) \\ \frac{\partial x_{dyn_2}}{\partial t} = f_{DH.D.C_M}(x_{dyn_2}, x_{stat_3}) \\ 0 = x_{stat_1} - f_{DH.D.n_T}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_1, u_2) \\ 0 = \frac{x_{stat_2 i} - x_{stat_2 i-1}}{\Delta r} - f_{DH.D.P}(x_{stat_1}, x_{stat_2}, r, x_{stat_3}, x_{stat_4}, x_{stat_5}, x_{stat_6}, x_{stat_7}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \\ 0 = \frac{x_{stat_3 i} - x_{stat_3 i-1}}{\Delta r} - f_{DH.D.T}(x_{dyn_1}, x_{dyn_2}, x_{stat_1}, x_{stat_2}, x_{stat_3}, r, x_{stat_6}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \\ 0 = x_{stat_4} - f_{DH.D.x_{Ar}}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_2) \\ 0 = \frac{x_{stat_5 i} - x_{stat_5 i-1}}{\Delta r} - f_{DH.D.x_{CH_4}}(x_{dyn_1}, x_{dyn_2}, x_{stat_1}, x_{stat_2}, x_{stat_3}, r, x_{stat_5}, x_{stat_7}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \quad (42) \\ 0 = x_{stat_6} - f_{DH.D.x_{C_2H_4}}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_2) \\ 0 = \frac{x_{stat_7 i} - x_{stat_7 i-1}}{\Delta r} - f_{DH.D.x_{C_2H_6}}(x_{dyn_1}, x_{dyn_2}, x_{stat_1}, x_{stat_2}, x_{stat_3}, r, x_{stat_5}, x_{stat_7}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \\ 0 = \frac{x_{stat_8 i} - x_{stat_8 i-1}}{\Delta r} - f_{DH.D.x_{C_3H_6}}(x_{dyn_1}, x_{dyn_2}, x_{stat_1}, x_{stat_2}, x_{stat_3}, r, x_{stat_5}, x_{stat_7}, x_{stat_8}, x_{stat_9}, x_{stat_{10}}) \\ 0 = x_{stat_9} - f_{DH.D.x_{C_3H_8}}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_2) \\ 0 = x_{stat_{10}} - f_{DH.D.x_{H_2}}(x_{stat_5}, x_{stat_7}, x_{stat_8}, u_2) \\ y = g_{DH}(x) \end{array} \right.$$

## 4.6 Manipulation of open loop simulation of the DH phase

### 4.6.1 Organization of the files

As the system is complicated, in order to well organize the coding of the model, we have several files as follows:

- a function main.m program used to start the simulation
- a function initialize\_offline\_all\_constants.m allows to initialize the constants parameters
- a function initialize\_offline\_initial\_state\_model.m to initialize the initial condition
- a function compute\_dh\_model.m allows computing online the model
- a function compute\_S0\_or\_process\_state\_dh.m allows to specify, the dynamic equations of the process and (S0 model)
- a function split\_x\_dyn\_k\_x\_stat\_k.m allows to transfer the matrix of states into matrix of static states and dynamic states
- a function merge\_x\_dyn\_k\_x\_stat\_k.m allows to transfer the matrix of static states and dynamic states into matrix of states
- a function plot\_my\_figures.m allows to plot the final results
- 17 functions compute\_dh\_function.m allows to compute the factors we need in the calculation of the system

### 4.6.2 Initialization of all constants parameters

We construct a function [constant,c,m,o,p,t]=initialize\_offline\_all\_constants that will be called at the beginning of main.m in order to define constant, model parameters and time parameters. We give each of them a structure.

By example, all the model parameters are set as

- m.parameter for the simple parameters
- m.size.paramter for initialize the size of the matrix
- m.u.openloot.parameter for the controls

### 4.6.3 Function of the dynamic equations of the process

As all constants have been initialized, we can start coding of the function of the system. According to (30), we initialize the 2 dynamic model states as xdyn and 10 static states as xstat, with the matrix size of which is defined in the structure m.

Ode15s receive and return a column vector, so in the beginning; we have to transpose all the model states.

As the model is complicated, we call 17 function established to calculate the factors in the equations.

With the finite difference method, according to (42), each model states is defined as a vector of size  $r_i$ , where the finite number points of discretization  $r_i$  for  $i = \{0, 1, \dots, N\}$ . Each element

of the matrix gives the dynamic of the system.

#### 4.6.4 simulation with ode15s

As described in 4.4, we have to initialize a singular mass matrix M in order to separate the dynamic states and static states.

With a lot of work in the Ode15s, the result of simulation is not satisfied because the dynamic of the system is not clear. We observed that the model states stay always at the initial condition.

### 4.7 Correction of the coding

#### 4.7.1 Verification of ode15s

As we haven't found the error with several tries, we started to verify if the ode15s is correct.

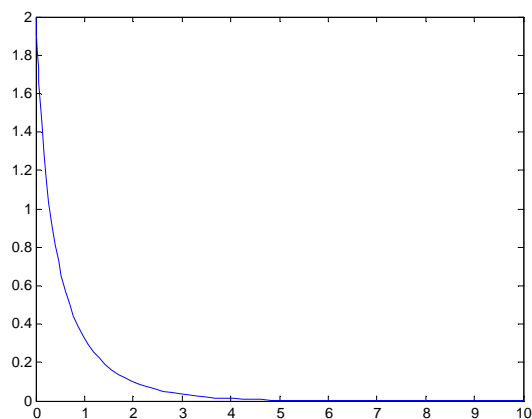
##### 4.7.1.1 Try with a simple DAE (finite dimension)

Considering a system as follows:

$$\begin{cases} y_1' = -y_1 + y_2 \\ y_1^2 + y_2 = 0 \end{cases} \quad (43)$$

We set M as [1 0 ; 0 0], and the initial condition for  $y_1$  as 2

We obtained the figure as follows:



(figure 5)

The figure of y1 verifies that ode15s operated well in this case.

#### 4.7.1.2 Try with a simple DAE (infinite dimension)

Considering a system as follows:

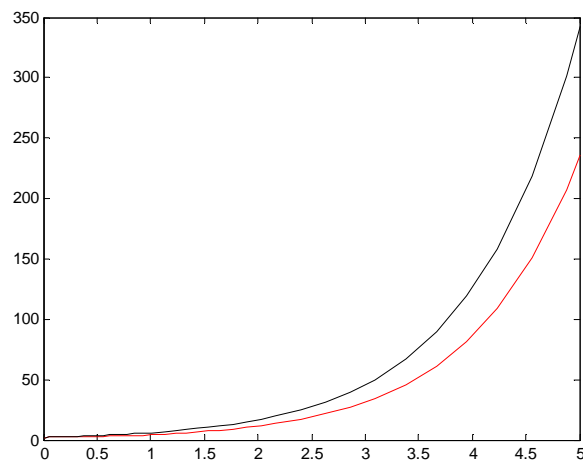
$$\begin{cases} \frac{\partial x_1}{\partial t} = x_1 + x_2 \\ \frac{\partial x_2}{\partial r} = x_1 x_2 \end{cases}$$

(44)

which has the same type of our complicated system .

We consider the size of vector or number of discretization points as 3. The boundary condition of x2 is 1, the initial condition for x1 x2 is [2 2 2;1 1 1],and set M with the same method in 4.5.4

We obtained the figure as follows:



(figure 6)

The figure of the 2 first points of y1 verifies that ode15s operated well in this case.

As a result of the simulation of two simple systems, the solver ode15s can solve our problem.

#### 4.7.2 Options of ode15s

In order to find where the problem lays in, we tried to check all the options of ode15s

#### 4.7.2.1 RelTol, AbsTol

Our problem is that the values of the system do not move. I think the numerical problem most probable is that the tolerance too small for the function to integrate.

Considering  $\frac{\Delta x}{x} = 0.1\%$ , this step size tolerance of integration permit us to calculate the system. So we have to set the absolute error tolerances AbsTol as a column matrix as  $m.AbsTol=[10^{-12} \ 10^{-12} \ 10^{-3} \ 10^{-1} \ 10^{-1} \ 10^{-4} \ 10^{-4} \ 10^{-4} \ 10^{-4} \ 10^{-4} \ 10^{-4} \ 10^{-4}]'$ ,

Then we set the scalar relative error tolerance RelTol 1e-3 by default.

After the simulation, the system stay the same error, so there will be some other problem.

#### 4.7.2.2 JPattern

In the help of matlab concerning ode15s, we find the sentences as follows:

If there are many differential equations, it is important to exploit sparsity:

- Return a sparse  $M(t,y)$ .
- Supply the sparsity pattern of  $\frac{\partial f}{\partial y}$  using the JPattern property or a sparse  $\frac{\partial f}{\partial y}$  using the Jacobian property.

After the try, unfortunately, this did not work.

#### 4.7.2.3 Mass

As we have described at 4.4,we should set a matrix 'Mass' in order to separate the algebraic equations and differential equations.

#### 4.7.2.4 Mass Singular

In 4.6.1, we have simulated two systems with ode15s.As the Mass is singular; we set yes for this option. However, in this case where the system is complicated, even if the Mass is always singular, I get the error message:

??? Error using ==> daeic12 at 167  
Need a better guess y0 for consistent initial conditions.

Maybe the initial guess is too far away from the correct value, and the solver fails. We have to start from a physically senseful solution because it is this solution which is the basis for the following time integration.



We tried to calculate this solution by using MATLAB's `fsolve` before calling the DAE integrator.

### 4.7.3 Consistent initial conditions

#### 4.7.3.1 FSOLVE

`x = fsolve (fun, x0, options)` solves the equations with the optimization options specified in the structure options. Use `optimset` to set these options.

FSOLVE attempts to solve equations of the form:  
 $F(X) = 0$  where  $F$  and  $X$  may be vectors or matrices.

In our case, in order to calculate the consistent initial condition, we set the fun in the form  $F(X) = 0$ , with the equations obtained in 4.6.3 by finite difference method. And the initial condition of `fsolve` is the initial condition of the model.

When we start the simulation, the problem appears. Matlab shows: "fsolve stopped because the relative size of the current step is less than the selected value of the step size tolerance, but the vector of function values is not near zero as measured by the selected value of the function tolerance." That means the integration stops before the solver finds the minimal value. We consult the value we have found with the calculate. There are jumps of values in the last number in the vector of the variable. Some values became negative, which is not available physically. The problem lies in the boundary condition at  $r=r_0$  with the states  $C_M, C_m, C_2H_4, C_2H_6, C_3H_6, CH_4, H_2$

As some values of the states become negative, we try to limit the states in the functions, or try another solver.

#### 4.7.3.2 lsqnonlin

`Lsqnonlin` can solve the equations limiting the values positive. We have tried the same method to calculate the consistent initial condition.

When the program is simulated, Matlab shows " Optimization terminated: search direction less than TolX."

In order to solve this problem, we have lower the TolX. However, even if we set TolX  $10e-20$ , the problem remains.

## 5 Conclusion and perspective

### 5.1 Conclusion

We are interested in the synthesis of the model and using the optimal control (which has never been studied for this process by LAGEP) to control the system. However, we haven't arrived the step of control.

The work consists of modeling of the process and simulation of the system. We had written the full model form of PDE dynamic system exploitable from an automatical viewpoint. We have worked for the numerical simulation for the model of dehydrogenation. With 31 matlab files and 1774 lines of codes, we tried to simulate the system with the finite difference method. Unfortunately the dynamic of the system do not work, even if a lot of works have been realized in searching the error.

### 5.2 Perspective

It's not easy to communicate with the ECUST specialist in distance, if there is some problem in the model. In my opinion, the problems where I can't succeed to simulate the system are:

- problem of the model(initial condition is not consistent or some value of model is not available)
- check if all constants, including those remaining in the equations, are expressed numerically in the right SI units
- inside code problem matlab(some options we haven't recognized)

We have to discuss with ECUST for ask

- if the dynamic equations (especially for  $C(t)$ ) is from an experimental analyze with a certain manipulated variable already chosen
- if the system is just available for this manipulated variable.

As the system to simulate is complicated and there is a new part for me also for my teacher Mr. Dufour. We suggest having a system less complex which is reduced. We should have started the work for the control.

And our plan for the control study is the following:

- open loop study of the DH phase
  1. code validation
  2. MV sensitivity analysis
  3.  $T_{DH}$  sensitivity analysis
- open loop study of the RG phase
  1. code validation
  2. MV sensitivity analysis
  3.  $T_{DH}$  sensitivity analysis

- open loop study of DH+RG+DH+RG... for different  $T_{DH}/T_{RG}$  ratio ( $T_{DH}$  and  $T_{RG}$  constant)
  - MV sensitivity analysis: 1 MV during DH + 1 MV during RG
  - MV sensitivity analysis: 2 MV during DH + 1 MV during RG
  - MV sensitivity analysis: 1 MV during DH + 2 MV during RG
  - MV sensitivity analysis: 2 MV during DH + 2 MV during RG
  
- Closed loop study of DH+RG+DH+RG... for different  $T_{DH}/T_{RG}$  ratio ( $T_{DH}$  and  $T_{RG}$  constant)
  - 1 MV during DH + 1 MV during RG
  - 2 MV during DH + 1 MV during RG
  - 1 MV during DH + 2 MV during RG
  - 2 MV during DH + 2 MV during RG

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## 7 Annexes

### 7.1 DH model additional equations

#### 7.1.1 Gas heat capacity

The correlation for gas heat capacity is a series expansion in temperature [7]:

$$\begin{cases} c_{pAr}(T) = 20.786 + 2.82591 \cdot 10^{-7} T - 1.46419 \cdot 10^{-7} T^2 + 1.09213 \cdot 10^{-8} T^3 - 3.66137 \cdot 10^{-8} / T^2 \\ c_{pCH_4}(T) = 25.360 + 168.678 \cdot 10^{-4} T + 713.121 \cdot 10^{-7} T^2 - 408.371 \cdot 10^{-10} T^3 \\ c_{pC_2H_4}(T) = 3.798 + 156.498 \cdot 10^{-3} T - 834.666 \cdot 10^{-7} T^2 + 175.615 \cdot 10^{-10} T^3 \\ c_{pC_2H_6}(T) = 8.181 + 161.465 \cdot 10^{-3} T - 400.710 \cdot 10^{-7} T^2 - 694.209 \cdot 10^{-11} T^3 \\ c_{pC_3H_6}(T) = 5.084 + 225.639 \cdot 10^{-3} T - 999.265 \cdot 10^{-7} T^2 + 133.106 \cdot 10^{-10} T^3 \\ c_{pC_3H_8}(T) = -5.338 + 310.239 \cdot 10^{-3} T - 164.640 \cdot 10^{-7} T^2 + 346.908 \cdot 10^{-10} T^3 \\ c_{pH_2}(T) = 29.062 - 0.820 \cdot 10^{-2} T + 1.9903 \cdot 10^{-6} T^2 \end{cases} \quad (45)$$

Mixture heat capacity is calculated using the following expression:

$$C_{pm}(x_i, T) = \sum x_i c_{pi}(T) \quad i \in \{Ar, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, H_2\} \quad (46)$$

#### 7.1.2 Gas mixture viscosity

The correlation for gas mixture viscosity is also a series expansion in temperature [9]:

$$\begin{cases} \mu_{Ar}(T) = 0.26324 - 9.3755310^{-4} T + 1.2768 \cdot 10^{-6} T^2 - 5.33333 \cdot 10^{-10} \cdot T^3 \\ \mu_{CH_4}(T) = -0.08525 + 3.4353810^{-4} T - 3.7285 \cdot 10^{-7} T^2 + 1.5 \cdot 10^{-10} \cdot T^3 \\ \mu_{C_2H_4}(T) = -0.03837 + 1.6706910^{-4} T - 1.596 \cdot 10^{-7} T^2 + 6.66667 \cdot 10^{-11} \cdot T^3 \\ \mu_{C_2H_6}(T) = 0.02496 - 7.1819310^{-5} T + 1.3095 \cdot 10^{-7} T^2 - 5 \cdot 10^{-11} \cdot T^3 \\ \mu_{C_3H_6}(T) = 0.03908 - 1.3223910^{-4} T + 2.0825 \cdot 10^{-7} T^2 - 8.33333 \cdot 10^{-11} \cdot T^3 \\ \mu_{C_3H_8}(T) = 0.05118 - 1.7194910^{-4} T + 2.469 \cdot 10^{-7} T^2 - 1 \cdot 10^{-11} \cdot T^3 \\ \mu_{H_2}(T) = -0.07956 + 3.24538 \cdot 10^{-4} T - 3.7285 \cdot 10^{-7} T^2 + 1.5 \cdot 10^{-10} \cdot T^3 \end{cases} \quad (47)$$

Mixture gas mixture viscosity is calculated using the following expression:

$$\mu(x_i, T) = 10^{-3} \cdot \sum x_i \mu_i(T) \quad i \in \{Ar, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, H_2\} \quad (48)$$

#### 7.1.3 Reaction heat

Respectively, reaction heat of propane dehydrogenation and cracking is as follow [7]:

The ultimate expressions of reaction heat are as follows: [9]

$$\begin{cases} H_1(T) = (116.0754 + 39.484 * 10^{-3}T - 46.4 * 10^{-6}T^2 + 222.346 * 10^{-10}T^3 - 53.4505 * 10^{-13}T^4) \cdot 10^3 \\ H_2(T) = (75.8671 + 34.4960 * 10^{-3}T - 68.45 * 10^{-6}T^2 + 508.3 * 10^{-10}T^3 - 144.916 * 10^{-13}T^4) \cdot 10^3 \\ H_3(T) = (-130.5246 - 24.6790 * 10^{-3}T + 6.5835 * 10^{-6}T^2 + 138.0177 * 10^{-10}T^3 - 61.2590 * 10^{-13}T^4) \cdot 10^3 \end{cases} \quad (49)$$

## 7.2 RG model: additional equations

### 7.2.1 Heat capacity of gas mixture

$$\begin{cases} C_p(T, x_{O_2}) = c_{pN_2}(T)x_{N_2} + c_{pO_2}(T)x_{O_2} \\ c_{pN_2}(T) = 26.092 + 8.218801 \cdot T - 1.976141 \cdot T^2 + 0.15924 \cdot T^3 + 0.044434 / T^2 \\ c_{pO_2}(T) = 29.659 + 6.137261 \cdot T - 1.186521 \cdot T^2 + 0.09578 \cdot T^3 - 0.219663 / T^2 \\ x_{O_2} + x_{N_2} = 1 \end{cases} \quad (50)$$

### 7.2.2 gas viscosity

calculation for gas viscosity (Leonard-Jones model) [7]:

$$\begin{cases} \mu_i(T) = 2.669 \frac{(M_i T)^{1/2}}{Q_i^2 \Omega_v(T)} & i \in \{N_2, O_2\} \\ \Omega_v(T) = \frac{1.16145}{T_N(T) 0.14874} + \frac{0.52487}{\exp(0.77320 T_N)} + \frac{2.16178}{\exp(2.43787 T_N(T))} \\ T_N(T) = \frac{T}{k_{vi}} \end{cases} \quad (51)$$

and mixing rules (Sutherland rules) is given by [7]:

$$\begin{cases} \mu_{mix}(T, x_i) = \sum_{i=1}^n [x_i \mu_i(T) / (\sum_{j=1}^n x_j \phi_{ij}(T))] & i \in \{N_2, O_2\} \\ \phi_{ij}(T) = \frac{[1 + (\mu_i(T) / \mu_j(T))^{1/2} (M_j / M_i)^{1/4}]^2}{[8(1 + M_i / M_j)]^{1/2}} \\ \phi_{ji}(T) = (\mu_j(T) / \mu_i(T)) (M_i / M_j) \phi_{ij}(T) \end{cases} \quad (52)$$

In our model, we have N2 and O2, which gives [7]:

$$\begin{cases}
\mu_{mix}(T, xO_2) = x_{N_2}\mu_{N_2}(T)/(x_{N_2}\phi_{11}(T) + x_{O_2}\phi_{12}(T)) + x_{O_2}\mu_{O_2}(T)/(x_{N_2}\phi_{21}(T) + x_{O_2}\phi_{22}(T)) \\
\text{where} \\
\phi_{11}(T) = ((1 + (\mu_{N_2}(T)/\mu_{N_2}(T))^2 \cdot (M_{N_2}/M_{N_2})^4))^2 / (8(1 + M_{N_2}/M_{N_2}))^2 \\
\phi_{12}(T) = ((1 + (\mu_{N_2}(T)/\mu_{O_2}(T))^2 \cdot (M_{N_2}/M_{O_2})^4))^2 / (8(1 + M_{N_2}/M_{O_2}))^2 \\
\phi_{21}(T) = (\mu_{O_2}(T)/\mu_{N_2}(T)) \cdot (M_{N_2}/M_{O_2})\phi_{12}(T) \\
\phi_{22}(T) = ((1 + (\mu_{O_2}(T)/\mu_{O_2}(T))^2 \cdot (M_{O_2}/M_{O_2})^4))^2 / (8(1 + M_{O_2}/M_{O_2}))^2
\end{cases} \quad (53)$$

### 7.2.3 gas thermal conductivity

$$\begin{cases}
\lambda_{mix}(T, x_{O_2}) = \frac{\sum_{i=1}^n x_i \lambda_i(T)}{\sum_{j=1}^n x_j A_{ij}(T)} & i, j \in \{N_2, O_2\} \\
A_{ij}(T) = \frac{1}{4} \left\{ 1 + \left[ \frac{\mu_i(T)}{\mu_j(T)} \left( \frac{M_j}{M_i} \right)^{3/4} \frac{T + S_i}{T + S_j} \right]^{1/2} \right\}^2 \frac{T + S_{ij}}{T + S_i} \\
S_i = 1.5(T_{bi}) \\
S_{ij} = S_{ji} = (S_i S_j)^{1/2}
\end{cases} \quad (54)$$

gas thermal conductivity values was got from regression of experimental data:

$$\begin{cases}
\lambda_{N_2}(T) = -0.03502 + 0.01051T - 6.66313e-6T^2 + 2.66786e-9T^3 \\
\lambda_{O_2}(T) = 0.01272 + 0.00978T - 4.11708e-6T^2 + 1.3853e-9T^3
\end{cases} \quad (55)$$

### 7.2.4 Influence of pore diffusion

The effectiveness factor  $\eta$  is the ratio of the rate constant with pore diffusion resistance to the intrinsic rate constant. The effectiveness factor and so-called Thiele modulus expression (for a coked catalyst with a uniform carbon load BC) is given by [1]:

$$\begin{cases}
\eta(C_M, C_m, P, T_{as}) = \frac{1}{\phi(C_M, C_m, P, T_{as})} \left( \frac{1}{\tan(3\phi(C_M, C_m, P, T_{as}))} - \frac{1}{3\phi(C_M, C_m, P, T_{as})} \right) \\
\phi(C_M, C_m, P, T_{as}) = \frac{V_m}{A_m} \sqrt{\frac{k(T_{as})(C_M + C_m)}{D_{eff,A}(P, T_{as})}}
\end{cases} \quad (56)$$

where [9]:

$$k(T_{as}) = k_0 e^{\left( \frac{-1000E_a}{R} \left( \frac{1}{T_{as}} - \frac{1}{T_0} \right) \right)} \quad (57)$$

More details about constant and variables are in tables (in the annex).

The effective diffusivity of oxygen in the porous catalyst is defined as [1]:

$$\left\{ \begin{array}{l} D_{eff,A}(P, T_{as}) = \frac{\varepsilon_p}{\tau_p} D_{A,pore}(P, T_{as}) \\ D_{A,pore}(P, T_{as}) = \left( \frac{1}{D_{A,mol}(P, T_{as})} + \frac{1}{D_{A,knu}(T_{as})} \right)^{-1} \\ D_{A,mol}(P, T_{as}) = \frac{1 \times 10^{-7} T_{as}^{1.75} \sqrt{1/M_{O_2} + 1/M_{N_2}}}{P \left[ (V_{O_2})_1^{1/3} + (V_{N_2})_2^{1/3} \right]^2} \\ D_{A,knu}(T_{as}) = 97 d_{pore} \sqrt{\frac{T_{as}}{32}} \end{array} \right. \quad (58)$$

More details about constant and variables are in tables (in the annex).

## 7.2.5 Influence of external diffusion

Mass transfer coefficients  $k_G$  and heat transfer coefficients  $h_s$  can be calculation from j factors of mass transfer and heat transfer correlation equations as follow:

$$\left\{ \begin{array}{l} j_D = \frac{k_G(G, T, x_{O_2}) \rho(P, T, x_{O_2})}{G} (Sc(P, T, x_{O_2}))^{2/3} = \frac{0.725}{(\text{Re}(G, T, x_{O_2}))^{0.41} - 0.15} \\ \Rightarrow k_G(P, G, T, x_{O_2}) = \frac{G \cdot 0.725}{\rho(T, x_{O_2}) (Sc(P, T, x_{O_2}))^{2/3} ((\text{Re}(G, T, x_{O_2}))^{0.41} - 0.15)} \\ j_H = \frac{h_s}{Gc_p(T, x_{O_2})} (\text{Pr})^{2/3} = \frac{1.10}{(\text{Re}(G, T, x_{O_2}))^{0.41} - 0.15} \\ \Rightarrow h_s(G, T, x_{O_2}) = \frac{Gc_p(T, x_{O_2}) \cdot 1.10}{(\text{Pr}(T, x_{O_2}))^{2/3} ((\text{Re}(G, T, x_{O_2}))^{0.41} - 0.15)} \end{array} \right. \quad (59)$$

$$\left\{ \begin{array}{l} \text{Re}(G, T, x_{O_2}) = \frac{D_p G}{\mu_{mix}(T, x_{O_2})} \\ Sc(P, T, x_{O_2}) = \frac{\mu_{mix}(T, x_{O_2})}{\rho(P, T, x_{O_2}) D(P, T)} \\ \text{Pr}(T, x_{O_2}) = \frac{c_p(T, x_{O_2}) \mu_{mix}(T, x_{O_2})}{\lambda_{mix}(T, x_{O_2})} \end{array} \right. \quad (60)$$

$$\left\{ \begin{array}{l} \rho(P, T, x_{O_2}) = \frac{PM_g(x_{O_2})}{RT} \\ M_g(x_{O_2}) = M_{N_2}(1-x_{O_2}) + M_{O_2}x_{O_2} \end{array} \right. \quad (61)$$



$$D(P,T) = \frac{0.001 \cdot T^{1.75} \sqrt{\frac{1}{M_{O_2}} + \frac{1}{M_{N_2}}}}{P(V_{O_2}^{\frac{1}{3}} + V_{N_2}^{\frac{1}{3}})^2} \quad (62)$$

More details about constant and variables are in tables (in the annex).

### 7.3 Tables

Table1: list of molecules involved in this work

Symbol	Name
CH4	Methane
C2H4	Ethylene
C2H6	Ethane
C3H6	Propene or propylene
C3H8	Propane
Pt-Sn/Al2O3	Catalyst
H2	Hydrogen
O2	Oxygen

Table2: list of variables involved in the DH model.

$A(r)$	Surface of the reactor	$m^2$
$a(C_M, C_m, T)$	catalyst activity	[-]
$C_m(r, t)$	coke concentration in monolayer	mg coke / mg catalyse
$C_M(r, t)$	coke concentration in multilayer	mg coke / mg catalyse
$c_{pi}(T)$	heat capacity of component i	J / (mole · K)
$C_{pm}(x_i, T)$	Mixture heat capacity	J / (mole · K)
$f_r(n_T, r, T, x_i)$	variable from(48),(59)	[-]
$G(n_T, r, x_i)$	flow rate	kg / (s · m <sup>2</sup> )
$H(T)$	reaction heat	J / mole
$K_1(T)$	propylene adsorption equilibrium constant	[-]
$K_{eq}(T)$	propane dehydrogenation reaction equilibrium constant	pa
$k_i(T)$	reaction rate constant	mg catalyse(mg coke) <sup>-1</sup> min <sup>-1</sup>
$k_{ic}(T)$	reaction rate constant of coke generation	mg catalyse(mg coke) <sup>-1</sup> min <sup>-1</sup>
$M_g(x_i)$	molar mass of gas	kg/mol

$n_T(n_T^0, x_{CH_4}, x_{C_2H_6}, x_{C_3H_8}, x_{H_2}^0)$	<i>transient total flow rate</i>	<i>mol/s</i>
$P(r,t)$	<i>Pressure of gas</i>	<i>pa</i>
$Re(n_T, r, T, x_i)$	<i>Reynolds number</i>	<i>[-]</i>
$r_1(P, T, x_{C_3H_6}, x_{C_3H_8}, x_{H_2})$	<i>Reaction rate of DH</i>	<i>mol/(kg.s)</i>
$r_2(P, T, x_{C_3H_8})$	<i>Reaction rate of cracking</i>	<i>mol/(kg.s)</i>
$r_3(P, T, x_{C_2H_4}, x_{H_2})$	<i>Reaction rate of ethylene hydrogenation</i>	<i>mol/(kg.s)</i>
$T(r,t)$	<i>Temperature of gas</i>	<i>K</i>
$T_{DH}(t)$	<i>duration of phase DH</i>	<i>s</i>
$u(n_T, P, r, T, x_i)$	<i>flow rate</i>	<i>m/s</i>
$x_i(r,t)$	<i>transient mole fraction of component i</i>	<i>[-]</i>
$\alpha_1(T)$	<i>activity variable</i>	<i>(g.cat)(g.coke)<sup>-1</sup></i>
$\mu(T)$	<i>gas mixture viscosity</i>	<i>pa.s</i>
$\mu_i(T)$	<i>mixture viscosity of component i</i>	<i>10<sup>-3</sup> pa.s</i>
$\rho_g(P, T, x_i)$	<i>Gas mixture density</i>	<i>kg/m<sup>3</sup></i>

Table 3. Constant values involved in the DH model.

<i>parameter</i>	<i>Signification</i>	<i>Value(units)</i>
$C_{max}$	<i>maximum coke concentration in monolayer</i>	<i>0.000682(g coke /g cat)</i>
$ds$	<i>equivalent diameter of particle</i>	<i>0.0035m</i>
$E_{a1}$	<i>constant reaction rate1</i>	<i>34573(J/mol)</i>
$E_{a2}$	<i>constant reaction rate2</i>	<i>137310 (J/mol)</i>
$E_{a3}$	<i>constant reaction rate2</i>	<i>154540 (J/mol)</i>
$E_{a1c}$	<i>constant reaction rate3</i>	<i>38430(J/mol)</i>
$E_{a2c}$	<i>constant reaction rate4</i>	<i>125510 (J/mol)</i>
$E_{ar1}$	<i>constant reaction rate5</i>	<i>9610(J/mol)</i>
$K_{01}$	<i>constant reaction rate6</i>	<i>3450[-]</i>
$k_{01c}$	<i>constant reaction rate7</i>	<i>3.9(mg.cat)(mg.coke)<sup>-1</sup> s<sup>-1</sup></i>
$k_{02c}$	<i>constant reaction rate8</i>	<i>2.4167 · 10<sup>-8</sup> (mg.cat)<sup>-1</sup> s<sup>-1</sup></i>
$k_{01}$	<i>constant reaction rate 9</i>	<i>8.7367 · 10<sup>-8</sup> mol · (kg · s · pa)<sup>-1</sup></i>
$k_{02}$	<i>constant reaction rate 10</i>	<i>7.75 · 10<sup>-10</sup> mol · (kg · s · pa)<sup>-1</sup></i>

$k_{03}$	constant reaction rate 11	$3.9333 \cdot 10^{-11} \text{ mol} \cdot (\text{kg} \cdot \text{s} \cdot \text{pa})^{-1}$
$L$	length of reactor	15m
$n_t^0$	initial total molar flow rate	237.55 mol/s
$R$	Ideal gas constant	8.314 J/mol K;
$r_{01}$	activity constant 1	$948.92 (\text{g.cat})(\text{g.coke})^{-1}$
$T_m$	Reference temperature	793.15K
$x_{Ar}^0$	Initial molar fraction of Ar	2/3[-]
$x_{C3H8}^0$	Initial molar fraction of C3H8	1/3[-]
$\alpha_2$	activity constant 2	$399 (\text{g.cat})(\text{g.coke})^{-1}$
$\alpha_3$	activity constant 3	40.07[-]
$\rho_B$	density of catalyst	1000kg/m <sup>3</sup>
$\Delta H$	constant from(4)	-85817 (J/mol)
$\varepsilon$	Bed voidage	0.45[-]

Table 4: list of variables involved in the RG model.

$c_s(T)$	Heat capacity of catalyst	J/(g.K)
$c_p(T, x_{O_2})$	Heat capacity of gas mixture	J/(g.K)
$C_p(T, x_{O_2})$	gas heat capacity thermal capacity	J/(mol.K)
$D(P, T)$	gas diffusion coefficient	m <sup>2</sup> /s
$D_{A, \text{pore}}(P, T_{as})$	combined diffusivity of molecular diffusivity and Knudsen diffusivity	m <sup>2</sup> /s
$D_{A, \text{knu}}(T_{as})$	Knudsen diffusivity	m <sup>2</sup> /s
$D_{A, \text{mol}}(P, T_{as})$	molecular diffusivity	m <sup>2</sup> /s
$D_p(P, T)$	particle diameter	m <sup>2</sup> /s
$f_r(G, T, x_{O_2})$	variable from(106),(117)	[-]
$G(r, t)$	gas mass flow rate	kg/m <sup>2</sup> .s
$h_s(G, T, x_{O_2})$	heat transfer coefficient between fluid and catalyst particles	J/(m <sup>2</sup> .s.K)
$j_D(G, P, T, x_{O_2})$	j factor of mass transfer	[-]
$j_H(G, T, x_{O_2})$	j factor of heat transfer	[-]
$k_G(G, P, T, x_{O_2})$	mass transfer coefficient	m/s
$M_g(x_{O_2})$	Molar mass of gas	[-]
$P(r, t)$	Pressure of gas	Pa
$P_{as}(r, t)$	Pressure drop of bed	Pa

$Pr(T, x_{O_2})$	<i>Prandtl number</i>	<i>[-]</i>
$Re(G, T, x_{O_2})$	<i>Reynolds number</i>	<i>[-]</i>
$r_m(C, P_{as}, T_{as})$	<i>coke burning reaction rate</i>	<i>mol/g.s</i>
$Sc(P, T, x_{O_2})$	<i>schmidt number</i>	<i>[-]</i>
$T(r, t)$	<i>temperature of gas phase</i>	<i>K</i>
$T_{as}(r, t)$	<i>temperature of particle</i>	<i>K</i>
$T_{RG}(t)$	<i>Duration of RG phase</i>	<i>s</i>
$u(G, P, T, x_{O_2})$	<i>Flow rate</i>	<i>m/s</i>
$\eta(C, P, T_{as})$	<i>Effectiveness factors of internal diffusion</i>	<i>[-]</i>
$\lambda_i(T)$	<i>gas thermal conductivity</i>	$10^{-2} J/(m.K.s)$
$\lambda_{mix}(T, x_{O_2})$	<i>gas thermal conductivity</i>	$10^{-2} J/(m.K.s)$
$\mu_i(T)$	<i>gas viscosity</i>	<i>Pa.s</i>
$\mu(T, x_{O_2})$	<i>gas viscosity</i>	<i>Pa.s</i>
$\rho_g(P, T, x_{O_2})$	<i>gas density</i>	$kg/m^3$
$\phi(C, P, T_{as})$	<i>effectiveness factor</i>	<i>[-]</i>
$\Omega_v(T)$	<i>collision integral</i>	<i>[-]</i>

Table 5. Constant values involved in the RG model.

<i>parameters</i>	<i>Signification</i>	<i>Value</i>
$Am$	<i>surface area of particle</i>	$5.931310^{-5} m^2$
$a_m$	<i>effective external surface area per unit mass</i>	$0.9470 m^2/kg$
$Di$	<i>inner diameter of reactor</i>	$1.5m$
$Do$	<i>outer diameter of reactor</i>	$3m$
$Dp$	<i>Particle diameter</i>	$0.0032 m$
$Dpore$	<i>Average pore diameter</i>	$2.8010^{-8} m$
$kvN2$	<i>Characteristic energy parameters of N2 molecular motion k</i>	$71.4[-]$
$kvO2[9]$	<i>Characteristic energy parameters of O2 molecular motion k</i>	$106.7[-]$
$k_0$		$2.7960 \cdot 10^{-8} pa-l.s-l$
$L$	<i>length of reactor</i>	$15m$
$l$	<i>Particle length</i>	$0.0043 m$
$Ms$	<i>Molecule weight of Pt-Sn/Al2O3</i>	$0.101961 kg/mol$
$MO2$	<i>molecular weight of oxygen</i>	$0.032kg/mol$

$MN_2$	<i>molecular weight of nitrogen</i>	$0.028 \text{ kg/mol}$
$QN_2$	<i>Characteristic energy parameters of N2 molecular motion</i>	$3.79810^{-10} \text{ m}$
$QO_2$	<i>Characteristic energy parameters of O2 molecular motion</i>	$3.46710^{-10} \text{ m}$
$R$	<i>Ideal gas constant</i>	$8.314 \text{ J/mol K}$
$S_i$	<i>Sutherland constant</i>	$[-]$
$V_m$	<i>volume of particle</i>	$3.458310^{-8} \text{ m}^3$
$\Delta H$	<i>Reaction heat</i>	$-393.510^3 \text{ J/mol}$
$\Delta H_r$	<i>reaction heat</i>	$-393.510^3 \text{ J/mol}$
$\rho_B$	<i>Particle density</i>	$1000 \text{ g/m}^3$
$\epsilon_p$	<i>Catalyst particle porosity</i>	$0.56[-]$
$\tau_p$	<i>Tortuosity</i>	$1.3333-$
$\epsilon$	<i>Bed voidage</i>	$0.45[-]$