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EXECUTIVE SUMMARY OF THE THESIS

Improvement of MADSim reaction environment and case-study related to methanol production

LAUREA MAGISTRALE IN CHEMICAL ENGINEERING - INGEGNERIA CHIMICA

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1. Introduction

Process simulation rises as one of the most discussed topic regarding process systems engineering: the possibility to recreate a real facility or simulate even a non-existing system helps the engineer in his work, giving a reliable instrument. Therefore, the so called *digital twin* becomes crucial in accordance to its trustworthiness.

Nowadays, the description of unsteady behaviour draws the attention due to the lack of well-established dynamic simulators. Back in the days, *MADSim* was developed laying the foundations for a competitive and performing software.

As described by its author Russo [7], the program is coded in the C++ language, following the idea of *object oriented programming* (OOP): the high level of customization is reached by the modular approach, which is granted by the selected language, in fact *MADSim* stands for "*Modular Advanced Dynamic Simulation*". More more new elements can be added to existing core as done for the work proposed by this thesis project.

Since the absence of a heterogeneous kinetics model and of a generic tubular reactor, the topic

attracted the interest, inspiring the coding of such elements in the work here described. Moreover, the will of validating *MADSim* with an existing and well-established process led to the choice of methanol production: after an investigation on the subject, a simple model for a tubular reactor and the Vanden Bussche and Froment (VBF) kinetic model [3] were considered simulating the system in *MADSim*.

2. Heterogeneous kinetic model

Since the *ChemicalReaction* environment was incomplete due to the lack of a generalized model, the implementation of the heterogeneous kinetic was conducted. Starting with the existing classes capable to deal with basic situations, such as the *Arrhenius law* (equation 1) for the kinetic constant and the *power law* (equation 2) for homogeneous and pseudo-homogeneous reactions, the complete model was developed.

$$k_i = A_i \cdot \exp\left(-\frac{Ea_i}{RT}\right) \quad (1)$$

where k_i is the generic kinetic constant, A_i is the corresponding pre-exponential factor, Ea_i is the associated activation energy, R is the ideal gas constant, and T is the temperature of the

system. Both k_i and A_i have the same unit of measure which depends on the one of the reaction rate and the associated bases, therefore it can be anything as long as the accordance between units is present.

Furthermore, the *power law* is here presented.

$$r_j = k_j \cdot \prod_i^{NC} a_{ij}^{b_{ij}} \quad (2)$$

where k_j is the kinetic constant even here considered in accordance with the *Arrhenius* formulation, a_{ij} is the selected basis which could be both the concentration or the partial pressure for the species i in the reaction j , and b_{ij} is the associated exponent.

2.1. Proposed model

Following the description of the reaction environment as a multiple steps based system, comprehending different stages of reaction, some theories arise: Langmuir–Hinshelwood–Hougen–Watson (LHHW) proposal, the Eley–Rideal (ER) kinetics or even the redox derived formulations. For this reason the overall reaction is written as a composition of the contributions of the direct reaction, the inverse one, and all the adsorption-desorption related, where the first two appear in the numerator and all the catalyst-linked interactions are collected in the denominator term. Therefore, the final formulation it is here presented:

$$r = \frac{\overrightarrow{k}_{dir} \cdot \prod_i^{NC} a_i^{b_i} - \overleftarrow{k}_{inv} \cdot \prod_i^{NC} a_i^{b_i}}{\left(1 + \sum_j^{NK} K_j \cdot \prod_i^{NC} a_{ij}^{b_{ij}}\right)^n} \quad (3)$$

where \overrightarrow{k}_{dir} , \overleftarrow{k}_{inv} , and K_j are the kinetic constants of the direct, inverse and adsorption reactions respectively. These constants follow the *Arrhenius law* (equation 1). Continuing, NC is the number of components involved in the reaction, Π is the symbol of consecutive multiplications, and Σ is the symbol of consecutive summations. Finally, a_i is the considered basis describing the compound i , which is usually the partial pressure or the composition, and b_i is the associated exponent.

The formulation presented in equation 3 is supported by a similar format present in the Aspen HYSYS[®] environment, which is a well-established chemical process simulator, being

also a source of inspiration for MADSim, in particular for the just presented topic.

Returning to the rate construction, the function works according to the following steps:

1. collect all the kinetic constants as Arrhenius pointer, giving the pre-exponential factors and the activation energies, paying attention to divide them (during the setting procedure) into direct reaction, inverse one and vector of adsorption-desorption mechanisms (denominator side);
2. convert the vector of the denominator sub-reactions in the value which describes how many adsorption-desorption contributions are there, exploiting the *size* function;
3. extract the concentrations (for *Heterogeneous_KinModel_Concentration*) and eventually transform them into partial pressures (for *Heterogeneous_KinModel_PartialP*) thanks to *ideal gas law*;
4. calculate both the direct and the inverse reaction rate, and all denominator ones, knowing that they are singularly considered as power law (equation 2), exploiting a *for* cycle for the denominator rates;
5. construct the overall rate according to equation 3.

Once the kinetics is set, the system is completed with the insertion of the stoichiometry and the components. Then all the other calculations are described in *ChemicalReactions* class, where the information enters via the methods *setStoichiometry*, *setKinetics*, and *setComponents*.

2.2. Validation

The validation was attempted for the kinetics on the old alkylator reactor model. The output of the specific system for the benzene alkylation was compared with the reactor model proposed by Russo [7].

Since the unit is the same, the only difference lies on the operative kinetics: this evidence permitted a proper conduction of the comparison. Two images are proposed, one describing the evolution of molar fraction of the product, the ethylbenzene, the other shows the change of the temperature which results interesting to analyze thanks to the adiabatic nature of the reactor.

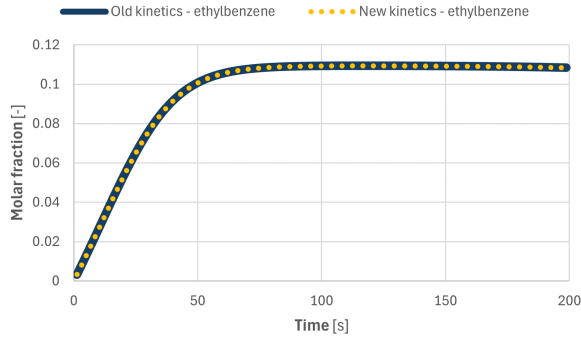


Figure 1: Comparison of the molar fraction of ethylbenzene evolution in time performing the simulation with the kinetics built by Russo [7] and the one proposed.

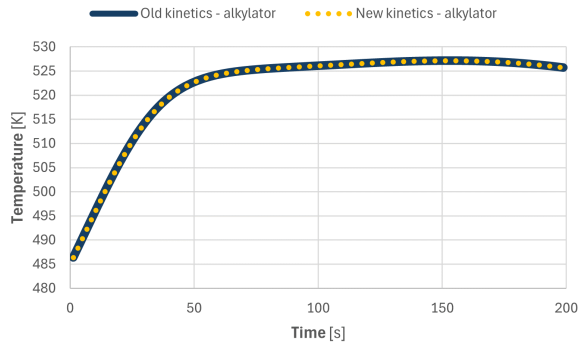


Figure 2: Comparison of the temperature evolution in time performing the simulation with the kinetics built by Russo [7] and the one proposed.

It is possible to appreciate the perfect fitting between the simulations performed exploiting the old model and the new one. For that reason the implementation of the kinetic model is proved as valid and fully functional.

3. Tubular reactor

To perform a good simulation, a tubular reactor model results to be a turning point; in fact, the presence of such a unit permits to cover a large assortment of different processes. It is possible to build a custom reactor starting with a simple model; the main operative choice falls on a tubular reactor, having the following characteristic:

- Cylindrical shape;
- Catalytic;
- Non adiabatic.

From the point regarding the shape of the reactor, the most immediate choice lies on a model

similar to a plug flow reactor (PFR), leading to a set of differential equations, even for the steady state simulation; for the reason of modeling, some simplifications occurred: the tube is simulated dividing its environment into ten different sub-volumes which are governed by the material balance equations (one for each species) presented as follows.

$$\frac{d\dot{n}_i}{dt} = \dot{n}_{in,i} - \dot{n}_{out,i} + \sum_j^{NK} \nu_{ij} r_j V \quad (4)$$

where $\frac{d\dot{n}_i}{dt}$ is the accumulation term, in particular, it is the time derivative of the molar flow of the species i , $\dot{n}_{in,i}$ is the molar inlet flow associated to species i , $\dot{n}_{out,i}$ is the molar outlet flow associated to species i . To be more precise, inlet and outlet flows are associated to the idea of having a continuity inside the reactor, therefore the inlet of a sub-volume is the outlet of the previous one. Continuing, NK is the number of reactions involved in the system, r_j is the rate associated to reaction j , ν_{ij} is the stoichiometric coefficient associated to the species i in the reaction j , and V is the volume of the sub-volume considering the vacuum coefficient since the remaining part is occupied by the catalyst.

To describe the non adiabatic nature of the reactor, or in other words, the presence of a cooling or heating system the following equation rises.

$$\frac{dT}{dt} = \frac{\dot{H}_{in} - \dot{H}_{out} - \sum_j^{NK} r_j \cdot \Delta H_{reac,j} \cdot V - \dot{Q}}{n_{tot} \cdot \tilde{c}_{p,mix}} \quad (5)$$

where $\frac{dT}{dt}$ is the time derivative of the temperature, \dot{H}_{in} is the inlet enthalpy flow, which is strictly related to the inlet mass stream and to its molar enthalpy, \dot{H}_{out} is the outlet enthalpy flow, which is strictly related to the outlet mass stream and to its molar enthalpy, NK is the number of reactions involved in the system, r_j is the rate associated to reaction j , $\Delta H_{reac,j}$ is the heat of reaction j , V is the control volume, n_{tot} is the total number of moles inside the control volume, and $\tilde{c}_{p,mix}$ is the specific heat of the mixture in molar basis. To better describe the equation, further explanation is presented: the considered control volume is the one of sub-volumes which form the overall equipment, at the denominator

n_{tot} and $\tilde{c}_{p,mix}$ are properties extrapolated via internal calculation in the software, $\Delta H_{reac,j}$ represents the enthalpy of reaction, having its own mathematical expression, obtained in a method inside the *ChemicalReactions* class, and finally, \dot{Q} is the element related to heat exchange. Moreover, the heat flux, due to the presence of the utility, is shown hereinafter.

$$\dot{Q} = U \cdot A_{lat} \cdot (T - T_{utility}) \quad (6)$$

3.1. Program interaction

The proposed model is inserted into the software via the *Builder* class: this procedure exploits the pattern methodology, and in particular the builder one which is categorized as a creational one due to its function. Continuing, in the dynamic simulation environment of MAD-Sim, the tubular reactor is seen as a flow device; this kind of representation is governed by flow conductance J as it is possible to appreciate in resistance equation presented hereinafter.

$$W = J \sqrt{\frac{\Delta P}{\rho}} \quad (7)$$

where W is the mass flow rate and Δ stands for difference between outlet and inlet, in this case of pressures. Finally, ρ is the density which is the one of exiting stream in the presented case; this last point is highlighted due to the fact that different choices can be made [6].

3.2. Validation

Focusing the attention on the tubular reactor model, a comparison between the alkylator simulated using the specific class and the one performed exploiting the generalized model, adjusted for the occasion, was conducted. The visual results were realized supplying two graphical elaborations: the first one provides for a plot of ethylbenzene (the valuable product) molar fraction changing in time (*figure 3*), while the second one represents the evolution of temperature in time (*figure 4*).

Even in this validation procedure the term of comparison is the old model taken from the work of Russo [7].

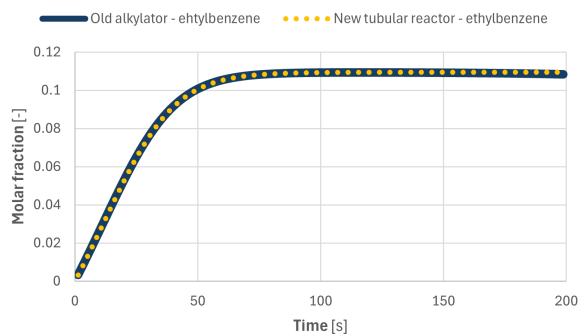


Figure 3: Comparison of the molar fraction of ethylbenzene evolution in time performing the simulation with the old alkylator by Russo [7] and the new tubular reactor.

Looking at the presented plot it is possible to affirm that the old alkylator and the new reactor model result in a similar behavior: this is true in the case of molar fraction, while in the next graph a slight deviation happens; for temperature-time diagram, the majority of the values coincide between the two simulations, near to the end instead, a different path is covered by the models. Even if the perfect fit is not observed in *figure 4*, this uncertainty should be supported or denied by mathematical evidence. Evaluating the percentage deviation of every point turns out that maximum value is 0.3%, proving in this way the validity of the proposal.

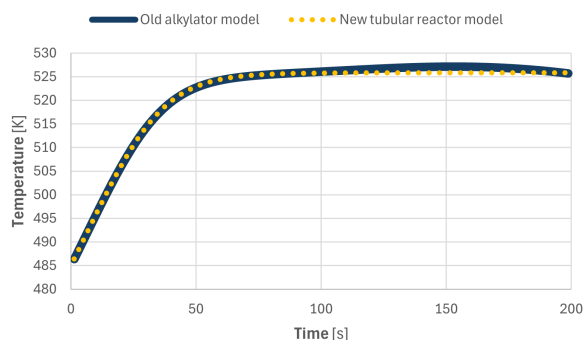


Figure 4: Comparison of the temperature evolution in time performing the simulation with the old alkylator by Russo [7] and the new tubular reactor.

4. Methanol

Since methanol is a key component in the chemical industry, being a widespread intermediate,

a solvent, and nowadays a largely studied hydrogen carrier, an investigation on the topic is conducted. Moreover, a simulation in MADSim is presented in order to cover both the subject around this compound and the proof of validity for the newly implemented heterogeneous kinetics and the tubular reactor models.

To characterize the stream fed to the reactor, in continuity with researches on exploitation of innovative sources, it is simulated as a recycled waste gas: the composition is based on the study conducted by Leonzio [5], while the operating conditions come from the theory [4]. To be precise the values used for the simulation, even if they resemble the reality, derive from arbitrary choices.

Hereinafter the simulated stream is shown.

Table 1: Composition and physical properties of the inlet gas stream (reagents).

Properties	Value	Unit
Mass flow rate F	0.01	[kg/s]
Temperature T	520	[K]
Pressure P	69.7	[bar]

Molar composition	Value	Unit
x_{CO_2}	0.21	[-]
x_{CO}	0.07	[-]
x_{H_2}	0.72	[-]
x_{H_2O}	0.00	[-]
x_{MeOH}	0.00	[-]

Continuing the reactor is sized according to the common practice: in particular, the geometrical configuration and flow conductivity are chosen in this way, exploiting typical numbers. For the catalyst, some extra investigations are conducted: the pellets utilized in this kind of process are usually made of copper, zinc and aluminium oxides as explained by Bozzano and Marenti [2]. Even in this instance the numbers used for the case-study are selected from typical ranges which can be find in real facilities. The final outcome for the design procedure is presented as follows.

Table 2: Design parameters for the catalytic tube.

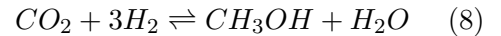
Parameters	Value	Unit
Flow conductance	$7 \cdot 10^{-6}$	[kg/m]
Radius	0.02	[m]
Length	9.0	[m]
Catalyst density	1170.0	[kg/m ³]
Vacuum fraction	0.387	[-]
Heat transfer coeff.	$3.7 \cdot 10^6$	[W/m ² /K]
Utility temperature	520.0	[K]

4.1. Vanden Bussche and Froment kinetic model

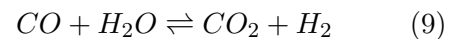
The simulation is performed exploiting the *Vanden Bussche and Froment kinetic model* [3]; the choice was done with support of the work presented by Bisotti et al. [1].

The model starts with the hypothesis of CO₂ as main source of carbon and passes through the idea of describing the reaction system considering the water gas shift, proceeding along a redox mechanism [3]. Moreover, the considered reactions are presented as follows.

- Carbon dioxide hydrogenation:



- Water gas shift (WGS):



As mentioned above, the simulation of the methanol reactor is performed in MADSim exploiting the kinetic model compiled with the value presented by Vanden Bussche and Froment [3].

4.2. Validation

To exhibit the dynamic nature of MADSim, the outlet stream, exiting from the reactor, starts with the same value imposed for the raw material (*table 1*). Being the inlet gas flow constant, the modifications happened are appreciable in the stream placed after the reactor. This evolution of composition and temperature are reported in the two graphs below.

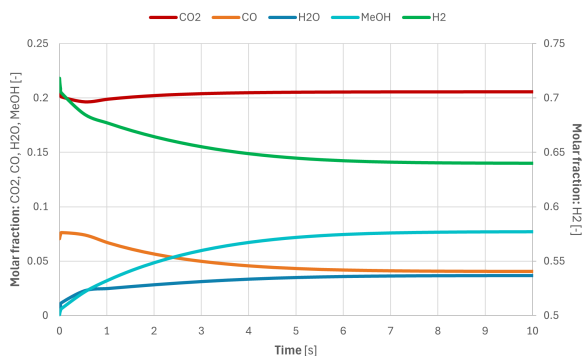


Figure 5: Molar fractions evolution in time performing the simulation of the methanol single tube reactor.

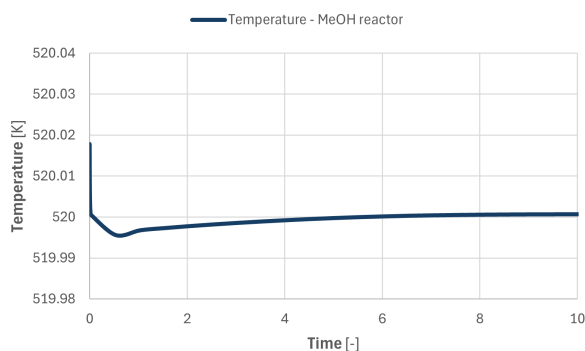


Figure 6: Temperature evolution in time performing the simulation of the methanol single tube reactor.

Furthermore, the analysis was also based on the comparison with an external source: Aspen HYSYS[®]. The final values so reached showed that MADSim properly works, in particular, the proposed models are fully functional and comparable with an established simulator.

5. Conclusions

The new kinetics model is capable to reliably represent a heterogeneous reaction environment. This statement was demonstrated within the validation performed in line with the previous works conducted in MADSim and within the study case regarding methanol.

The inclusion of a generic tubular reactor model results in a notable milestone. However, this should not be considered only a final destination but a new starting point for more complex implementations as well. What is suggested for the future developer is the addition of a cooling

system coded in a similar way to the existing heat exchanger model and the implementation of a multitubular reactor.

In order to be fully capable to accompany the users, the program needs extra efforts: the demand of a revamp on the *Species* class stands out since critical species are not handled in a correct way due to simplifications in the properties calculation. Moreover, a GUI (graphical user interface) attracts the interest, being an appealing matter for a future expansion of MADSim.

References

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