



POLITECNICO
MILANO 1863

SCUOLA DI INGEGNERIA INDUSTRIALE
E DELL'INFORMAZIONE

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

TESI DI LAUREA MAGISTRALE IN
CHEMICAL ENGINEERING - INGEGNERIA CHIMICA

Author: **Andrea Rinaldi**

Student ID: 222379

Advisor: Prof. Flavio Manenti

Co-advisors: Eng. Marcello Maria Bozzini

Academic Year: 2023-24

Abstract

The goal of this thesis project is to improve MADSim, expanding the existing chemical reaction environment and creating a general model for a tubular reactor. Before this work, the program permitted to construct the kinetics of reactions using built-in functions such as Arrhenius law and power law, while the remaining part was left to the user. In order to simplify the procedure a standard heterogeneous model was introduced. Similarly it happened for chemical reactors: a specific unit has been introduced by the first developer, while a generalized version was coded for this work.

Considering an increasingly predominant chemblock, methanol, a preliminary study on the thermodynamics, kinetics and industrial production of the compound was led with a consequently simulation in the MADSim environment, both validating the generic kinetics and the reactor model proposed. The software potential emerged as considerable, making it valuable thanks to the possibility to be customized and, at the same time, to perform interesting industrial applications. The program is capable to accompany the manufacturing.

Keywords: Kinetics, Reactor, Dynamic simulation, Methanol.

Abstract in lingua italiana

L'obiettivo di questa tesi è il miglioramento di MADSim, espandendo l'esistente ambiente di reazione e creando un modello generale di reattore tubolare. Prima di questo lavoro, il programma era in grado di processare la cinetica di reazione utilizzando le funzioni interne come la legge di Arrhenius e la legge di potenza, mentre tutto il resto era lasciato all'utente. Per semplificare questa procedura è stato introdotto un modello eterogeneo standardizzato. Similmente è accaduto per i reattori chimici: un'unità specifica è stata introdotta dal primo sviluppatore, mentre è stata codificata una versione generalizzata ai fini di questa tesi.

Considerando il metanolo, sempre più presente nella scena dell'industria chimica, è stato condotto uno studio preliminare sulla termodinamica di quest'ultimo, la cinetica a riguardo e i metodi di produzione di tale composto, con la conseguente simulazione nell'ambiente di MADSim, validando così i modelli proposti per la cinetica e il reattore tubolare. Il software si è mostrato come funzionale, donandogli valore e interesse grazie alla possibilità di essere personalizzato e, allo stesso tempo, di eseguire e seguire applicazioni di stampo industriale. Il programma è quindi capace di accompagnare la manifattura.

Parole chiave: Cinetica, Reattoristica, Simulazione dinamica, Metanolo.

Contents

Abstract	i
Abstract in lingua italiana	iii
Contents	v
1 Introduction	1
1.1 Dynamic process simulation	2
1.2 MADSim	4
1.2.1 Object-oriented programming	4
1.2.2 Code structure	6
1.2.3 Core calculation for the simulation	9
1.2.4 Global simulation algorithm	12
1.2.5 <i>PlantGraphTraversal</i> Algorithm	14
1.2.6 Some unit operation present in MADSim	17
1.3 Methanol synthesis	19
1.3.1 Methanol thermodynamics and catalyst	20
1.3.2 Methanol reactors	23
1.3.3 Kinetics in methanol synthesis	26
1.4 In this thesis	30
2 Methodology	31
2.1 <i>ChemicalReaction</i> Environment	32
2.1.1 Heterogeneous kinetic model	33
2.1.2 Coding part	35
2.2 Tubular reactor implementation	39
2.2.1 Tubular reactor model	41
2.2.2 Dynamic simulation derived characteristics	47
2.3 Methanol reactor simulation	49

2.3.1	Vanden Bussche and Froment kinetic model rearrangement	50
2.3.2	Methanol reactor sizing and operation condition	51
3	Results	55
3.1	Kinetics model validation	55
3.2	Tubular reactor validation	57
3.3	Methanol Simulation	58
4	Conclusions and future developments	63
	Bibliography	65
	List of Figures	69
	List of Tables	71
	Acknowledgements	73

1 | Introduction

Process simulators are useful instruments which are becoming increasingly popular due to the potential that they offer. In particular, the possibility to create a parallel version of a process, the so called *Digital Twin*, permits to study the process itself offline or, even, not existing system [7]. The available programs are capable to reliably represent steady state condition, i.e. units and plants at full regime. It appears clear that such an instrument supports the engineer throughout the project and design phase and during the control routine.

Some examples of chemical process simulators [22] are reported below:

- **Aspen HYSYS[®]** by Aspen Technology;
- **Aspen Plus[®]** by Aspen Technology;
- **DYNSIM[®]** by AVEVA;
- **DWSIM[®]** by D. Medeiros, G. León and G. Reichert;
- **UniSim[®]** by Honeywell.

As mentioned above the idea behind a process simulator is to create a virtual version of a plant, to do so the application of mathematics and first principles (i.e., conservation laws, thermodynamics, transport phenomena, and reaction kinetics) is involved. All the equipment is described using a specific set of balance equations, one for each state variables (temperature, pressure and composition), according to the physics of the unit operation and the given data, then the overall system is constructed passing the variables from one constituent to another.

The systems are built according to an ideal approximation where the variation in time is not considered, i.e. accumulation term is null, resulting in time derivative equal to zero.

More in general, the material and energy balances, governing the systems, appears to be:

- **Mass balance equation:**

$$\dot{m}_{in} - \dot{m}_{out} = \frac{dm}{dt} = 0 \quad (1.1)$$

- **Energy balance equation:**

$$\dot{H}_{in} - \dot{H}_{out} + \dot{Q} = \frac{dH}{dt} = 0 \quad (1.2)$$

where dm/dt is the time derivative of mass, \dot{m}_{in} is the mass flow rate entering the system, \dot{m}_{out} is the outlet mass flow rate, dH/dt is the time derivative of enthalpy, \dot{H}_{in} is the enthalpy flow rate entering the system, \dot{H}_{out} is the outlet enthalpy flow rate and \dot{Q} is the heat which affects the system.

Although the strong simplification introduced by the steady state hypothesis, chemical processes are composed by several units, each of which brings its balance equations. Moreover, the chemical engineering systems, by its own nature, are strongly not ideal, adding more challenges from the point of view of the mathematical resolution.

This issue requires a certain computational cost, therefore making the system more complicated, in normal situation should be avoided. To do so a common choice is to not analyze the dynamic behaviour, limiting the resolution only to the stationary problem. However explore continuously changing environment can be a really interesting field, which opens a wide range of possibilities, such as the study of start up, shut down of the plant and every situation linked to the instability brought by the noises and disturbances or even a change in process specifics.

1.1. Dynamic process simulation

Nowadays, the description of unsteady behaviour attracts more and more interest: the lack of well-established dynamic simulator is one of the major deficit of existing chemical process simulators.

The first notable different between a steady state simulator and a dynamic one lays on the fact that the first describes variables fixed in time, while the second considers variations. As a result some interesting phenomena cannot be dealt with common software, for example the start up or the shut down of a plant which require different approaches or external applications. Another remarkable difference is the possibility to represent the system more close to the reality, considering also the movement of the material. In partic-

ular, the flow of matter covers a considerable distance in the pipeline, having an impact on the propagation of every desired and undesired variations, disturbances and more in general noises. This kind of simulators provides a wider range of analysis, capable to deal with complex questions otherwise too difficult to answer.

Considering a system as dynamic makes the steady state condition no more acceptable. In fact, the possibility to have modification in time requires an accumulation term different from zero.

Therefore, the governing equations of this kind of process result to be:

- **Mass balance equation:**

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out} \quad (1.3)$$

- **Energy balance equation:**

$$\frac{dH}{dt} = \dot{H}_{in} - \dot{H}_{out} + \dot{Q} \quad (1.4)$$

The descriptive equations of dynamic systems are *ordinary* or even *partial differential equations*, which are often coupled with algebraic equations giving birth to the so called *differential algebraic equations (DAEs)* systems. Since the derivative term is considered, the way of resolution passes through a solving algorithm capable to provide a numerical solution. This is the reason why a higher level of difficulty compared to the steady state case arises; its handling, from a computational point of view, results in a more laborious and expensive operation.

If the application of such software clearly appears to be an interesting field of research several challenges emerge. Starting from a more complex and extended set of equation due to an higher level of accuracy, an expensive computational cost and a more intense effort for the machine is required. Therefore, the developers should work with dexterity, operating a trade off between accuracy, stability and complexity.

Back in the days simulators more and more specific have begun to be developed, such as *MADSim*.

1.2. MADSim

To answer the increasing challenges linked to the process system engineering, MADSim was developed. In particular, MADSim stands for "*Modular Advanced Dynamic Simulation*". As the name suggests, the idea behind is the development of a module-based software, segregating main components such as the solver, the equation and the unit models in order to allow the implementation of new functionalities.

1.2.1. Object-oriented programming

The existing models can be expanded, supported or even substituted thanks to the high flexibility of the framework; this is possible due to the object-oriented programming (OOP) adopted during the coding. The chosen language to do so was *C++*. Combined with the OOP methodology, it is possible to maintain the code in the most simple and lean way, avoiding the repetitions: every common functionality becomes a specific class. Thanks to the potential parental bound between classes, a clear structure for the program and a fast execution are provided. Moreover, this logic was applied for the equations of state (EoS), which are described in a shared class, from which every specific son function inherits the common features.

Furthermore, the OOP could be adapted to a wide range of situations adopting some coding strategies. The structure of the program follows the so called "*design patterns*". More in general a *pattern* is a specific response for common and repeated issues; they are identified by a name, a problem which they can solve and the solution itself. Due to the high flexibility level of such patterns a consistent use appears in the MADSim code.

The four patterns used in the simulator are here illustrated:

- **Composite pattern;**
- **Builder pattern;**
- **Strategy pattern;**
- **Adapter pattern.**

Composite pattern

The first presented method is the *composite pattern*. This family falls in the structural pattern category: capable of giving a defined scaffold, this element is largely implemented in the program, in order to outline a specific hierarchy inside the software. It works according to a *tree structure* (*figure 1.1*), with a shaft made of components, which are the elements made with the purpose of interacting with other elements, for that reason they are also known as containers. The leaf is the constituent with no children, being in the extremes of the tree. For this reason, it determines the behaviour of primitive objects in

the composition, being the components that typically handle most of the operations.

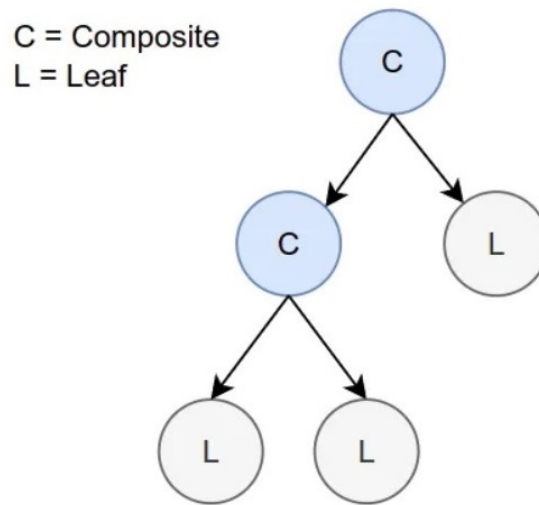


Figure 1.1: Simple representation of a tree structure in the composite pattern.

Builder pattern

On the other hand, the *builder pattern* is a creational pattern. Under this category goes the *MADSim Builder* class in which, as the name suggests, all the unit operations are constructed. This allows a link between the *main* function and the class of the unit operation models or better, it permits the segregation of the construction from its representation. This element is the component which allows an high level of modularity, being one of the main features of the software.

Strategy pattern

The *strategy patterns* encapsulate algorithms one with the other, donating the interchangeability. The same behaviour of different objects can be collected under an umbrella class with shared properties; as mentioned above, this happens once with the EoS family in general, and then within the cubic equation family.

Adapter pattern

The *adapter pattern* converts an adaptee to a target, via an adapter, according to the client request (*figure 1.2*). It is applied as it happens with the external library *CoolProp* [1], already implemented in the code. The *"wrapper"* converts the interface of class into the one expected by the client. In the *CoolProp* example, this pattern makes the library legible by MADSim as a built-in EoS.

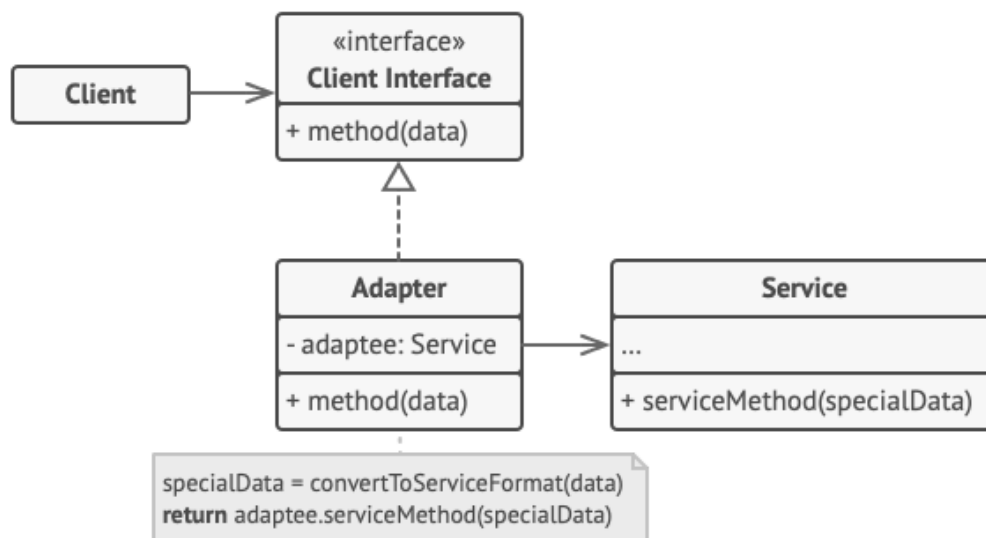


Figure 1.2: Unified Modeling Language diagram of the *adapter pattern*.

1.2.2. Code structure

As highlighted in the previous sections, one of the main characteristics of MADSim is the object-oriented framework, in other words, the management of the code in classes and interfaces. Furthermore, to better organize and consequently understand the script, both chemical process engineering and programming notions should be clear. What emerges from the previous statement is the logic behind the software, in particular a clarification of the structure is here presented. It is possible to categorize all the objects inside the script, putting them in one of the following areas of relevance:

- **Stream and unit operation modeling.** Every object which belongs to the *Base-Class* lies in this category. In particular, the main inheriting class are *Stream* and *Equip*;
- **Thermodynamics description and handling.** The physical systems are described by thermodynamics thus the simulation works at the same way. The description of the state of the matter and the handling of chemical reactions both lie in this group, being the descriptive interfaces *EquationOfState* and *ChemicalReaction* respectively;
- **Simulation solver.** The interfaces which process the solution stay under this classification. In particular, the *PressurFlowSolver* and the *Solver* are responsible for the final solution;
- **Software utilities.** This category collects all the remaining objects.

Going further into these categories, it is possible to state that the first group represents the pipelines, the machines, and more in general all the operations which can be found in a chemical plant. Also the interaction and how they are attached each other are included in this group. Some example will be shown later in the chapter, in the specific section.

Briefly, the solver works in order to give a solution that is time dependent and subjected to some driving forces. Those are the pressure distribution and the consequent flow generation, in other words, the difference in pressure triggers the movement of the mass. To describe this phenomenon, the *PressurFlowSolver* was developed.

The simulated flows of matter appear according to the physical states, and are described by their intrinsic properties, the so called *state variables*. Therefore, knowing temperature, pressure and composition is a key point to perform a good simulation. This task is solved exploiting the already mentioned EoS, with the addition of properties specific for each compound such as the critical temperature and the critical pressure.

Another topic coming from thermodynamics is the prominent subject regarding chemical reactions. How the components of a system interact together, in particular, when they transform into other compounds, results in an interesting, but complex matter of study. The equilibria are governed by the rules of thermodynamics, for that reason the derived calculation is included in the software.

Nowadays what is absent in the *ChemicalReaction* interface is a proper way to handle systems which are not at the equilibrium. To do so, the theory around chemical reaction kinetics is taken into account, moreover a general model for heterogeneous reaction environment is developed in order to deal with one of the most widespread way to work reactors. The discussion of this argument is addressed in the appropriate chapter (*chapter 2*).

Finally, the last group is here explained. In these categories lie different objects, first of all the *Plant* class. This interface permits to collect all the simulation elements. Once they are stored, the *PlantGraphTraversal* routine reads and organizes the simulated units thanks to a built-in algorithm, ready to transfer an ordained group of operations to the proper solver.

Then, the *Builder* class, written according to the pattern procedure, is used to simplify both the current developer, the future ones and eventually the user which has the permission to enter in the code. More in detail, this interface interacts directly with the streams (*Stream* class) and the equipment (*Equip* class), listing the functions which create and connect all the objects. The reason why the builder class exists is to make explicit the aforementioned procedures even if this routine could be done specifically for every unit. Therefore, the effort of adding this interface is clearly done for a question of usability. Once the creation of the streams and units and their connection are here declared, then

all this information are passed to *Plant*.

To operate a chemical process simulation a good database of compounds and their thermochemical properties is certainly required. This is the reason why the *Species* class is thought, in particular it serves as a storage and it interacts with the simulation via the *SimulationComponents* class. Nowadays the available species are:

- | | |
|---|---|
| 1. Hydrogen H ₂ ; | 12. Ethylene C ₂ H ₄ ; |
| 2. Nitrogen N ₂ ; | 13. Acetylene C ₂ H ₂ ; |
| 3. Oxygen O ₂ ; | 14. n-Propane C ₃ H ₈ ; |
| 4. Water H ₂ O; | 15. Propylene C ₃ H ₆ ; |
| 5. Methanol MeOH; | 16. Carbon monoxide CO; |
| 6. Ethanol EtOH; | 17. Carbon dioxide CO ₂ ; |
| 7. 2-Propanol 2prop; | 18. Ammonia NH ₃ ; |
| 8. n-Butane nBut; | 19. Benzene C ₆ H ₆ ; |
| 9. n-Octane nOct; | 20. Air Air; |
| 10. Methane CH ₄ ; | 21. Ethylbenzene EtC ₆ H ₆ ; |
| 11. Ethane C ₂ H ₆ ; | 22. Diethylbenzene DietC ₆ H ₆ . |

With the present components it is already possible to simulate a wide range of processes, however a viable development for MADSim in the future should be the addition of new species. The interaction with a specific library containing the thermochemical properties of families of molecules could be a doable solution other than manually adding the necessary information.

A critical point to be stressed is the handling of compounds which have unusual behaviour; in fact, the advantages of a program like MADSim is, for certain, the possibility to use "empty" formulation that are filled with the required properties of a specific chemical component. On the other hand some molecules, because of the lack of some properties or because of a behaviour that differs from the majority, the implemented models should be revised. An example of that is the very common molecule of *carbon dioxide* (CO₂) which does not have a normal boiling point since at atmospheric pressure exists as supercritical fluid, for that reason every calculation based on the normal boiling point does not work with this species. Some corrections was introduced, anyway a complete review on that should be an interesting starting point for a future thesis.

1.2.3. Core calculation for the simulation

One interesting feature of MADSim depends on its nature, in fact being a dynamic process simulator it inherits peculiar characteristics. Such type of simulator are *pressure driven* [21], or in other words the profile of pressure through the simulated plant governs the flow rate. This behaviour differs from the steady state simulator one where the contrary happens: the flows define pressures. Inspired on DYNOSIM[®], the software divides process equipment into two distinct families in accordance with pressure effect on connected streams.

- **Flow Devices (FD)**: governed by *resistance equations*, this equipment determines the flow rates of the stream passing through them, by means of the pressure difference across the device. This category includes instruments such as valves and heat exchangers;
- **Pressure Nodes (PN)**: governed by *volume balance equations*, this equipment defines pressures of connected streams. Typical pressure nodes are tanks, mixers and drums.

Due to the complexity of some unit operations, an equipment can be modelled as flow device, pressure node or even as a combination of the two.

A relevant fact lies on the impossibility to have two pressure nodes directly attached each other, leading to a mandatory flow device in between. On the other hand, consecutive flow devices are permitted; the reason of that is explained by the fact that stream must be univocally defined in its main characteristics (according to pressure driven nature of the software). It is clear that two consecutive objects capable to define the pressure of the same stream go against the just explained principle.

Focusing the attention on MADSim, the *Pressure-Flow Solver* is the element aimed to solve the aforementioned resistance equations, volume balance equations for the equipment and all the *general pressure and flow equations*.

Resistance equations

This kind of equations is used to define the stream of an equipment knowing the pressure profile. The key parameters for the calculation are the density of the fluid ρ and the conductance J as it is possible to appreciate in the *equation 1.5*.

- **Resistance equation** of a flow device:

$$W = J \sqrt{\frac{\Delta P}{\rho}} \quad (1.5)$$

where W is the mass flow rate and Δ stands for difference between outlet and inlet, in this case of pressures. The density can be calculated in different manners, as average between entering and exiting stream [12] or using directly the inlet stream value as operated in DYNsIM®.

Volume balance equations

This kind of equations describes how the pressure varies according to a variation of volume. In particular, it is written for any equipment having *hold ups*. The general form appears to be:

- **Volume balance equation** of a pressure node:

$$\frac{dP_h}{dt} = f(P, T, holdup, flows) \quad (1.6)$$

where P_h represents the pressure associated to hold ups.

According to Mohajer et al. [12], in MADsIm an alternative form is adopted:

- **Volume balance equation** (Mohajer et al.):

$$\frac{dV}{dt} = \delta V_P + \delta V_F + \delta V_T + \delta V_O \quad (1.7)$$

where δV_P is variation of volume caused by pressure, δV_F is variation of volume caused by flows, δV_T is variation of volume caused by temperature, and δV_O is variation of volume caused by other factors.

In the *Pressure-Flow Solver* typically only the terms δV_P and δV_F are considered. The other two are used during the update routine for pressure outside the solver.

General Pressure and Flow Relations

For each object considered both as pressure node and flow device a wider set of equations to solved is required. Pressure relations respond to the necessity for pressure relating the stream with the considered pressure node. On the other hand flow relations depend on the presence of a hold up, which is correlated to the stream thanks to this kind of equations.

The form of the relations changes from equipment to equipment, for this reason let analyze a simple example [18]. In particular, a mixer node is presented (*figure 1.3*): two streams enter the unit having their value of flow rates ($F1$, $F2$) and pressures ($P1$, $P2$), one stream exits the unit with its flow rate ($F3$) and pressure ($P3$). The pressure inside the equipment is also considered (P_{mix}).

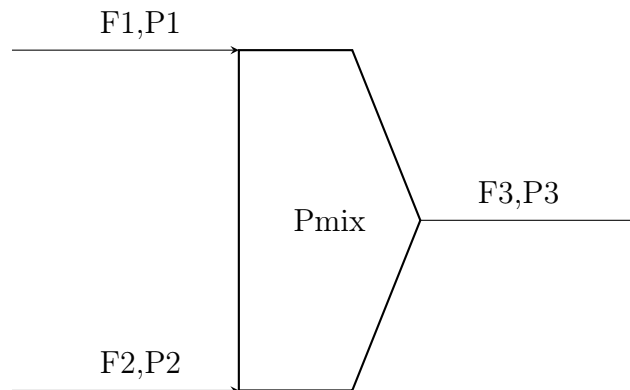


Figure 1.3: Example of a mixer with two entrance and one exit.

The presented mixer is modelled without the hold up, this implies that the flow relation does not present the accumulation term, leading to equation analogous to a steady state balance.

The equations for the model are the following.

- **Pressure relation** for the mixer:

$$P1 = P2 = P3 = P_{mix} \quad (1.8)$$

- **Flow relation** for the mixer:

$$F1 + F2 = F3 \quad (1.9)$$

Since the *equation 1.8* is very simple and directly satisfied setting the pressure of the unit, it can be not considered in mathematical resolution [12]. To evaluate the *Pressure-Flow scheme* is sufficient the knowledge of the resistance equations, while the mathematical solution must take volume balance equations and flow relations into account.

Hold ups

Since it is already mentioned, a brief explanation of *hold up* is here presented. It represents the presence of fluid inside of an equipment, which plays the role of the accumulation term in the mass balance equation (*equation 1.3*). Therefore, units modelled without hold ups does not present the accumulation term such as the mixer in the example above.

Two types hold up exist: *incompressible* and *compressible*. If in the majority of cases the *compressibility* is related to the physics, there are cases where the related equations result simplified. As an example, small volumes of gas can be modelled as incompressible hold ups.

Hereinafter a small presentation of the two is reported:

- **Incompressible hold ups:** it permits the evaluation of pressure outside the unit solving the Pressure Flow Network;
- **Compressible hold ups:** it makes necessary the exploitation of *Flash* calculation [18], which are associated to the thermodynamic equilibrium of phases.

Moreover, in the case of equipment without hold ups, the pressure is always evaluated by the Pressure Flow Solver.

1.2.4. Global simulation algorithm

The way in which the resolution is produced is another interesting characteristic of MAD-Sim, the overall simulation algorithm solves four different groups of equations:

- **Pressure-Flow relations.** They provide for pressure distribution and flow rate all over the process scheme;
- **Control and logic loops.** These are the equations linked to the control logic, associated to valves and similar equipment;
- **Energy calculations.** They include the energy balances around the units;
- **Composition and flash calculations.** The majority of the effort comes from these kind of equations. They are usually non-linear, more in general they describe the physical and chemical equilibria.

In other software such as Aspen HYSYS[®], Pressure-Flow relations are solved by the system every iteration, while the control and logic loops equations and the energy calculations solutions are performed every two iterations. The composition and flash calculations are processed only every ten iterations. It is important to notice that this last group is the most time consuming in term of calculation, for that reason the software routine performs the computing as few times as possible. For the matter of simplicity, MADSim solves all the equation every iteration. This choice opens new paths for future development of the program.

Going directly to the proper algorithm, MADSim requires the initial condition, chemical environment, and plant initialization setting, after that is ready to pass the equation through the solution routine.

Every iteration works in accordance to a steps succession here presented:

1. Evaluate the time step size for the iteration;
2. Update controllers parameters from t to time $t + \frac{dt}{2}$;
3. Update flow devices status from time t directly to time $t + dt$;
4. Store the current t status of all the equipment;
5. Pass the Pressure Flow Network through the Pressure Flow Solver, obtaining the solution;
6. Update each node and stream via the Model Integrator routine;
7. Evaluate if the difference between the newly evaluated pressures for compressible pressure nodes and the original ones is smaller than a certain threshold: if it is not, go to **point 5**, restore the old equipment state, and continue until the condition is satisfied;
8. Satisfied the compressible pressure nodes condition, the controllers are update from time $t + \frac{dt}{2}$ to time $t + dt$;
9. The results are printed and the routine restarts from **point 1**, until the simulation time is reached.

Moreover, the system performs a double update every iteration at $t + \frac{dt}{2}$ and $t + dt$. This splitting method is used to increase the efficiency of the program, then the update of every part is operated according to the needed accuracy.

1.2.5. *PlantGraphTraversal* Algorithm

Stressing the attention on *PlantGraphTraversal* routine it is possible to understand how the code is capable to read and identify the units and sorting them. This happens according to a built-in algorithm. The *plant graph traversal algorithm* was created by an hybridization of different ordering methodologies, to supply for a sequence of reading (and consequently order of solution) for the various nodes. This takes into account the possibility to have recycles, without involving any problem although the absence of a linear order. Moreover, the aim of the algorithm is to take the shortest path possible between connected vertices.

The parent algorithms are here presented and deeply discussed in the following subsection.

- **Breadth-first search** (BFS);
- **Depth-first search** (DFS).

Breadth-first search algorithm

Invented by Konrad Zuse (1945), this algorithm is one of the simplest method to sort elements of tree data structure, such as for a chemical process plant considering the units as vertices of the graph.

Every node of the graph belongs to one of the following categories:

- **Visited**: it represents a vertex already analyzed by the algorithm, its position is known as well as for all the connected vertices;
- **Marked**: it represents a vertex discovered by the algorithm, the marking procedure happens with the discovery of connected vertices of the visited one;
- **Unmarked**: it represents a vertex not discovered yet.

All the marked vertices are stored in a *queue*, in which the "*first in first out*" rule is adopted. In fact, the order of entrance into the list is the same utilized to extract the elements.

Starting from tree root, BFS explores the vertices at distance d before passing to a distance $d + 1$, it is possible thanks to the queue system. In this manner the sorting is disposed according to levels which are completely explored after the finishing of the previous and before the access to the subsequent.

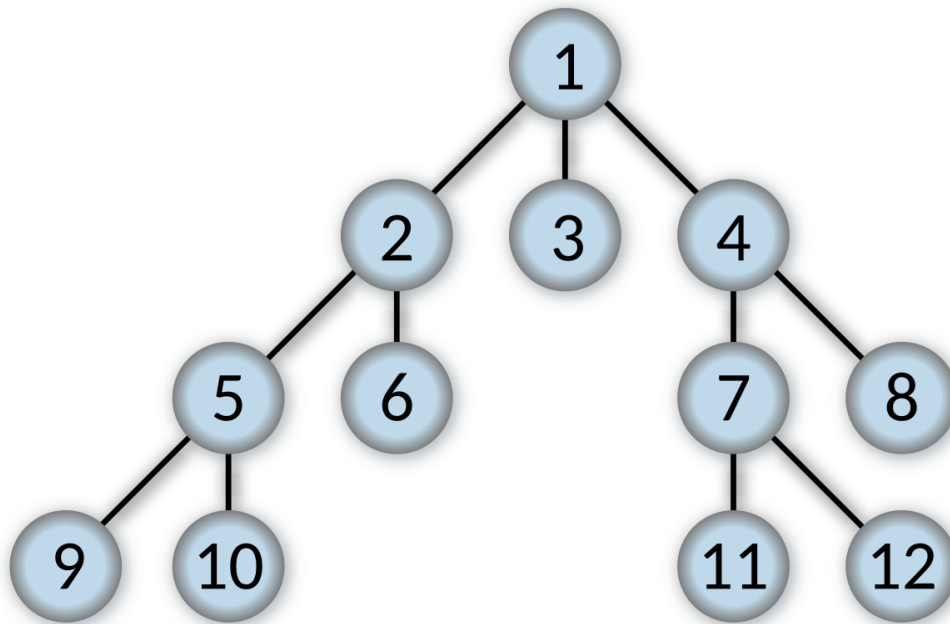


Figure 1.4: Tree structure ordained exploiting the BFS algorithm.

Depth-first search algorithm

Examined by Charles Pierre Trémaux (in 19th century), this algorithm, initially used for maze solving, inspired *PlantGraphTraversal* used in MADSim.

This algorithm works in contrast to BFS, in fact it does not prioritize the completion of levels but operates the exploration of a branch as deep as possible.

In this case a queue is no more needed and to make it work two methods are possible:

- **Iterative method:** a list of marked (discovered but not visited) vertices is used. In this case it takes the name of *stack* which works according to the "*first in last out*" rule. When a node is visited, its adjacent list is attached at the end of the stack. The algorithm continues until there is at least one vertex in the stack;
- **Recursive method:** Without the implementation of the stack, the algorithm operates recursively being called on the newest visited vector.

This algorithm is exploited for the capacity to deal with internal circles and to define a primary branch that works as a backbone.

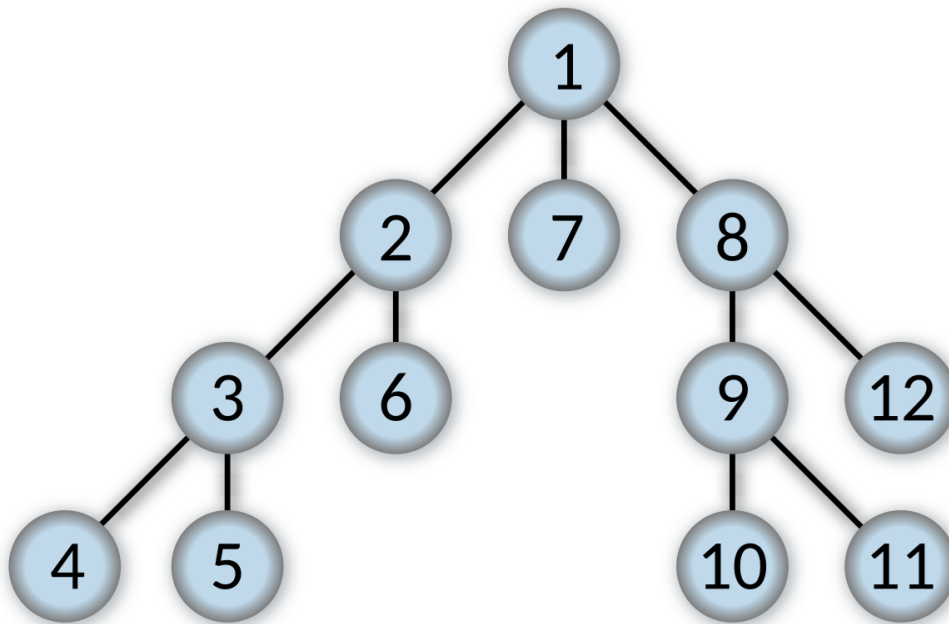


Figure 1.5: Tree structure ordained exploiting the DFS algorithm.

Hybridized algorithm functioning

The aim of *PlantGraphTraversal* is to define an optimal order of solution for the unit operations in the flowsheet and to identify all the recycles in the scheme. Considering a process flow diagram as *finite directed cyclic graph*, much simpler than graphs from other applications, it was possible to construct a suitable algorithm.

The existing algorithm was created combining BFS and DFS routines, which operates as explained hereinafter:

1. The algorithm starts choosing a *source* as its root node;
2. It works as a DFS until a *sink* is reached;
3. Once the initial *sink* is discovered, the algorithm switches from DFS to BFS and begins with all vertices marked during the DFS but not yet visited;
4. If other *sources* exist, it works as a BFS starting from them until all the vertices in the scheme are visited.

The *point 2* is made in order to define a backbone branch which gives to the system a first way to understand how and in which direction the streams flow.

Moreover, with the adoption of two different storage vectors, *PlantGraphTraversal* is able to identify the recycles, if they exist.

- **GraphTraversal** vector: it is the primary storage vector in which vertices are gradually inserted. At the end of the algorithm the vector becomes the final result, with the nodes ordered as desired;
- **Stack** vector: it is a temporary storage during the algorithm routine. Its elements are transferred to the **GraphTraversal** vector every time certain conditions are respected. This support element permits the achievement of the desired order in the **GraphTraversal**.

The algorithm deals with the creation of other supporting vectors such as the sinks and sources ones. In this way it can work with any kind of process, independently to which it is.

Since the chemical processes do not originate too big graphs, in the MADSim code it was preferred to push and enhance the accuracy side. In fact the time-space complexity and the computational costs are not touched in a considerable way by *PlantGraphTraversal* algorithm.

1.2.6. Some unit operation present in MADSim

Finally, a list of the unit operations already present in the software permits to understand both its functionality and the future perspective. In fact, one goal of this thesis project is to expand the inventory, in order to cover the most wide range of possible industrial applications. To achieve the objective a general tubular reactor model was implemented and accurately explained in the specific section of *chapter 2*.

Coming back to currently existing equipment, a list of the currently present units is illustrated hereinafter.

1. **MadSource**: it represents the inlet stream source, being the analogue of a prime matters entrance of a *process flow diagram* (PFD);
2. **MadSink**: it represents the outlet stream discharge, being the analogue of a product exit of a *process flow diagram* (PFD);
3. **MadFlash**: it is a one stage separation unit, which is usually a drum;
4. **MadDistillationColumn**: it is a multiple stages separation unit. In the code it appears as repeated series of trays, where every tray works similarly to a flash unit, the only exceptions are the top and bottom trays and the one attached to the fed stream;
5. **MadMixer**: it is a node of convergence of multiple different streams giving as a result a single exiting flow;
6. **MadSplitter**: it is the contrary of a mixer, one entrance is divided in multiple exits according to splitting factors;
7. **MadPump**: it is a machine capable to increase the pressure of incompressible fluids;
8. **MadHeatExchanger**: it is a complex unit where two streams interact each other inside the equipment. One side works as coolant and the other one absorbs the released heat;
9. **MadValve**: it is the control element capable to change the value of flow rates of the attached stream;
10. **MadExpander**: it is a particular type of valve that lowers the pressure, it is usually coupled with separation units such as the flash.

In the MADSim inventory a reasonable number of units already exists, a possible outcome for a future project could be the addition of new units to improve the program pool. Partially in this thesis, it was conducted a similar proposal, in particular the absence of a generic reactor model raised the necessity to implement it.

A more detailed description of MADSim and how it was developed are well explained by its creator in the associated thesis project [18].

1.3. Methanol synthesis

In this work, a simple process to perform a validation procedure was chosen, in particular a tubular reactor for the methanol synthesis. This kind of synthesis clearly results to be the most efficient one to reach the desired goal for several reasons such as: the huge presence of methanol in the market and the possibility to figure out the reactor as a tubular one.

Methanol is a very common and widespread chemblock with a considerable amount of thermochemical information in databases: this is the reason why it emerges as an interesting study case, considering also the simplicity to verify the calculation thanks both to Aspen HYSYS[®] and several studies on the subject.

To prove the aforementioned statements the key aspects of methanol are explored, dwelling in particular on its production and the relative market.

Starting from the chemistry of the molecule it is possible to understand the extensive field of application only examining the atomic components: carbon, hydrogen and oxygen, being CH_3OH the formula (*figure 1.6*). From each atom some notions can be comprehended, the presence of carbon leads to the field of organic chemistry, being the methanol a typical reagent. Furthermore, because of the occurrence of oxygen the production of this molecule results linked to carbon monoxide (CO) and carbon dioxide (CO_2); while they are usually pollutants and by-products, here they cover a key role as reagents (*equation 1.10* and *equation 1.11*). Finally hydrogen conduces to one of the most discussed and studied topic in modern chemical industry: the green chemistry related to green hydrogen production. It is precisely this aspect that makes methanol a suitable candidate for the hydrogen transport and exploiting, other than be a good target for the carbon capture and utilisation (CCU) technologies.



Figure 1.6: Fischer projection and 3D structure of the methanol molecule.

Nowadays methanol is largely exploited as a solvent in many processes, but its utilization resides primarily as intermediate: it is involved in the production of acetic acid, alcohols,

methyl formate, formaldehyde, methyl amines, and ethers.

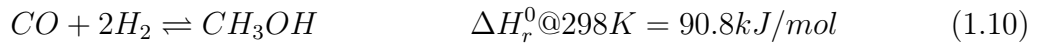
Moreover, technologies which employ methanol in energy sector are rising, in particular in the transport field. In fact, methanol can be used directly in internal combustion engines or by mixing it with gasoline and diesel. This second application exploits its energy value as a low carbon content molecule (considering in proportion to its total mass) in order to reduce emissions. Methanol can be used as a fuel either directly in methanol fuel cells (DMFC) or after prior reforming in proton exchange membrane fuel cells [13].

In the following sections thermodynamics is explicated; moreover, the state of the art for the methanol synthesis is shown, focusing in the reactors area. Finally, a discussion on the kinetic models is conducted, following with the choice of the most convenient one.

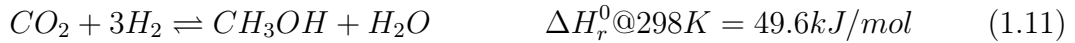
1.3.1. Methanol thermodynamics and catalyst

The main reactions involved in the synthesis of methanol are:

- **Carbon monoxide hydrogenation:**



- **Carbon dioxide hydrogenation:**



To complete the system another reaction should be coupled with the two methanol synthesis reactions:

- **Water gas shift (WGS):**



This last reaction plays a key role in the management of a methanol reaction system: in fact it permits to obtain higher conversion of carbon dioxide at high temperature, appearing in the form of *reverse water gas shift* (RWGS). In particular, this is the manner of which the kinetic models are constructed. Despite the higher conversion of CO₂ at high temperature the reaction is favored at low temperature.

One problem emerged in the past is the operative temperature of catalysts, which were originally active only at high temperatures. Therefore, the pressure had to be very high (from 250 to 350 bar) to reach acceptable conversions. These original catalysts were used

in the so called "*classical methanol processes*" until the end of the 1960s. More active catalysts (copper-based) were discovered; unfortunately they were not resistant to feed impurities such as sulfur. Only the ability to produce sulfur-free syngas, reached in the late 1960s, allowed the use of these very active catalysts, the new generation thus obtained are known as "*low-pressure plants*" [9].

To clarify the statement above, in *figure 1.7* the equilibrium conversion of carbon monoxide to methanol is presented:

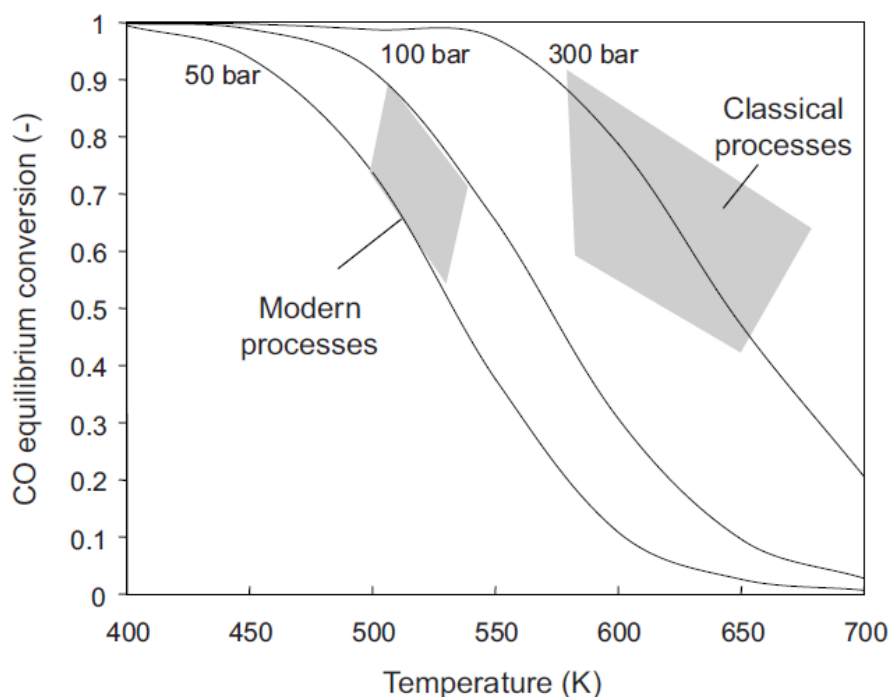


Figure 1.7: Equilibrium CO conversion to methanol feeding a 2 : 1 mol_{H₂}/mol_{CO}.

In the figure the difference between the classical and the modern process can be appreciate, in fact the newest catalysts are active at lower temperature which makes possible to operate at lower pressures (between 50 and 100 bar), while maintaining the same conversion reached with the old processes.

From a thermodynamic perspective, lowering the temperature is profitable, in addition, the highly active catalysts are sensitive to sintering, which progresses with temperature. On the other hand a low temperature vanishes the presence of the catalysts making them no longer active. Both the theory and the practice impose an high limit of 570 K, although the suggested operative point is around 520 K [9].

For this reason, a good pressure for the simulated reactor utilized during the validation procedure is around 70 bar, while the temperature chosen is 520 K.

State of the art: catalysts

The development of a catalyst for methanol synthesis resulted more challenging than ammonia and other common chemicals synthesis because of the criticality of selectivity. The formation of higher alcohols and hydrocarbons during the hydrogenation of carbon monoxide is predictable since it is quite common [9]. The catalyst needs to be very selective due to the large number of possible by-products [19]: for this reason, the selectivity of modern catalysts reaches values over 99%.

The most commonly adopted catalyst for industrial application is CuO/ZnO/Al₂O₃ [10]. The feature which varies from a producer to another is the composition: the copper oxide (CuO) ranges between 20% and 80% in weight, zinc oxide (ZnO) ranges between 15% and 50% and Allumina (Al₂O₃) ranges from 4% to 30%. Additives can also be present. For example, magnesia (MgO) is added as a promoter and acts as catalyst stabilizer as well. In *table 1.1* commercial variants of CuO/ZnO/Al₂O₃ are shown [5]. In particular, the attention is stressed on catalyst compositions and eventual additives.

Table 1.1: Compositions of CuO/ZnO/Al₂O₃ catalyst variants from different manufacturers.

Manufacturer	Cu wt%	Zn wt%	Al wt%	Other	Ref.
IFP	45 – 70	15 – 35	4 – 20	Zr-2-18	[20]
ICI	20 – 25	15 – 50	4 – 20	Mg	[20]
BASF	38.5	48.8	12.9	rare earth oxide -5	[20] [20]
Shell	71	24	12		[20]
Süd Chemie	65	22	31		[20]
Dupont	50	19	17		[20]
United Catalysts	62	21	17		[20]
Haldor Topsoe MK-121	> 55	21 – 35	8 – 10		[20]
Mitsubishi Gas Chemical Co.	63.6	33.4	3		[2]
Ammonia Casale	30	50	3	Cr(16)	[2]
Lonza	40	20		Zr(40)	[2]
AIST, RITE	45.2	27.1	4.5	Zr(22.6)	[2]
				Si(0.6)	[2]
YYK Corporation	76.3	11	12.7		[2]

1.3.2. Methanol reactors

The reactor plays a key role in the industrial facility, in fact the process capable to transform the raw material in valuable product happens in its environment. Certainly the upstream and downstream parts of a process have its importance. For example in the upstream line of methanol production the provenience of carbon sources (syngas, CCU and etc...) has its relevance due to the impact of the different feed compositions. Even the separation of methanol and water from the raw gas, often recycled, and between methanol and water themselves raise interest, however all the attention is stressed on reactors.

A summary of the main features of a methanol reactor and a collection of all the existing technologies, divided into macro-families, are introduced hereinafter. The reaction is conducted in gaseous phase on a catalyst bed at operating conditions well above the boiling temperature of involved compounds. Therefore, the equipment is projected as a tubular reactor: here the differences between technologies come out. Before illustrating the different possibilities (*figure 1.8*), another important common feature, which is treated in different manner according to the reactor, is the cooling system. As it is possible to understand from the chemistry (*equations 1.10, 1.11 and 1.12*) the overall process consists in a highly exothermic environment, leading to a necessary control system for the increasing temperature.

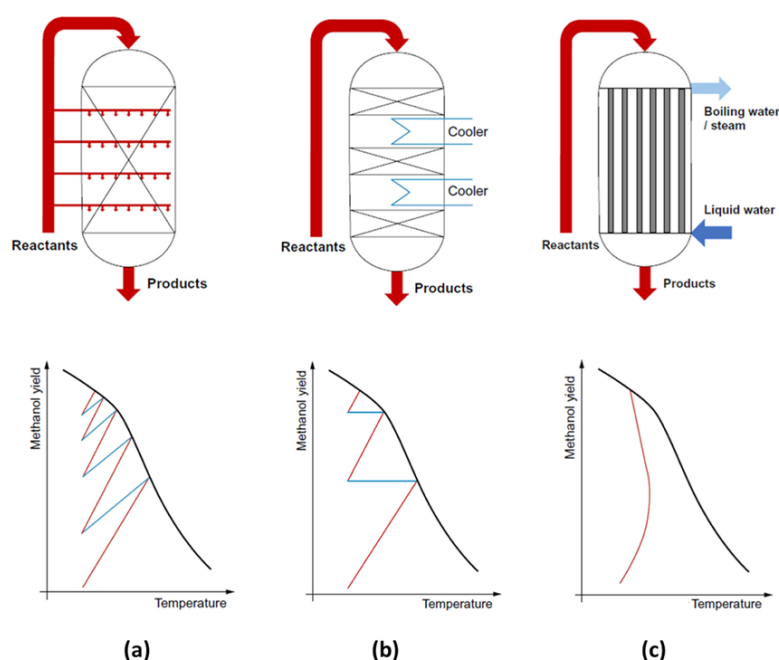


Figure 1.8: Most common commercial methanol technologies and relative temperature profile: (a) direct quenching, (b) indirect cooling, and (c) quasi-isothermal boiling water reactor. Picture adapted from Palma et al. [16] by Bisotti et al. [3].

The figure illustrates three typologies of reactor, the first one comprehends a multiple injection of fresh feed to quench the main stream along the tube while the second presents adiabatic segments of reactor alternating indirect cooling. The third typology is composed of a set of tubes refrigerated by boiling water: since the change in phase is an isothermobaric process, the reactor can be considered isothermal.

With the addition of a generic tubular reactor model inside the MADSim software all the previous macro-families of methanol reactor can be simulated. For the same reason the processes which are thought according to a similar physics can be simulated as well. Returning to the analysed case, group **(a)** can be seen as a series of alternated tubular reactors and mixers, where the first ones are interpreted as adiabatic and the seconds can be attached to the main inlet stream adopting splitting nodes representing the continuous extraction. Group **(b)** appears to be easier, in fact a series of adiabatic tubular reactors and heat exchangers results sufficient for the scope. Finally, group **(c)** is just a parallel set of tubes operated as isothermic, or to be more specific with a very high heat exchanging coefficient. For a matter of simplicity, a single tube coming from this last group is simulated in the apposite chapter as demonstration of the validity of the newly introduced models in MADSim and in continuity with the discussion about methanol.

State of the art: reactors

The better way to prove the aforementioned statements is the discussion about real examples. To show the current state of the art it was adopted the list of major technologies in the field of methanol synthesis by Bisotti et al. [3]. All the presented technologies are available on the market, therefore their *Technology Readiness Level* (TRI) has reached its maximum value of 9/9, the only exception is the AirProducts (LPMEOH) as explained below.

- **Johnson Matthey:** a quench reactor that mixes radial and axial flows. Its ideal operating condition is at 270°C (533 K) and with a pressure in a range between 50 and 100 bar. The scale of application results small, having a production of less than 2200 ton/day;
- **ICI:** similar to the Johnson Matthey it presents an improved quenching and well separated catalyst beds. In this way it achieves better performances up to an extra 20% of methanol;
- **Haldor Topsøe and Casale SA:** A gas quench reactor having the gaseous (catalyst part) stream flowing radially while the quenching stream flows axially. The catalytic beds are disposed in plates. By doing so it achieves the condition of reduced pressure

drops;

- **Kellogg Brown & Root (KBR)**: A series of adiabatic beds with intermediate cooling. The peculiar aspect is the spherical shape;
- **Toyo Technology Company**: A radial flow passes through a concentric catalytic bed. It has an optimal temperature control due to intermediate cooling via boiling water (isothermal condition). Other notable features are the low pressure drops, an easy scale-up, and a considerable saving in catalyst up to 30% less than conventional usage;
- **Linde**: A tube reactor with an axial gas flow and a helical cooling conduit (indirect cooling). Its last characteristic permits the elimination of radial temperature gradients;
- **Lurgi (multitubular BWR)**: A simple design for a multitubular reactor coupled with boiling water (BWR) as cooling medium. It has a reasonable yield and low manufacturing costs;
- **Lurgi (MegaMethanol)**: Two reactor united in one, a BWR and a GCR (gas catalytic reactor). The inlet stream enters in the GCR tube side receiving the effluent heat stream coming from the catalytic bed on shell side. The BWR works both as an intermediate cooling and a quasi-isothermic step. It has low recycle ratio;
- **Mitsubishi Heavy Industries**: A reactor with double-walled pipes works as an integrated BWR and CGR. The feed gas is preheated working as a coolant passing in the inner tube, while the catalytic bed is disposed on the external annular part where the reagent gas flow is cooled both by the inner side and the external boiling water;
- **AirProducts (LPMEOH)**: A slurry reactor working at mild pressure (from 30 up to 50 bar). Nowadays it is at pilot scale and has a low production volume with less than 2000 ton/day.

As shown a wide range of possible reactors for the methanol synthesis is available, moreover recently developing technologies are emerging. It is also possible to understand which typology results more successful and effective, in fact the vast majority of the illustrated units belong to the macro-family of quench reactors or to the quasi-isothermal group. Another ever more present feature is the adoption of circle-based shapes, having the reactant flow in hybrid regime (axial and radial) respect to the full axial one.

1.3.3. Kinetics in methanol synthesis

If thermodynamics gives all the information about the equilibrium, kinetics represents the velocity of the change of the concentration of reactants and products, therefore the study of reaction rates acquires interest.

A very concerning issue lies in the fact that the equilibrium cannot be usually reached due to the residence time inside the reactor, the intervention of safety limitations and any other opposing phenomena. Since the catalyst is present, and it is necessary to overcome the otherwise impassable activation energy, it makes the temperature bounded below, in fact catalysts require quite high temperature to perform; on the other hand, thermodynamics suggests to work at the lowest temperature possible whenever the main reaction is exothermic, and this is true in the case of methanol synthesis as already seen in the apposite section (delta enthalpy of the reactions in *equations 1.10 and 1.11*). In addition, the heterogeneous environment of reaction (gas–solid) in the methanol production introduces new problematic related to transport phenomena: it is not possible to find a simple rate model able to represent reality, without considering the adsorption on the catalyst and the presence of hydrogen, the smallest molecule in universe which for definition enhances the diffusion phenomena; these occurrences increase the effects on the formation rates.

To build up a good kinetic model it is necessary to keep in mind notions regarding transport phenomena and thermodynamics, as already explained, with the addition of a good knowledge about reactants and feed composition focusing on the mutual proportion between components. Some parameters to evaluate the efficacy of a given feed in relation with the system and the kinetic model will be shown later in the discussion. Finally, a set of experiments is carried out followed by the mathematical derivation of the model.

A wide list of kinetic models is presented by Bozzano and Manenti [5]. The considered cases range between the 1976 and 2014, covering the most recent applications. Other than studying new kinetics model, it is possible to refit the parameters of an existing model, as it happened with Graaf et al. kinetics [8] in the work of Bisotti et al. [4].

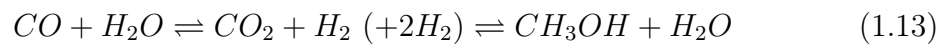
For the matter of simplicity some assumptions were done. First the formation of byproducts was not considered, discharging models and discussions as the one suggested by Park et al. [17], where it was considered also the formation of dimethyl ether. The proposed hypothesis is supported by the fact that the current catalysts reached a level of selectivity to methanol above 99%. In addition, the case-study simulated in MADSim has involved the adoption of CO_2 as main source of carbon, thus required an appropriate model. Therefore the chosen kinetics results to be the one proposed by Vanden Bussche and Froment [6]. This fact permitted to rearrange the formulation according to the software needs, supported by Bisotti et al. [4]. VBF model considers only two reactions to

describe the system, in particular the carbon dioxide hydrogenation to methanol and the reverse water gas shift shown in *equation 1.11* and *equation 1.12*. This last reaction is presented as a direct water gas shift, an extra attention is required during the set of the system in the software, inverting the sign of all stoichiometric coefficients.

Vanden Bussche and Froment kinetic model

Vanden Bussche and Froment kinetic 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 [6]. The reactions shown in *equation 1.11* and *equation 1.12* are coupled as follows.

- **Water gas shift and carbon dioxide hydrogenation coupling:**



If the initial point is where the carbon dioxide is present, the adoption of the reverse water gas shift results evident. Moreover the reaction scheme, starting with the CO₂, is here presented:

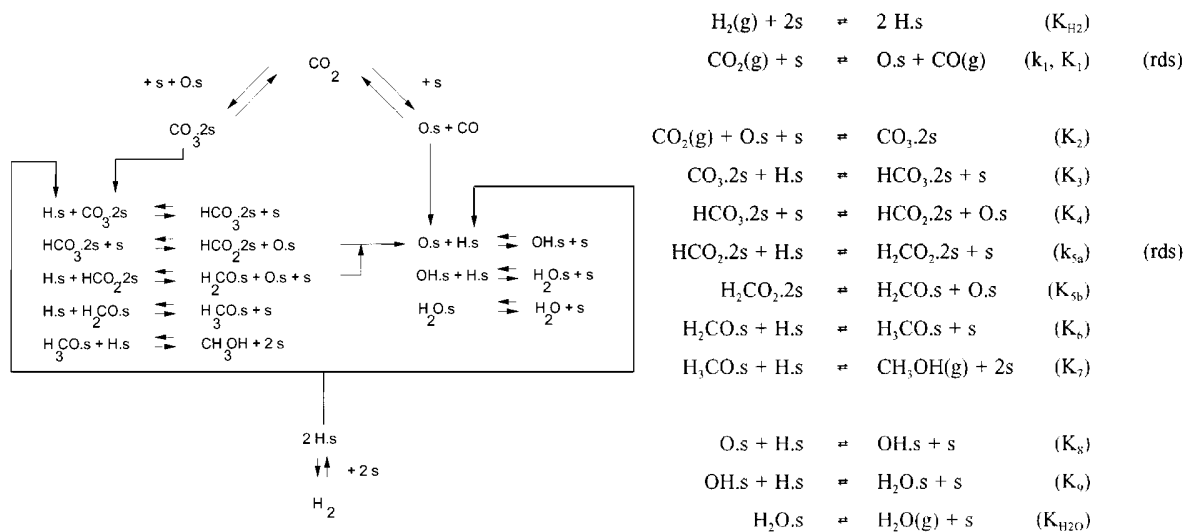


Figure 1.9: Reaction scheme for methanol synthesis: CO₂ hydrogenation and WGS. *rds* stands for rate determining step. Picture adapted from Vanden Bussche and Froment [6].

All further assumptions and simplifications are explained by Vanden Bussche and Froment [6].

The final result is a couple of rates related to the two considered reaction as shown hereinafter.

- **Reaction rate of CO₂ hydrogenation:**

$$r_{CO_2/MeOH} \left[\frac{mol}{g_{cat}S} \right] = \frac{k_1 p_{CO_2} p_{H_2} \left(1 - \frac{p_{MeOH} p_{H_2} O}{p_{H_2}^3 p_{CO_2} K_{eq,CO_2/MeOH}} \right)}{\left(1 + K_1 \frac{p_{H_2} O}{p_{H_2}} + \sqrt{K_2 p_{H_2}} + K_3 p_{H_2} O \right)^3} \quad (1.14)$$

- **Reaction rate of RWGS:**

$$r_{RWGS} \left[\frac{mol}{g_{cat}S} \right] = \frac{k_2 p_{CO_2} \left(1 - \frac{p_{CO} p_{H_2} O}{p_{H_2} p_{CO_2} K_{eq,RWGS}} \right)}{\left(1 + K_1 \frac{p_{H_2} O}{p_{H_2}} + \sqrt{K_2 p_{H_2}} + K_3 p_{H_2} O \right)} \quad (1.15)$$

where p_{CO_2} is the partial pressure of carbon dioxide, p_{CO} is the partial pressure of carbon monoxide, p_{H_2} is the partial pressure of hydrogen, p_{H_2O} is the partial pressure of water, p_{MeOH} is the partial pressure of methanol, all measured in bar, and more in general those are considered the *bases* for the reaction rate calculation. Continuing, k_1 is the kinetic constant for direct reaction in the CO₂ hydrogenation, k_2 is the kinetic constant for direct reaction in the RWGS, $K_{eq,CO_2/MeOH}$ is the equilibrium constant of the CO₂ hydrogenation, $K_{eq,RWGS}$ is the equilibrium constant of the RWGS, K_1 , K_2 , and K_3 are kinetic constants involved in adsorption or desorption phenomena as presented in the complete scheme (*figure 1.9*). All the kinetic constants follow the Arrhenius law (*equation 1.16*).

- **Arrhenius law:**

$$k_i = A_i \cdot \exp \left(-\frac{Ea_i}{RT} \right) \quad (1.16)$$

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.

Performance parameters

To characterize the composition of the reactant gas fed to the reactor two parameters are used. The *stoichiometric number* (SN) and the *carbon oxide ratio* (COR) permit to understand if the inlet stream can be described according to the chosen kinetic model: a further discussion is carried on later in the text.

The expressions for SN and COR are reported as follows.

- **Stoichiometric number (SN):**

$$SN = \frac{x_{H_2} - x_{CO_2}}{x_{CO} + x_{CO_2}} \quad (1.17)$$

- **Carbon oxide ratio (COR):**

$$COR = \frac{x_{CO_2}}{x_{CO} + x_{CO_2}} \quad (1.18)$$

where x_{H_2} is the molar fraction of hydrogen in the feed stream, x_{CO} is the molar fraction of carbon monoxide in the feed stream and x_{CO_2} is the molar fraction of carbon dioxide in the feed stream.

The objective is to work with an excess of hydrogen, therefore a value of SN higher than 2 is highly recommended. In fact, $SN < 2$ indicates an excess of carbon oxides with respect to hydrogen which would lead to larger by-product formation [15]. The value of 2 is not casual: in this case it means that the reacting mixture is at perfect stoichiometric conditions. The value of SN depends on the process and on the catalyst as it is possible to understand consulting different feed listed and studied by Leonzio [11]. More in general, SN ranges between 1.5 and 3.0, lower values are associated to new sources while the interval 2.8–3.0 is achieved exploiting syngas from natural gas reforming [5].

According to the assumptions of CO_2 as main source of carbon an high value of COR is expected; on the other hand, COR is usually kept under 0.6 [14] since higher amounts of CO_2 lead to drops in the reaction kinetics and fast catalyst deactivation.

Those parameters were used in the simulated reactor in order to have a believable feed and as a consequence a functioning system.

1.4. In this thesis

The objective of this thesis project is to improve MADSim, expanding the existing chemical reaction environment and creating a general model for a tubular reactor. The program permitted to construct the kinetics of a reaction utilizing the built-in functions such as Arrhenius law and power law, while the remaining part was left to the user, in order to simplify the procedure a standard heterogeneous model was introduced. By the way, the already present reactor, had been used for a validation of a specific industrial facility, being an element particularly created for that role, therefore the need of customizable models emerged. Starting from the alkylator one, a more generic tubular reactor was developed. (*chapter 2*).

Finally validation procedures were conducted. Starting from the generic kinetics proposed in this thesis, a comparison with the one proposed by Russo [18] was led (*chapter 3*).

An increasingly predominant chemblock was considered: methanol. A preliminary analysis on the thermodynamics, kinetics and industrial production of the compound was led and argued in the previous section of this introduction. A consecutive simulation in the MADSim environment, both validating the generic kinetics and reactor model (*chapter 3*), was carried on. Moreover a section in *chapter 2* is dedicated to the sizing of a methanol reactor and to the adjustment of an existing kinetic model in order to fit in the MADSim structure.

It was demonstrated the potential of MADSim to be customized and, at the same time, to perform interesting industrial applications, making the program capable to support the manufacturing in the future.

2 | Methodology

A model is a convenient arrangement of key points capable to reproduce a more complex object, thus implies that a model should be an accessible, empty structure which a user can fill according to the necessity. The lack of a framework for a generic tubular reactor and a kinetic model capable to cover a vast range of cases opened the opportunity to investigate them.

The reaction related theory, in which most of the phenomena and their complexities are considered, is in the case of heterogeneous environment; in particular, the fluid phase reagents, which could be both gaseous or liquid, react with the solid catalyst. The coexistence of multiple phases implies the presence of extra terms, describing the transport phenomena other than the reaction itself, the sum of which composes the overall rate of formation.

For the reactor it was chosen to implement a generic tubular reactor, for instance, such a model should consider different cases. In the specific, a cooling system was inserted and a set of parameters, e.g. the catalyst density and void ratio, were introduced as well. These contributions specifically fit into the aforementioned chemical kinetic representation. Therefore, the most convenient way to proceed suggested to start with the existing alkylator. Taking inspiration from it, the structure of the specific reactor was expanded and generalized: a new model was developed in order to satisfy more complex application. Finally, a simple procedure for the characterization of a methanol reactor is shown; the catalytic tube was sized as presented hereinafter, moreover the *Vanden Bussche and Froment kinetic model* [6] was adjusted in accordance to the heterogenous kinetic model introduced in MADSim via this thesis project.

2.1. *ChemicalReaction* Environment

Inside the MADSim code a *ChemicalReaction* environment is present. Before the intervention made by this thesis, the framework was already composed by the following few classes:

- ***KineticConstant***. It permits the calculation of the kinetic constant according to the given temperature. The child classes are *Constant*, which keeps the value unchanged, and *Arrhenius*; this last class requires empiric information other than temperature, as shown in *equation 1.16*, such as the activation energy and the pre-exponential factor;
- ***Kinetics***. It is predisposed to evaluate the proper reaction rate, which is the key element that affects material and energy balances. The only child class present was *PowerLaw*: it is a simple model that covers a small range of application, in particular in case of homogeneous and pseudo-homogeneous environments of reaction;
- ***ChemicalReactions***. It contains all the methods utilized to describe the system. It deals with the reaction rate, evaluated via *Kinetics*, calculating the heat of reaction and the formation rates for each species belonging to the simulated system.

Since the aforementioned classes have worked in a good way, the majority of the effort lies on the creation of new child classes for *Kinetics*. Once this is done, *ChemicalReactions* performs all the extra calculation, being already capable to handle the reaction rate to derive the other information. In fact, the insertion of the stoichiometry in the main function, the components and the empiric data for the *Kinetics* class is sufficient to make the system work.

A brief discussion is conducted hereinafter, comprehending a short explanation of the heterogeneous kinetic theory and how it was implemented in the program.

2.1.1. Heterogeneous kinetic model

Most of the chemical processes involve the presence of catalysts in order to improve the production rate. Moreover, the raw materials are fed to the system and treated in gaseous or liquid phase, while the catalyst is a metal or an oxide at solid state: this difference in phases makes the system heterogeneous.

Description of involved phenomena

The kinetics does not describe only the chemical transformation, in fact the most complete theory includes all the transport phenomena around, on and in the catalyst other than reaction itself. To clarify this concept the seven steps of a reaction are here illustrated and shown in *figure 2.1* too.

1. **Film diffusion** (entering): the reactants flow from the bulk environment into the boundary layer around the catalyst; this phenomenon is governed both by the mutual interaction between the involved species and by the geometry of the catalyst;
2. **Porous diffusion** (entering): the reactants enter inside the pores of the catalyst. The path inside these tunnels depends on their quantity, the *vacuum fraction* and the *tortuosity*;
3. **Adsorption on the catalyst**: the reactants interact with the active surface of the metal or the oxide. The attaching sites are called *active sites*;
4. **Chemical reaction**: adsorbed species and even free reactants (if they exist) interact each other transforming themselves into new compounds, the products;
5. **Desorption from the catalyst**: since it is the reverse of the adsorption, the species detach from the active surface of the catalyst;
6. **Porous diffusion** (exiting): the products and not reacted species travel through the pores, the controlling elements of this stage are the same described for the entering porous diffusion;
7. **Film diffusion** (exiting): being it is analogous to the entering film diffusion, the species go from the boundary layer to the bulk.

An illustrative scheme, presenting the seven steps, is shown hereinafter:

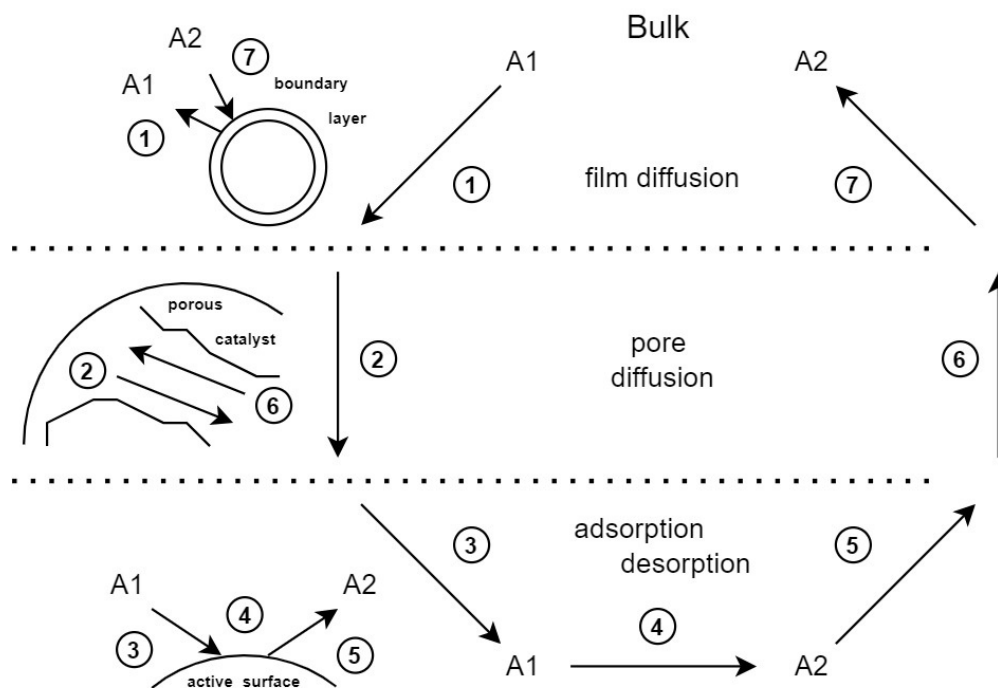


Figure 2.1: Seven steps of heterogeneous catalyst reactions: (1) film diffusion, (2) porous diffusion, (3) adsorption on the catalyst, (4) proper chemical reaction, (5) desorption from the catalyst, (6) porous diffusion, (7) film diffusion.

Since steps (1), (2), (6), and (7) are pure transport phenomena, their representation in the reacting system could be done considering tortuosity and vacuum fraction. During the evaluation of the catalyst density and of the empty volume filled with the reagent stream, the reaction rate in $[\text{mol/s/g}_{\text{cat}}]$ becomes a multiplicative factor which allows to obtain the exiting molar flow in $[\text{mol/s}]$. Therefore, the kinetic scheme of reaction is written as a sum of sub-reactions, considering also the adsorption and desorption mechanisms as it is possible to appreciate in the methanol synthesis example (VBF model in *figure 1.9*). Some theories which build up the rate in accordance to the aforementioned statement are the Langmuir–Hinshelwood–Hougen–Watson (LHHW) theory, the Eley–Rideal (ER) kinetics and the redox derived formulations.

The proposed model

Since the difference between the various theories lies on the choice of the sub-reactions of the scheme, based both on theoretical assumptions and empirical proofs, the final formulation of the reaction rates results similar.

- **Heterogeneous kinetic model.** The aforementioned assumptions can be summarised as follows:

$$r = \frac{\overrightarrow{r}_{dir} - \overleftarrow{r}_{inv}}{\left(1 + \sum_j^{NK} r_{j,ads}\right)^n} = \frac{\overrightarrow{k}_{dir} \cdot \prod_i^{NC} a_i^{b_i} - \overleftarrow{k}_{inv} \cdot \prod_i^{NC} a_i^{b_i}}{\left(1 + \sum_j^{NK} K_j \cdot \prod_i^{NC} a_{ij}^{b_{ij}}\right)^n} \quad (2.1)$$

where \overrightarrow{r}_{dir} is the direct reaction rate, \overleftarrow{r}_{inv} is the inverse reaction rate, $r_{j,ads}$ are the NK different adsorption and desorption rates and n is the exponent of the denominator, which depends on the chosen theory, usually related to the active site interaction and the associated stoichiometry. In addition, the second formulation presents the expansion of the various rates, 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 1.16). 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.

2.1.2. Coding part

After the preliminary discussion on the argument, the acquired notions are transformed into code logic to be inserted in the MADSim structure. Some choices were operated in order to properly fit in the OOP and in the already existing program as well. Hereinafter, all the presented topic are explained.

External input

To begin the programming of the heterogeneous kinetic model, some external inspirations were taken, choosing Aspen HYSYS[®] as starting point. It is one of the most widespread simulator used, its chemical reaction environment works properly, it is easy to understand, and it can be used without excessive effort.

In the following image the *Kinetic Equation Help* of Aspen HYSYS[®] is illustrated.

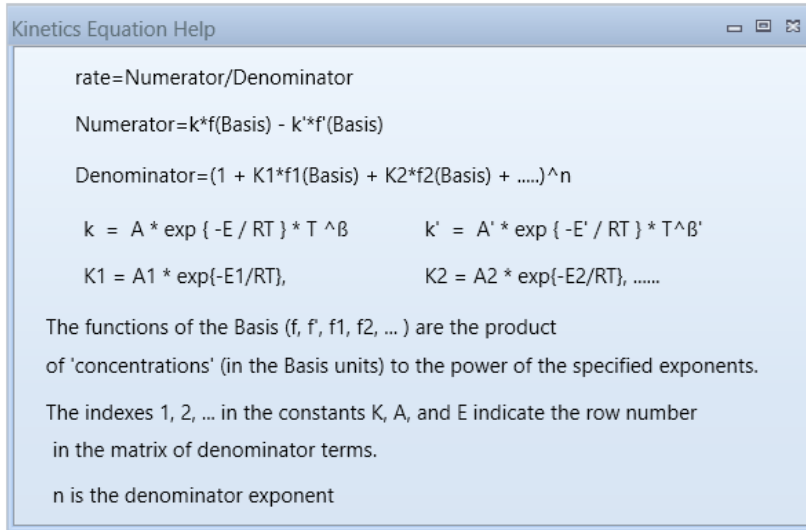


Figure 2.2: The *Kinetic Equation Help* GUI from Aspen HYSYS® chemical reaction environment.

In the figure above, the methodology implemented in Aspen HYSYS® is shown: in order to evaluate the kinetic constants of the numerator, it considers an extra dependence on temperature which is external to the exponential of the Arrhenius law. For a matter of simplicity, the formulation proposed by the software is rewritten in order to make it comparable with one illustrated in *equation 2.1*. In this way, the terms related to temperature become appreciable as it emerges in the following expression.

- **Heterogeneous kinetic model** (Aspen HYSYS®):

$$r = \frac{\overrightarrow{k}_{dir} \cdot T^{c_{dir}} \cdot \prod_i^{NC} a_i^{b_i} - \overleftarrow{k}_{inv} \cdot T^{c_{inv}} \cdot \prod_i^{NC} a_i^{b_i}}{\left(1 + \sum_j^{NK} K_j \cdot \prod_i^{NC} a_{ij}^{b_{ij}}\right)^n} \quad (2.2)$$

where all the parameters equal to the ones shown in *equation 2.1* are the same, T represents the temperature of the system, and c_j is the exponent in the associated sub-rate. Hence, the *equation 2.2* results to be more detailed, making its formulation more complicated. In particular, extra experimental data are required; on the other hand, the vast majority of the model does not consider this dependence on the temperature so prominent. It is also true that the addition of a second model based on partial pressure, starting from one concentration-based, as discussed below, introduces an indirect dependence on temperature with the advantage to not require the specification of the exponents associated to the temperature. In this way, the code is maintained clean and extra external numbers, during the setting of the system, are not necessary.

Programming choices

Initially MADSim was programmed in a way where the reaction rates were written as functions of concentration; on the other hand a multitude of systems is better described taking into account the partial pressure of the components or even their fugacity, which is the deviation of the real gases from the ideal ones. To resolve the issue, the proposed heterogeneous kinetic model has firstly been coded exploiting the concentrations as bases (*Heterogeneous_KinModel_Concentration* class) and only secondarily it was revamped introducing another class (*Heterogeneous_KinModel_PartialP* class) in order to deal with the largely diffused utilization of partial pressure based reaction rates. Fugacity was not considered, making the implementation of a specific class a viable work for a future project. Moreover, a unified class could be a valid solution thanks to the *switch* function. To perform the transformation from a concentration to a partial pressure the ideal gas approximation was introduced.

- **Ideal gas law** (partial pressure adjustment):

$$P_i = \frac{C_i}{RT} \quad (2.3)$$

where P_i is the partial pressure of the species i , C_i is the concentration of the compound i , T is the temperature of the system and R is the ideal gas constant. Since the partial pressure depends on temperature *Heterogeneous_KinModel_PartialP*, that is based on *equation 2.1*, implicitly works as the *equation 2.2*. The only difference is that the exponents associated to the temperature are not required and the system proceeds smoothly and with less effort: less empiric data are necessary.

If the mathematical formulations are already explained above, to enter in the proper coding part some notions should be clear. First of all, the utilization and the consequent understanding of characteristic coding cycles such as *for*, *if*, and *while* is a fundamental topic: multiple similar operations are condensed in a small number of code lines. Another element of interest is the harmonic interaction of the newest lines with the existing program: a consistent use of the existing classes was conducted.

The possible outcomes of *equation 2.1* are infinite due to the NC and NK numbers. Since in the analyzed system the components could be any possible combination of all the existing ones, and because of the selected model, which influences the amount of involved adsorption–desorption mechanisms, the denominator term could present a huge variety of different sub–rates, becoming an issue that the code must be capable to deal with. Therefore, it was decided to write the classes *Heterogeneous_KinModel_Concentration* and *Heterogeneous_KinModel_PartialP* in the way where all the information related to

the kinetic constant are distinctly collected in order to define the number of associated sub-reactions; this is true because every rate composing the overall one is written according to a power law, as presented hereinafter.

- **Power law:**

$$r_j = k_j \cdot \prod_i^{NC} a_{ij}^{b_{ij}} \quad (2.4)$$

where k_j is the kinetic constant even here considered in accordance with the Arrhenius formulation (*equation 1.16*). For the resolution, the already existing *Arrhenius* class and the method to calculate the kinetic constants were exploited inside the model, thanks to the *pointer* interactions. In fact, the *pointer* results to be an useful object in C++, permitting the link between different classes; moreover it is possible to affirm that it is one of the key component to understand the OOP.

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 *equation 2.3*;
4. calculate both the direct and the inverse reaction rate, and all denominator ones, knowing that they are singularly considered as power law (*equation 2.4*), exploiting a *for* cycle for the denominator rates;
5. construct the overall rate according to *equation 2.1*.

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. Tubular reactor implementation

The core section in a chemical process plant is the transformation environment, having in the reactor its main component. Inside this type of equipment the chemical reaction happens transforming the raw material in valuable product.

This unit can have a huge variety of configurations, depending on the reagents, the products or even the phase in which the process is conducted. Hence, a multitude of configurations exists and, consequently, their mathematical model. To simplify the treatment of this topic, two fundamental approximations rise:

- **Continuous stirred tank reactor (CSTR).** This equipment simulates a perfectly mixed tank in which every point presents the same composition, in the specific, the result of the chemical reaction. The corresponding material balance (per single species) is shown as follows.

$$\dot{n}_{in,i} - \dot{n}_{out,i} + \sum_j^{NK} \nu_{ij} r_j V = 0 \quad (2.5)$$

where $\dot{n}_{in,i}$ is the molar inlet flow associated to species i , $\dot{n}_{out,i}$ is the molar outlet flow associated to species i , 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 tank.

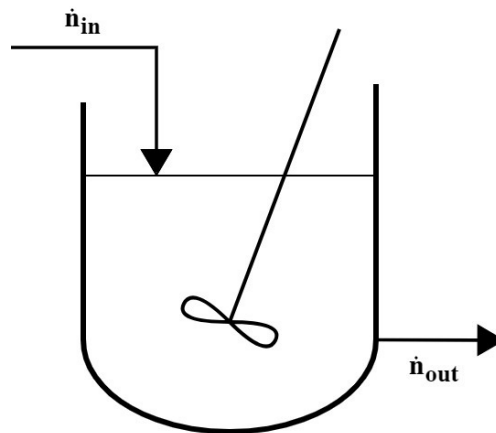


Figure 2.3: Simple representation of a continuous stirred tank reactor.

- **Plug flow reactor (PFR).** This unit represents a tube in which the concentration is constant in the radial distribution and it varies along the axial coordinate. It is possible to imagine a plug that moves inside the equipment; keeping the focus on its movement can be useful to describe and understand the evolution of the reaction system. Therefore, this unit can be analyzed according to its volume or even by the residence time. Hereinafter, its mathematical model is shown; the formulation appears to be a differential equation (and no more an algebraic one as it happens for the CSTR, *equation 2.5*).

$$\frac{d\dot{n}_i}{dV} = \sum_j^{NK} \nu_{ij} r_j \quad (2.6)$$

where $d\dot{n}_i/dV$ is the molar flow derivative in the volume associated to species i , 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 dV is the derivative of the volume.

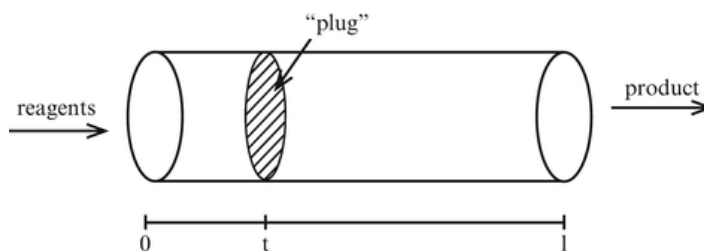


Figure 2.4: Simple representation of a plug flow reactor.

Furthermore, *equation 2.5* and *equation 2.6* are presented in the simplest case, when both units have reached the steady state condition. Since the main argument of this thesis is MADSim which is a dynamic simulator, these are the starting points of the discussion; in fact in the next sections it is possible to appreciate how this base is developed to fulfil the objective of a proper model of reactor interacting into a dynamic environment.

Moreover, to model a real reactor a suggested methodology is to visualize it as a combination of CSTR and PFR. Moreover the CSTR could be rendered as a PFR imagining the tube encircled by an infinite recirculation; the same could be done for the PFR. A tubular reactor could be seen as infinite series of CSTR, hence, a good approximation could be the visualization of a PFR as a considerable number of tank reactors in line; this procedure permits also to avoid the resolution of a differential equation substituting it with a manageable quantity of algebraic equations.

Since in this thesis a focus on tubular shaped reactor is considered, a discussion starting from simple PFR reactor (*figure 2.4*) arriving to a catalytic tubular one is consequently conducted.

2.2.1. Tubular reactor model

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. Moreover, as already discussed for the presented families of reactors in methanol production (*chapter 2*) and in the previous section, it is possible to build a custom reactor starting with a simple model.

The choice falls on a tubular reactor, having the following characteristics:

- **Cylindrical shape.** The development of this kind of unit lies on the fact that it can be figured as an advanced version of a PFR reactor. Hence, the properties explained above are the starting point for a new model presenting new features related to the successive characteristics;
- **Catalytic.** The considered tube is no more empty, being filled with a catalyst; it presents a structure alternating the active metal with void. The reagent fluid flows in the gap between the catalytic pellets or in the tunnel of a structure that had been previously customized for the specific issue;
- **Non adiabatic.** Based on the real practice, the presence of a cooling or heating system is quite common since the vast majority of reactions are controlled thanks to their strong dependence on temperature; assuming that allows to deal with safety issues and process target requirements.

PFR based reactor

Some possibilities could be taken into consideration. Since the reactor is proposed as a PFR model, the governing equations, which describe the evolution of concentration of the involved species, results to be *equation 2.6*. However this procedure adds to an hypothetical simulated plant extra differential equations, in this case evaluated on the geometry (volume or length) of the unit, making the calculation of the dynamic simulator more time consuming. For that reason, the segregating approach emerges as a better choice; in fact, the description of such equipment is led by a considerable number of algebraic equations (*equation 2.5*). In addition, it is meant as a reminder that the mathematics requires an infinite quantity of successive CSTR to simulate an ideal PFR; on the other hand, a functional and limited value could be find. It is possible to make this number customizable, for the reason of simplicity 10 results to be an acceptable solution, being sufficient for the scope. This decision is supported by other simulators e.g. Aspen HYSYS®.

Furthermore, some specifications on the way the volume V (*equation 2.5*) is calculated

and how the equations themselves are modified, in order to reflect the intrinsic nature of time–driven dynamic simulations, are shown into a specific section below.

Temperature controlling system

To begin the explanation of the governing equation and, therefore, the physics behind the change in temperature in the reactor environment, talking about an adiabatic reactor may result clarifying. In this situation the temperature only depends on the phenomena residing inside the unit: external contribution is not considered eliminating the possibility of an entering or exiting heat flow. In this way the evolution of temperature is described by the internal energy of the involved matter and by the heat released or absorbed by the reactions. This also happened in the study case proposed by Russo in his thesis project: alkylator reactor in the benzene alkylation facility [18]. To make it clear the equation used to describe the system is made explicit hereinafter.

- **Energy balance equation** (adiabatic reactor):

$$\frac{dT}{dt} = \frac{\dot{n}_{in} \cdot \tilde{h}_{in} - \dot{n}_{out} \cdot \tilde{h}_{out} - \sum_j^{NK} r_j \cdot \Delta H_{reac,j} \cdot V}{n_{tot} \cdot \tilde{c}_{p,mix}} \quad (2.7)$$

where $\frac{dT}{dt}$ is the time derivative of the temperature, $\dot{n}_{in,i}$ is the total molar inlet flow, \tilde{h}_{in} is the molar enthalpy associated to the inlet stream, $\dot{n}_{out,i}$ is the total molar outlet flow, \tilde{h}_{out} is the molar enthalpy associated to the outlet stream, 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 and finally \tilde{h}_{in} , \tilde{h}_{out} and $\Delta H_{reac,j}$ represent the enthalpies in various situations, having each one its own mathematical expression.

For the enthalpies are here reported the way their are processed and where the calculation are performed inside the software:

- **Inlet molar enthalpy** \tilde{h}_{in} . The information is extrapolated from the entering stream being all the thermochemical properties known. The calculation is conducted in the EoS environment according to the chosen one;
- **Outlet molar enthalpy** \tilde{h}_{out} . Being this information dependent on the temperature, which is the unknown of the balance, the definition is governed even this time by the chosen EoS. The only difference lies in the way the EoS is reached, in this case the followed route passes through an apposite method called *getMolarEnthalpy*, which is part of the *BaseClass*;
- **Heat of reaction** $\Delta H_{reac,j}$. As mentioned during the description of the chemical environment of the software, the used method *HeatOfReaction* is part of the *ChemicalReactions*, the one predisposed for every kind of calculation based on the reaction rate which is calculated itself in the *Kinetics* class. Moreover, the mathematical expression is here presented:

$$\Delta H_{reac,j}(T) = \sum_i^{NC} \nu_{ij} \cdot \left(\Delta H_{f,i}^0 @ (T_{rif}) + \int_{T_{rif}}^T \tilde{c}_{p,i} dT + WatsonRelation(T) \right) \quad (2.8)$$

where NC is the number of involved compounds, ν_{ij} is the stoichiometric coefficient of the species i in the reaction j , $\Delta H_{f,i}^0 @ (T_{rif})$ is the enthalpy of formation of the compound i at the reference temperature T_{rif} (in the case is considered as 273.15K or 0°C), $\int_{T_{rif}}^T \tilde{c}_{p,i} dT$ is the deviation from the reference temperature to the desired one thanks to the integration of the specif heat $\tilde{c}_{p,i}$, which is a function of the temperature, related to species i , and finally the *WatsonRelation*(T).

Since the shown case is valid only for the adiabatic reactor, to complete the formulation which is able to fit with a wider range of situations, an extra member is added to *equation 2.7*. This element wants to represent the possibility to have an external heat flux (entering or exiting) which interacts with the equipment. The presented concept can be appreciate in the simple representation that follows.

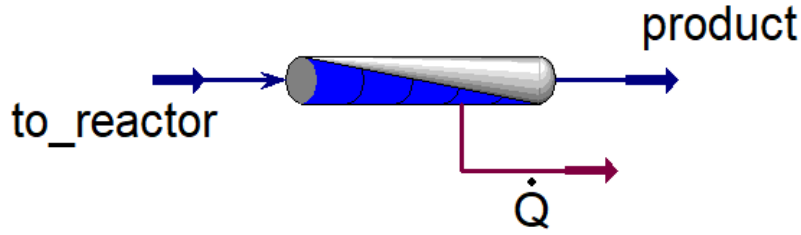


Figure 2.5: Simple representation of a non-adiabatic tubular reactor in the Aspen HYSYS[®] flowsheet. The inlet flow (*to_reactor*), the outlet flow (*product*) and the heat flux between equipment and external environment (\dot{Q}) are shown.

It appears clear that the aforementioned newly introduced term is the heat flux displayed as \dot{Q} , which is disposed in the new energy balance equation as proposed hereinafter.

- **Energy balance equation** (generic reactor):

$$\frac{dT}{dt} = \frac{\dot{n}_{in} \cdot \tilde{h}_{in} - \dot{n}_{out} \cdot \tilde{h}_{out} - \sum_j^{NK} r_j \cdot \Delta H_{react,j} \cdot V - \dot{Q}}{n_{tot} \cdot \tilde{c}_{p,mix}} \quad (2.9)$$

where all the presented elements are the same shown and explained for the *equation 2.7* with the addition of \dot{Q} . This last term could be treated in many different ways depending on the level of precision adopted and on the reactor typology which is wanted to be represented. In fact, there is the possibility to build a parallel flow in which the utility fluid passes through, having its own description and development. This model requires to construct a more complex system similar to the existing *MadHeatExchanger*, present in the code, with the addition of a reacting system; this approach was discharged for a simpler case which is already capable to cover a good quantity of processes without the involvement of extra difficulties. However, this topic opens an interesting perspective for a future development of MADSim, being plausibly a good starting point for new thesis projects.

Returning to the main argument, a clarification on \dot{Q} is carried out. Supported by other simulators, as it happens for Aspen HYSYS[®], the utility side is not considered as a complete flow of matter, leaving only the effect, in term of heat flux, on the main stream. Doing so, the mathematical expression results in a short formulation easy to be understood and handled.

The proposed formula is shown as follows.

- **Heat flux** (main stream side).

$$\dot{Q} = U \cdot A_{lat} \cdot (T - T_{utility}) \quad (2.10)$$

where U is the heat transfer coefficient, A_{lat} is the exchanging area, which in this case is considered as the lateral area of the cylindrical sub-volume, T is the temperature of the system, and $T_{utility}$ is the temperature of the utility. Notice that the parameter U can vary from zero to infinite covering all the possible outcomes. An heat transfer coefficient equal to zero means that the heat flux does not exit re-proposing, in this way, the adiabatic case; on the other hand, a huge value of U makes the energy transfer so fast that the system can be considered isothermic. In the between of this limit cases all the other situation lies on. Furthermore, $T_{utility}$ is used as a constant value which means that the fluid maintains its temperature: this could be the case of a utility operated as a changing in phase (coolant or heat medium) or due to very high heat capacity.

Design parameters

To operate a reactor in real practice, the design operation anticipates the construction of such equipment. Similarly it happened during the coding, since some numbers are required in order to project and simulate a unit.

The parameters which are acted to represent the unit may be categorized into four different families:

1. **Dynamic related parameters;**
2. **Geometric parameters;**
3. **Catalyst related parameters;**
4. **Utility related parameters.**

To be precise, in *dynamic related family* only one element appears: the flow conductance J . It is present due to the nature of the unit which is coded as a flow device, as explained below.

In the *geometric parameters* are defined both the length of the tube and its radius. Thanks to this two elements only, all the others are defined, knowing also that the tube is imagined as cylindrical. In particular, the remaining geometric properties are the cross section area (circle), the lateral area (rectangular) and the volume. All of that are then divided into their smaller counterpart for the ten sub-volumes; notice that the tubular reactor is simulated as a series of ten CSTR as illustrated in the apposite section.

Because of the presence of the catalyst inside the equipment two elements differ: the free

volume and the kinetic model. The volume becomes occupied by the catalytic pellets or by the catalytic structure inserted in the reactor; therefore, a parameter that describes the remaining space is required. For the case the vacuum fraction ϵ is used to describe the behavior being a multiplicative factor of the volume. The free volume, so decreased from the overall cylinder, is the one coupled with the rates to provide for the formation rates and the reaction heats. Then, the mass of the catalyst is taken into account in the form of density ρ . This parameter permits the conversion of the rate from the form expressed in $[\text{mol}/\text{g}_{\text{cas}}/\text{s}]$ into the one figured in $[\text{mol}/\text{m}^3/\text{s}]$, which is the format used in the balances (r in *equation 2.11* and *equation 2.9*).

Since the proposed model is the widest possible, it can be performed with some modifications; for example, in the case of a PFR without the catalyst, it is possible to set the vacuum factor ϵ equal to one in order to consider the entire volume of the cylinder as empty. In the same way, the catalyst density ρ could be avoided considering its value as one as input, writing the rate directly in $[\text{mol}/\text{m}^3/\text{s}]$; please note that the unit of measure of the chemical rate only depends on the parameters given during the kinetics setting procedure as mentioned in the specific section.

The *utility related parameters* describe the heat flux as shown in *equation 2.10*. As mentioned above those elements appear to be the heat transfer coefficient U and the temperature of the utility T_{utility} .

With all the shown criteria the reactor can run in the program simulating the unit, hence, the effort is now shifted on the user who should give reasonable numbers to MADSim. This happened for the methanol reactor simulated as study case to perform the validation; the results are shown in *chapter 3*, while the design procedure and the utilized value are presented in the apposite section of this chapter.

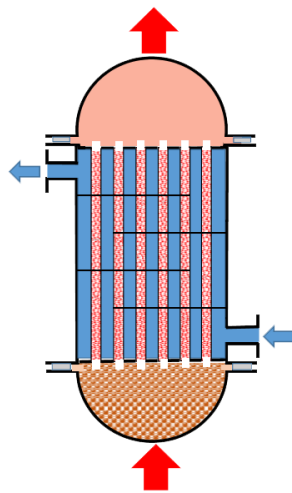


Figure 2.6: Example of a multitubular reactor.

In *figure 2.6* is illustrated a multitubular reactor, a typical unit employed in several process facilities. Because of the proposed model, which can be imagined as the equipment shown in *figure 2.5*, it emerges that a future perspective may consider the possibility to implement such unit; at the moment, it is possible to use parallel single tube reactor simulated with the class described in this work, preceded by a splitter (*MadSplitter*) and then followed by a mixer (*MadMixer*). However, the possibility to condense the splitter, the set of parallel reactors and the mixer exists, making necessary a new parameter which represents the *number of tube*. Because this path was not considered, it is left to a developer interested in the argument. Notice that not only the need of a new number raises but also the description of two new sub-units which bring the characteristics of pressure nodes equipment. In fact, the simple tube is simulated by the only appointment of the flow device implementation, while a multitubular reactor requires a more complex description.

2.2.2. Dynamic simulation derived characteristics

Since the majority of the theories regards the steady state condition, some topics were presented generalizing the discussion as a consequence of a good flowing treatment. In this section, an in-depth analysis and considerations on the dynamic purpose of MAD-Sim are well explained hereinafter.

In particular, the steady state equations are modified in order to describe the dynamic condition, fulfilling the purpose of such simulator, as displayed and consequently explained. Moreover, how the equipment is figured out in the program becomes a point of interest, for which an apposite section is deserved; even a small section that focuses its attention on the insertion of the equipment in the coding environment is presented.

From steady state to dynamic

As already mentioned above, *equation 2.5* is subject to some modifications. In particular, the accumulation term has to be considered due to the intrinsic nature of the simulator (this aspect can be understood with a reference to the initial part of *chapter 1*, where the differences between static and dynamic simulators are discussed). To be more precise, this element represents the internal build-up inside the unit, being a sort of small hold up repeated as many times as the parts the tube is divided into. This follows the reality, in fact a real tubular unit may run into over or under pressure due to external disturbances or during special procedures (startups and shutdowns) having as a consequence an irregular flow which results to be some times accelerated and some others slowed down.

The equations describing the change in concentration due to the reactive environment are

here presented.

- **Tubular reactor sub–volume species balance equation** (dynamic):

$$\frac{d\dot{n}_i}{dt} = \dot{n}_{in,i} - \dot{n}_{out,i} + \sum_j^{NK} \nu_{ij} r_j V \quad (2.11)$$

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 as already discussed.

To complete the set of equations for each sub–volume, the energy balance should be considered other than the species balance equations. As opposite to what is done for the material balances, the formulation presented in *equation 1.4* is already written in the form ready for a dynamic simulator such as MADSim.

A notable mention of the *BzzMath* library should be done: since the aforementioned system appears to be a DAE (differential algebraic equations), a mathematical instrument capable to deal with the issue emerges as fundamental; for the case, a C++ library developed by Professor Buzzi-Ferraris at the Politecnico di Milano is adopted. It implements numerical methods to solve several issues, in particular the root finding, algebraic and differential systems of equations, and others are solved by the employment of this library inside the MADSim environment. To be more precise, the *BzzDaeObject* is used to construct the systems, while the variables are provided via the *BzzVector*.

Flow device

The presented model is a tubular reactor, for this reason, in the dynamic simulation environment of MADSim, it is seen as flow device. As mentioned above the discussion is conducted on a single tube unit avoiding the implementation of pressure nodes inside the unit structure.

The parameter which governs this kind of representation is the flow conductance J as it is possible to appreciate in *equation 1.5*. As explained in the appropriate section in *chapter 1*, the difference in pressure ΔP is taken from the proximal pressure nodes, while for the density ρ it is chosen to use the exiting stream one; this last point is highlighted due to the fact that different choices can be made.

Insertion in *Builder* class

In accordance to the exploitation of programming patterns, every piece of equipment is collected in the *Builder* class. In this way the builder pattern is used giving to the software the capability to construct the units via a unified interface, which is the *Builder* class itself. This happens calling the equipment through a method of such class according to *builder.EquipmentName()*, in particular, the tubular reactor is called as *builder.TubularReactor()*, with inside the parenthesis all the parameters shown above, the stream attached to the unit and the identification label.

Please notice that inside the builder the object is constructed while the aforementioned method recalls the class dedicated to the description of the equipment. Every unit is coded separately, often scripting multiple classes which compose the complete object, as happens for the tubular reactor: in fact, it is described with its own class that contains the link to the one used for the definition of the sub-volumes.

For a matter of order, all the classes created for the delineation of the reactor are collected into two different pages of code: the header (.h) for the declaration and the code (.cpp) for the definition. In particular, these two are *MadTubularReactor.h* and *MadTubularReactor.cpp*.

2.3. Methanol reactor simulation

To complete the theoretical description introduced in the previous chapter, in continuity with the development of new features inside the MADSim environment, a simple simulation is conducted. For this reason a catalytic single tube extracted from a plausible multitubular reactor is replicated. If the results are collected in *chapter 3*, how the simulation is performed is presented in the following section.

To be more precise, two operations were done to fulfil the requirements for the simulation: first of all, the adjustment of the Vanden Bussche and Froment kinetic model [6] is operated in order to fit into the MADSim kinetics environment (the rearrangement procedure is supported by the research of Bisotti et al. [4]); then the second part is dedicated to the sizing of the reactor. A simple procedure is proposed and the value used for the simulation are presented in *table 2.2* and *table 2.3*.

2.3.1. Vanden Bussche and Froment kinetic model rearrangement

As explained in the introduction (*chapter 1*), for the methanol case-study the Vanden Bussche and Froment kinetic model was chosen. The VBF kinetics [6] was proposed according to the following descriptive reactions: the carbon dioxide hydrogenation and the reverse water gas shift; in particular, these are rendered by the rate equations shown in the aforementioned section (*equation 1.14* and *equation 1.15*).

To properly fit in the model proposed in this thesis project, a rearrangement was acted. In fact, the mathematical formulation under consideration is the one which can be appreciate in *equation 2.1*. For this reason the VBF appears with a equivalent form where the new equations are displayed hereinafter.

- **Reaction rate of CO₂ hydrogenation** (rearranged):

$$r_{CO_2/MeOH} \left[\frac{mol}{m^3 s} \right] = \frac{k_{1,dir} p_{CO_2} p_{H_2} - k_{1,inv} p_{MeOH} p_{H_2} p_{H_2}^{-2}}{\left(1 + K_1 p_{H_2} p_{H_2}^{-1} + \sqrt{K_2} p_{H_2}^{0.5} + K_3 p_{H_2} \right)^3} \quad (2.12)$$

- **Reaction rate of RWGS** (rearranged):

$$r_{RWGS} \left[\frac{mol}{m^3 s} \right] = \frac{k_{2,dir} p_{CO_2} - k_{2,inv} p_{CO} p_{H_2} p_{H_2}^{-1} p_{CO_2}^{-1}}{\left(1 + K_1 p_{H_2} p_{H_2}^{-1} + \sqrt{K_2} p_{H_2}^{0.5} + K_3 p_{H_2} \right)} \quad (2.13)$$

Please notice that all the partial pressures are the same as in *equation 1.14* and *equation 1.15*, maintaining their respective exponents. The real difference lies on the formulation of the kinetic constants. Being those written according to the Arrhenius law (*equation 1.16*), rearranging their values means modify the activation energy Ea_i and the pre-exponential A_i factor in accordance to the properties of exponential operator.

Moreover, the formulations proposed above are arranged in the form where the rate is seen in $[mol/m^3/s]$. For this adjustment on the unit of measure, the density of the catalyst is multiplied to the pre-exponential factors of the direct and indirect kinetic constants $k_{1,dir}$, $k_{1,inv}$, $k_{2,dir}$, and $k_{2,inv}$.

Starting from the work of Vanden Bussche and Froment [6], confronting with the one of Bisotti et al. [4], the final values so reached are presented in the following table.

Table 2.1: Kinetic parameters of the reformulated VBF model.

Reaction	Kinetic constant	A_i	Ea_i
CO ₂ hydrogenation	$k_{1,dir}$	$1.98 \cdot 10^3$	$-3.67 \cdot 10^4$
	$k_{1,inv}$	$7.75 \cdot 10^{13}$	$2.20 \cdot 10^4$
RWGS	$k_{2,dir}$	$2.26 \cdot 10^{13}$	$9.48 \cdot 10^4$
	$k_{2,inv}$	$2.11 \cdot 10^{11}$	$5.51 \cdot 10^4$
Adsorbtion constant	K_1	$3.45 \cdot 10^3$	0.0000
	$\sqrt{K_2}$	$4.99 \cdot 10^{-1}$	$-1.72 \cdot 10^4$
	K_3	$6.62 \cdot 10^{-11}$	$-1.24 \cdot 10^5$

Notice that the activation energies Ea_i unit of measure is [J/mol], which is the one used to run MADSim correctly. Furthermore, the units of measure of the kinetic constants are all different coherently to the overall rate unit and the bases with they are multiplied with. Finally the partial pressures are processed in [bar].

2.3.2. Methanol reactor sizing and operation condition

Every user can build its own reacting system; to do so many theories, empiric ways, or even trial and error procedures can be adopted.

One methodology for the characterization of the reactor as simple design procedure arises as a doable path, showing the know how of this elaboration in the next sections.

Moreover, the final numbers thus produced had been inserted in MADSim as a proof of validity (*chapter 3*).

Hereinafter, the mathematical elaboration is reported together with some side considerations.

Stream characterization

Before the proper sizing of a reactor, knowing (at least as an approximation) the reactant stream, which is processed in the unit, becomes fundamental. This step defines the thermochemical conditions for the process: how the raw gases are composed and how they should be treated to have the best possible results. Then, some limitations rise due to different factors such as the material involved for the construction, the economy or also safety issues.

Even if the choice was arbitrary, the composition was defined in order to reproduce flue

gases that are processed with hydrogen, resulting similar to the stream shown in the work of Leonzio [11]. Furthermore, this practice follows the modern trend for the carbon abatement (CCU), making clear the intention to study topics that have been discussed a lot nowadays and showing the possibility to do that with the backing of MADSim.

To define the working conditions, and therefore the physical properties of the stream, values that are conform to the modern practice were selected, as it is explained in the *chapter 1* and supported by the theory [9].

Hereinafter, the mass flow rate of the reagent stream, its composition and the physical properties are reported.

Table 2.2: 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	[-]

To conclude the characterization of the feed, the evaluation of the performance parameters is done. It is meant as a reminder that these numbers are the *stoichiometric number* SN and the *carbon oxide ratio* COR , already described in *equation 1.17* and *equation 1.18* respectively.

In the presented work they results to be:

1. $SN = 1.82$;
2. $COR = 0.75$.

SN appears to be a little lower than two as expected for a source coming from waste gases and, in particular, less than the typical range of consolidated process path (such as methanol from syngas [5]). COR exceeds the value of 0.6, unlike what was expected, being that the typical value for the main methanol production line [14]: the reason of this surplus is related to the unconventional source. Since the objective is to abate the carbon dioxide it is normal to have an extra amount of CO_2 respect to the one suggested for syngas-based facilities.

Catalytic tube design

Starting with the assumption of a single tube reactor, the first observation lies on the choice of a pipe narrow enough: the diameter of such tube (40 mm) was selected from standard values for the application. However, the length was derived from the volume, recalling that the pipe has a cylindrical shape, which was obtained exploiting an heuristic methodology: GHSV (gas hourly space velocity) and the standard volumetric flow rate interact to provide for the catalyst volume, which is further processed with the void fraction. The formulation describing such methodology is here reported.

- **Reactor volume - GHSV relation:**

$$V_{reactor} = \frac{V_{catalyst}}{(1 - \epsilon)} = \frac{\dot{V}}{GHSV \cdot (1 - \epsilon)} \quad (2.14)$$

where $V_{reactor}$ is the volume of the reactor, $V_{catalyst}$ is the volume occupied by the catalyst, $GHSV$ is the gas hourly space velocity, which is expressed in [1/h], \dot{V} is the volumetric flow rate in [STDm³/h], and ϵ is the void fraction.

Methanol synthesis requires a moderate GHSV in order to ensure adequate conversion while maintaining reasonable reactor sizes: a typical range for this value spans from 5,000 to 20,000 h⁻¹. For the case 10000 h⁻¹ was adopted.

Another arbitrary choice, based on industrial practise, applies to the catalyst selection. The density, which is similar for all the elements of the list presented in *table 1.1*, was defined as 1170 kg/m³; it happens similarly for the proposed vacuum ratio.

For the heat transfer coefficient, otherwise, a huge number was exploited to represent a nearly isothermic condition, where the quasi-constant temperature is approximately the one of utility. This last property respects the characteristic condition adopted in the methanol synthesis [9].

Finally the flow conductance is the one capable to maintain the flow rate utilized (*table 2.2*), recalling the attention on *equation 1.5*, since the tubular reactor is performed as flow device.

The final numbers thus obtained are shown as follows:

Table 2.3: Design parameters for the catalytic tube.

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

3 | Results

As largely discussed in the previous chapters, some validating simulations were done. Starting with the approval of the kinetic model, the case-study of the alkylator proposed by Russo [18] was taken into account. Since it was already implemented in the code as an example, it was used to proceed with the validations.

Similarly, the tubular reactor proposed in this work was compared with the specific implementation of the alkylator, being the study case of the previous developer of MADSim, as stated above.

Finally, a completely new system was analyzed and simulated: a single tube extracted from a plausible tubular reactor for the methanol production. How the design was conducted and the choices made are explained in *chapter 2*.

3.1. Kinetics model validation

As anticipated above, the first 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 [18].

It is correct to spend some words about the old alkylator model, which is the inspiration for the one proposed in this thesis; it works in the same way as the generic tubular reactor with few differences: the reactor does not present a cooling system due to its adiabatic nature and the equations are written specifically for the situation having the same structure of the new reactor model.

Since the unit is the same, the only difference lies on the operative kinetics: in this way the comparison was properly conducted. 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.

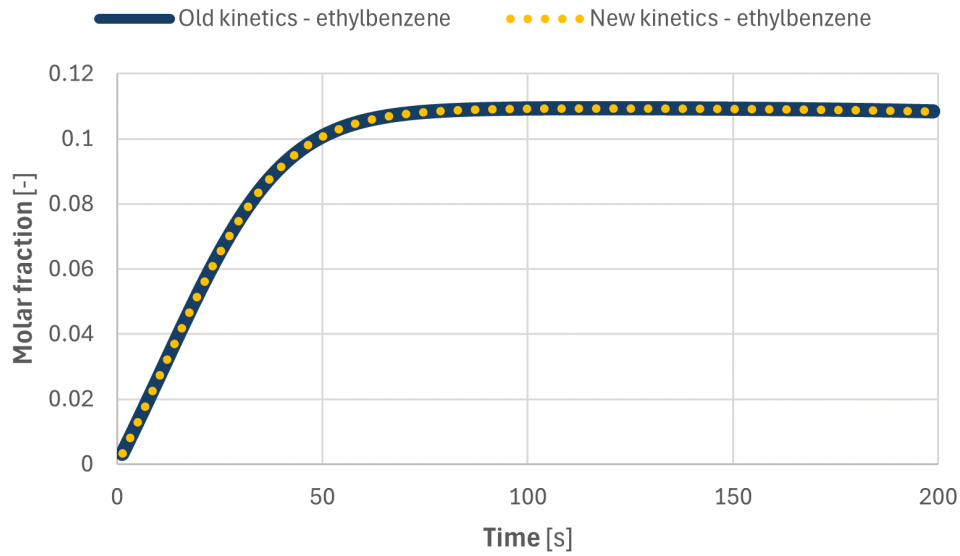


Figure 3.1: Comparison of the molar fraction of ethylbenzene evolution in time performing the simulation with the kinetics built by Russo [18] and the one proposed. The system utilized for the case is the alkylator described by Russo [18].

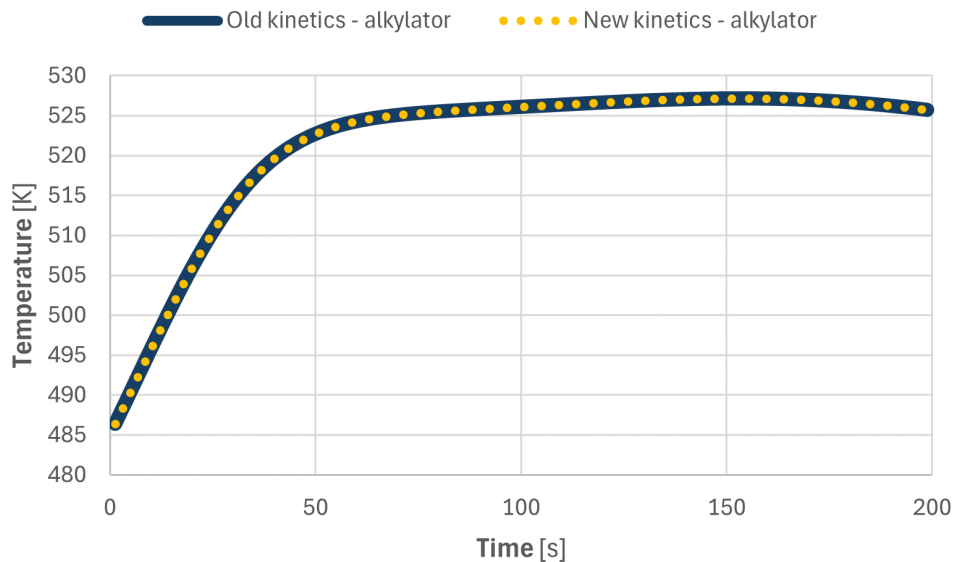


Figure 3.2: Comparison of the temperature evolution in time performing the simulation with the kinetics built by Russo [18] and the one proposed. The system utilized for the case is the alkylator described by Russo [18].

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.

Every future applications of MADSim can exploit the generalized heterogeneous kinetics; moreover, a rising challenge is represented by the creation of GUI (graphical user interface), getting closer and closer to the idea of a commercial simulator.

3.2. Tubular reactor validation

Moving 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 3.3*), while the second one represents the evolution of temperature in time (*figure 3.4*).

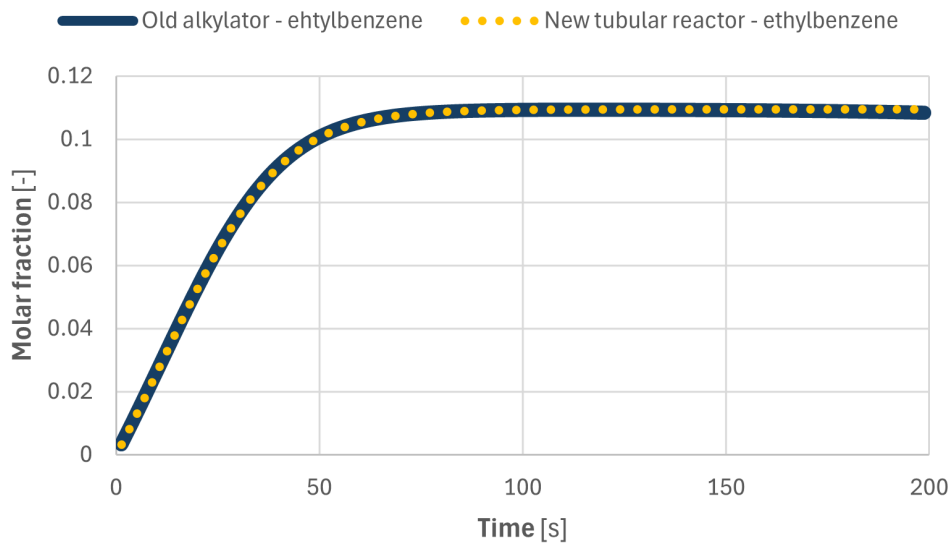


Figure 3.3: Comparison of the molar fraction of ethylbenzene evolution in time performing the simulation with the old alkylator by Russo [18] and the new tubular reactor.

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 3.4*, 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.

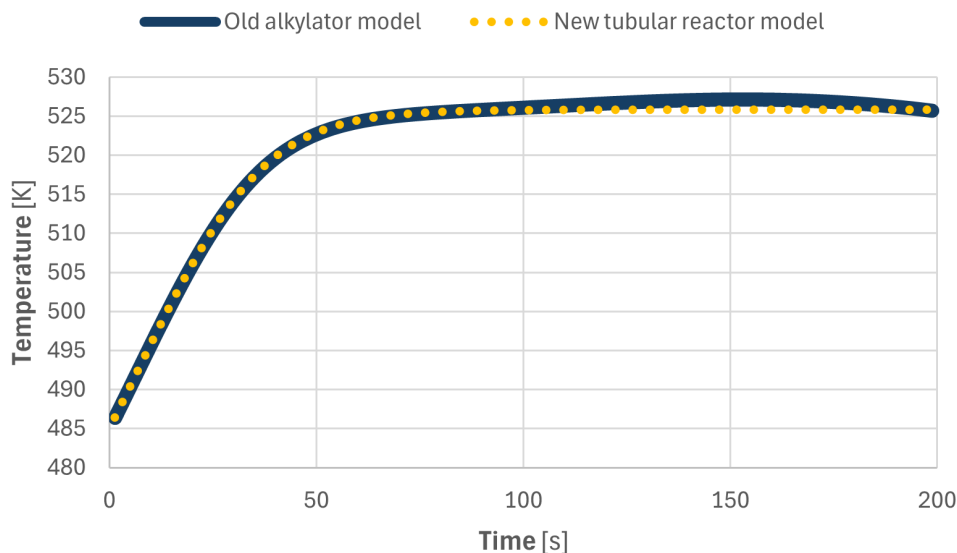


Figure 3.4: Comparison of the temperature evolution in time performing the simulation with the old alkylator by Russo [18] and the new tubular reactor.

3.3. Methanol Simulation

Since both the kinetics model and tubular reactor one are proved as valid, relying on the alkylator example by Russo as validation system, a completely new process was simulated. For the case, the single tube for the methanol production is reproduced both in the MADSim environment and in the Aspen HYSYS[®] one: this is done to compare the software with an existing and well established simulator. Because of the different scopes of the two instruments, what is confronted is the steady state produced by Aspen HYSYS[®] and the equilibrium reached by the system processed in MADSim.

Both the softwares work with the VBF kinetic model illustrated in the previous chapters: the descriptive parameters for reaction rates are shown in *table 2.1*. The same was followed for the unit: the design criteria are the ones presented in *table 2.3* for the equipment simulated in MADSim and for the one performed in Aspen HYSYS[®] as well.

MADSim

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 2.2*). 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.

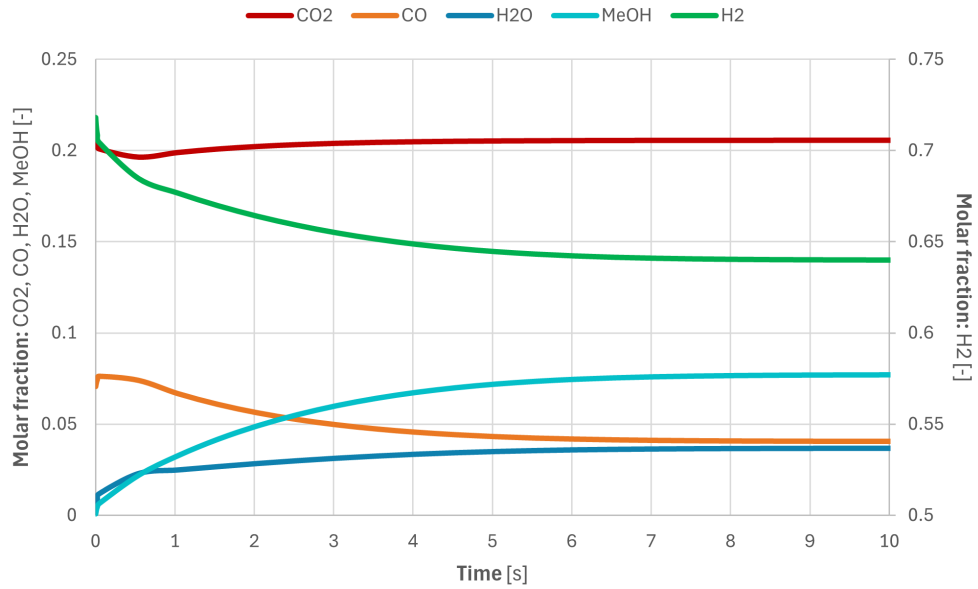


Figure 3.5: Molar fractions evolution in time performing the simulation of the methanol single tube reactor.

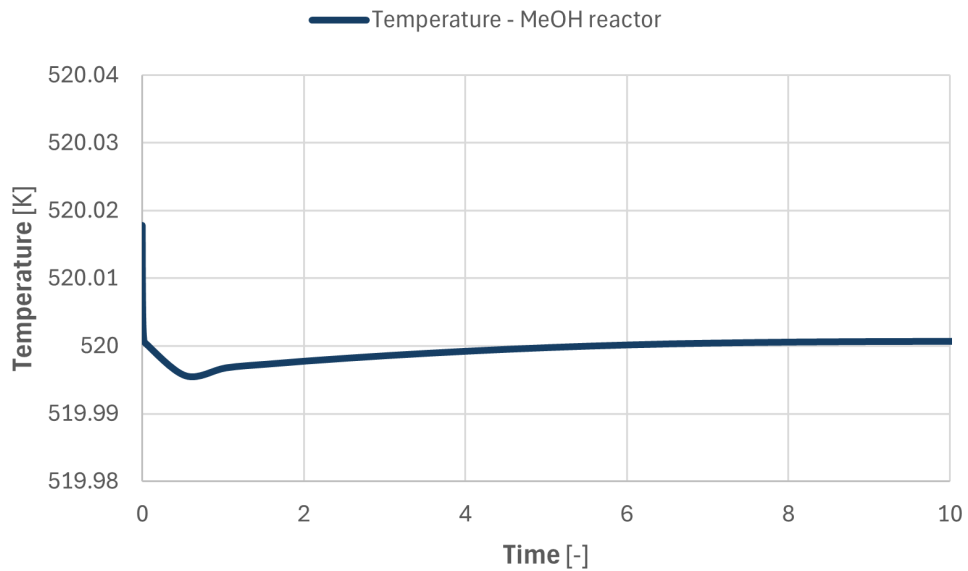


Figure 3.6: Temperature evolution in time performing the simulation of the methanol single tube reactor.

For the objective of comparison between MADSim and Aspen HYSYS[®], the composition

presented by the system once the steady state had been reached is collected in the table hereinafter.

Table 3.1: Final composition reached by the simulated reactor in MADSim.

Species		Molar fraction	Unit
Carbon dioxide	CO ₂	0.205646	[-]
Carbon monoxide	CO	0.040397	[-]
Hydrogen	H ₂	0.640016	[-]
Water	H ₂ O	0.036767	[-]
Methanol	CH ₃ OH	0.077174	[-]

Comparison with Aspen HYSYS

The aforementioned statement on the properties and sizing parameters is valid; it is wanted to stress the attention to the only difference between Aspen HYSYS[®] and MADSim. In fact, the kinetics is set with the same value in both cases, the same happens for the geometrical and catalyst-related parameters for the reactor. On the other hand, the cooling system is simplified, requiring only the imposition of the temperature of the exit stream; since the system is simulated as isothermal, such value of temperature turned out to be 520K.

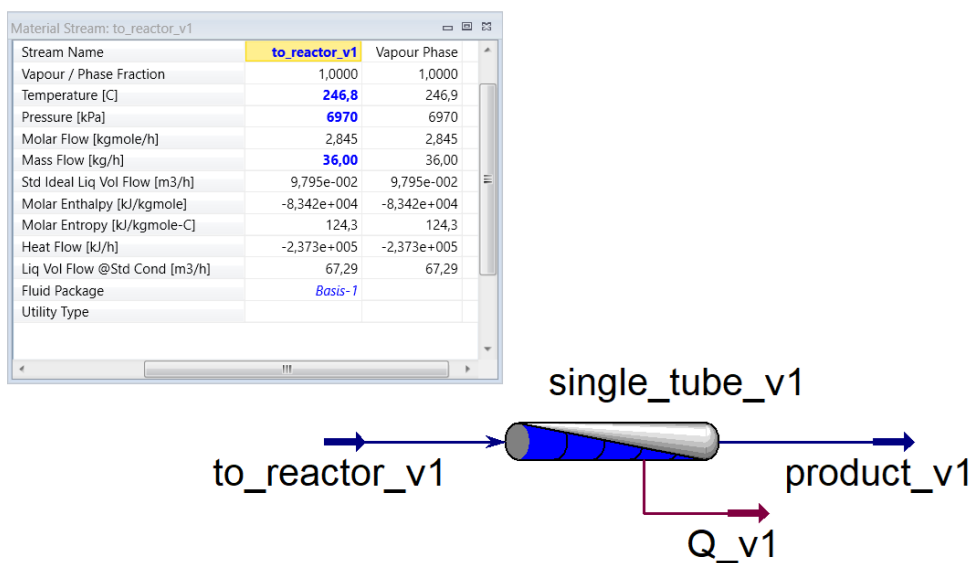


Figure 3.7: Simulated single tube reactor in Aspen HYSYS[®]. The properties of the inlet flow (*to_reactor_v1*) are shown as well.

In figure above, it is shown an extract from Aspen HYSYS®: the reactor and the GUI of the inlet stream are highlighted. In particular, this last one is meant to be as an inspiration for a future development of MADSim, pursuing the idea of making the software easier to be understood and handled by a generic user.

Finally, the composition of the outlet stream so obtained is collected in the following table.

Table 3.2: Composition of the simulated steady state reactor in Aspen HYSYS®.

Species		Molar fraction	Unit
Carbon dioxide	CO ₂	0.205645	[-]
Carbon monoxide	CO	0.040077	[-]
Hydrogen	H ₂	0.639295	[-]
Water	H ₂ O	0.037076	[-]
Methanol	CH ₃ OH	0.077907	[-]

Please notice that the outcomes of this last simulation, shown above, and the ones produced by MADSim (*table 3.1*) are comparable, with a grade of similarity at least on the second decimal digit. This is the final prove which confirms the reliability of the software, validating another time the newly implemented models.

4 | Conclusions and future developments

As it is possible to understand looking to the results shown in *chapter 3* this work was concluded with a success. The new kinetics environment, following the commercial simulators trend, is capable to reliably represent a heterogeneous reaction environment. This statement was demonstrated both for the *Heterogeneous_KinModel_Concentration* and *Heterogeneous_KinModel_PartialP* with the validation performed in line with the previous works conducted in MADSim and within the study case regarding methanol. On the other hand the necessity of a revamp on the *Species* class stands out: critical species are not handled in a correct way due to simplifications in the properties calculation.

As regards the tubular reactor model it is possible to affirm that it is a notable milestone for the software, being fully functional. However, this should be not considered only a final destination but a new starting point for more complex implementations as well. What is suggested for the future developer is to start from here: adding a cooling system coded in a similar way to the existing heat exchanger model and implementing a multitubular reactor model rise as interesting topics and challenges.

Finally, a suggest of this thesis work, more than a goal, is the will to research, to apply and to study always new arguments. In the discussion, an overview on the word of methanol was addressed: a field of research linked to modern issue opens a wide range of possibilities. Learning how to deal with increasingly predominant chemicals results in a bright path for the future. What was achieved with this project lies on the successful exploitation of MADSim to simulate a methanol reactor, paving the way for the time when the program will be fully capable to accompany the users.

Bibliography

- [1] I. H. Bell, J. Wronski, S. Quoilin, and V. Lemort. Pure and pseudo-pure fluid thermophysical property evaluation and the open-source thermophysical property library coolprop. *Industrial & Engineering Chemistry Research*, 53(6):2498–2508, 2014. doi: 10.1021/ie4033999. URL <https://doi.org/10.1021/ie4033999>.
- [2] M. Bertau, H. Offermanns, L. Plass, F. Schmidt, and H.-J. Wernicke. *Methanol: The Basic Chemical and Energy Feedstock of the Future: Asinger's Vision Today*. 01 2014. doi: 10.1007/978-3-642-39709-7.
- [3] F. Bisotti, M. Fedeli, K. Prifti, A. Galeazzi, A. Dell'Angelo, M. Barbieri, C. Pirola, G. Bozzano, and F. Manenti. Century of technology trends in methanol synthesis: Any need for kinetics refitting? *Industrial Engineering Chemistry Research (Process Systems Engineering)*, 2021. doi: 10.1021.
- [4] F. Bisotti, M. Fedeli, K. Prifti, A. Galeazzi, A. Dell'Angelo, and F. Manenti. Impact of kinetic models on methanol synthesis reactor predictions: In silico assessment and comparison with industrial data. *Industrial Engineering Chemistry Research (Process Systems Engineering)*, 2022. doi: 10.1021.
- [5] G. Bozzano and F. Manenti. Efficient methanol synthesis: Perspectives, technologies and optimization strategies. *Progress in Energy and Combustion Science*, 56:71–105, 2016. doi: <https://doi.org/10.1016/j.pecs.2016.06.001>. URL <https://www.sciencedirect.com/science/article/pii/S0360128515300484>.
- [6] K. Bussche and G. Froment. A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial cu/zno/al₂o₃catalyst. *Journal of Catalysis*, 161(1):1–10, 1996. doi: <https://doi.org/10.1006/jcat.1996.0156>. URL <https://www.sciencedirect.com/science/article/pii/S0021951796901566>.
- [7] T. E. Casavant and R. P. Côté. Using chemical process simulation to design industrial ecosystems. *Journal of Cleaner Production*, 12(8):901–908, 2004. ISSN 0959-6526. doi: <https://doi.org/10.1016/j.jclepro.2004.02.034>. URL <https://www>.

- sciencedirect.com/science/article/pii/S0959652604000794. Applications of Industrial Ecology.
- [8] G. Graaf, E. Stamhuis, and A. Beenackers. Kinetics of low-pressure methanol synthesis. *Chemical Engineering Science*, 43(12):3185–3195, 1988. doi: [https://doi.org/10.1016/0009-2509\(88\)85127-3](https://doi.org/10.1016/0009-2509(88)85127-3). URL <https://www.sciencedirect.com/science/article/pii/0009250988851273>.
- [9] M. J.A., M. M., and van Diepen A.E. *Chemical Process Technology*. Wiley, 2013.
- [10] K. Klier, V. Chatikavanij, R. Herman, and G. Simmons. Catalytic synthesis of methanol from CO₂: Iv. the effects of carbon dioxide. *Journal of Catalysis*, 74(2): 343–360, 1982. doi: [https://doi.org/10.1016/0021-9517\(82\)90040-9](https://doi.org/10.1016/0021-9517(82)90040-9). URL <https://www.sciencedirect.com/science/article/pii/0021951782900409>.
- [11] G. Leonzio. Mathematical modeling of a methanol reactor by using different kinetic models. *Journal of Industrial and Engineering Chemistry*, 85:130–140, 2020. doi: <https://doi.org/10.1016/j.jiec.2020.01.033>. URL <https://www.sciencedirect.com/science/article/pii/S1226086X20300538>.
- [12] M. Mohajer, B. R. Young, and W. Svrcek. Comparing pressure flow solvers for dynamic process simulation. *Chemical Product and Process Modeling*, 3(1), 2008. doi: [doi:10.2202/1934-2659.1119](https://doi.org/10.2202/1934-2659.1119). URL <https://doi.org/10.2202/1934-2659.1119>.
- [13] H. Nazir, N. Muthuswamy, C. Louis, S. Jose, J. Prakash, M. E. Buan, C. Flox, S. Chavan, X. Shi, P. Kauranen, T. Kallio, G. Maia, K. Tammeveski, N. Lymperopoulos, E. Carcadea, E. Veziroglu, A. Iranzo, and A. M. Kannan. Is the H₂ economy realizable in the foreseeable future? part iii: H₂ usage technologies, applications, and challenges and opportunities. *International Journal of Hydrogen Energy*, 45(53), 2020. doi: <https://doi.org/10.1016/j.ijhydene.2020.07.256>. URL <https://www.sciencedirect.com/science/article/pii/S0360319920329311>.
- [14] F. Nestler, M. Krüger, J. Full, R. J. Hadrich, M. J. and White, and A. Schaadt. Methanol synthesis – industrial challenges within a changing raw material landscape. *Chemie Ingenieur Technik*, 90:1409–1418, 2018. doi: [DOI:10.1002/cite.201800026](https://doi.org/10.1002/cite.201800026).
- [15] F. Nestler, A. Schütze, M. Ouda, M. Hadrich, A. Schaadt, S. Bajohr, and T. Kolb. Kinetic modelling of methanol synthesis over commercial catalysts: A critical assessment. *Chemical Engineering Journal*, 394:124881, 2020. doi: <https://doi.org/10.1016/j.cej.2020.124881>. URL <https://www.sciencedirect.com/science/article/pii/S138589472030872X>.

- [16] V. Palma, E. Meloni, C. Ruocco, M. Martino, and A. Ricca. Chapter 2 - state of the art of conventional reactors for methanol production. In A. Basile and F. Dalena, editors, *Methanol*, pages 29–51. Elsevier, 2018. doi: <https://doi.org/10.1016/B978-0-444-63903-5.00002-9>. URL <https://www.sciencedirect.com/science/article/pii/B9780444639035000029>.
- [17] N. Park, M.-J. Park, Y.-J. Lee, K.-S. Ha, and K.-W. Jun. Kinetic modeling of methanol synthesis over commercial catalysts based on three-site adsorption. *Fuel Processing Technology*, 125:139–147, 2014. doi: <https://doi.org/10.1016/j.fuproc.2014.03.041>. URL <https://www.sciencedirect.com/science/article/pii/S0378382014001453>.
- [18] F. Russo. Development of an object-oriented programming framework for dynamic simulation of chemical processes: Madsim. Master’s thesis, Chemical Engineering - Politecnico di Milano, May 2023.
- [19] G. P. Somerville-Marrs. The protection of batch chemical reactors against overpressure. 1987. URL <https://api.semanticscholar.org/CorpusID:137976076>.
- [20] P. L. Spath and D. C. Dayton. Preliminary screening – technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas. 12 2003. doi: 10.2172/15006100. URL <https://www.osti.gov/biblio/15006100>.
- [21] I. Thomas, B. Wunderlich, and S. Grohmann. Pressure-driven dynamic process simulation using a new generic stream object. *Chemical Engineering Science*, 215:115171, 2020. doi: <https://doi.org/10.1016/j.ces.2019.115171>. URL <https://www.sciencedirect.com/science/article/pii/S0009250919306621>.
- [22] Wikipedia contributors. List of chemical process simulators — Wikipedia, the free encyclopedia. https://en.wikipedia.org/w/index.php?title=List_of_chemical_process_simulators&oldid=1202131443, 2024.

List of Figures

1.1	Simple representation of a tree structure in the composite pattern.	5
1.2	Unified Modeling Language diagram of the <i>adapter pattern</i>	6
1.3	Example of a mixer with two entrance and one exit.	11
1.4	Tree structure ordained exploiting the BFS algorithm.	15
1.5	Tree structure ordained exploiting the DFS algorithm.	16
1.6	Fischer projection and 3D structure of the methanol molecule.	19
1.7	Equilibrium CO conversion to methanol feeding a 2 : 1 mol _{H₂} /mol _{CO}	21
1.8	Most common commercial methanol technologies and relative temperature profile: (a) direct quenching, (b) indirect cooling, and (c) quasi-isothermal boiling water reactor. Picture adapted from Palma et al. [16] by Bisotti et al. [3].	23
1.9	Reaction scheme for methanol synthesis: CO ₂ hydrogenation and WGS. <i>rds</i> stands for rate determining step. Picture adapted from Vanden Bussche and Froment [6].	27
2.1	Seven steps of heterogeneous catalyst reactions: (1) film diffusion, (2) porous diffusion, (3) adsorption on the catalyst, (4) proper chemical reaction, (5) desorption from the catalyst, (6) porous diffusion, (7) film diffusion.	34
2.2	The <i>Kinetic Equation Help</i> GUI from Aspen HYSYS [®] chemical reaction environment.	36
2.3	Simple representation of a continuous stirred tank reactor.	39
2.4	Simple representation of a plug flow reactor.	40
2.5	Simple representation of a non-adiabatic tubular reactor in the Aspen HYSYS [®] flowsheet. The inlet flow (<i>to_reactor</i>), the outlet flow (<i>product</i>) and the heat flux between equipment and external environment (\dot{Q}) are shown.	44
2.6	Example of a multitubular reactor.	46

3.1	Comparison of the molar fraction of ethylbenzene evolution in time performing the simulation with the kinetics built by Russo [18] and the one proposed. The system utilized for the case is the alkylator described by Russo [18].	56
3.2	Comparison of the temperature evolution in time performing the simulation with the kinetics built by Russo [18] and the one proposed. The system utilized for the case is the alkylator described by Russo [18].	56
3.3	Comparison of the molar fraction of ethylbenzene evolution in time performing the simulation with the old alkylator by Russo [18] and the new tubular reactor.	57
3.4	Comparison of the temperature evolution in time performing the simulation with the old alkylator by Russo [18] and the new tubular reactor.	58
3.5	Molar fractions evolution in time performing the simulation of the methanol single tube reactor.	59
3.6	Temperature evolution in time performing the simulation of the methanol single tube reactor.	59
3.7	Simulated single tube reactor in Aspen HYSYS [®] . The properties of the inlet flow (<i>to_reactor_v1</i>) are shown as well.	60

List of Tables

1.1	Compositions of CuO/ZnO/Al ₂ O ₃ catalyst variants from different manufacturers.	22
2.1	Kinetic parameters of the reformulated VBF model.	51
2.2	Composition and physical properties of the inlet gas stream (reagents). . .	52
2.3	Design parameters for the catalytic tube.	54
3.1	Final composition reached by the simulated reactor in MADSim.	60
3.2	Composition of the simulated steady state reactor in Aspen HYSYS®. . . .	61

Acknowledgements

Nel lontano settembre 2019 non avrei mai pensato che la mia carriera università mi avrebbe permesso di affrontare sfide tanto entusiasmanti quanto faticose. Tutto questo è stato possibile grazie ad una solida base costruita durante la laurea triennale, ma soprattutto grazie a tutti coloro che mi hanno sostenuto in tutto questo tempo, permettendomi di crescere non solo come ingegnere, ma anche come persona.

Un ringraziamento a tutti i miei amici. Grazie Lorenzo che da anni mi supporti e che mi sopporti. Grazie Mirko che dal primo giorno in università ci sei sempre stato, fino all'ultimo mi sei stato accanto. Grazie Sofia e Davide, siete sempre stati affidabili compagni, mi avete assistito in molteplici lavori condividendo gioie e fatiche. Grazie a Federico e Gabriele, alleggerite le mie giornate e mi donate puri momenti di distacco.

La mia gratitudine va anche a tutte le persone che ho conosciuto, provenienti dai più disparati angoli della Terra. Mi avete permesso di conoscere culture e mondi diversi aprendo la mia mente in vista del futuro, un futuro che forse sarà quaggiù, forse da qualche parte in Europa o chissà dove nel mondo. Grazie per avermi insegnato a interagire con tutti e in tutte le situazioni: in qualche modo ci si fa capire. Thank you Jawad, Ali, Amin , Sebastian, Pablo... thank you all guys!

Un grazie a chi mi hanno ispirato, in particolare al professor Manenti e all'ingegner Bozzini: mi avete seguito, sostenuto, dato un esempio che tengo stretto; conserverò il ricordo di voi come mie guide, miei mentori sperando presto di raggiungere un livello pari al vostro.

Dulcis in fondo, a chi era lì e lì sempre sarà, alla mia famiglia: a voi va un grande, anzi enorme grazie. Grazie mamma, grazie papà, mi avete protetto e conservato in questi anni, avete permesso la mia riuscita in questo percorso, avete spianato le strade del mio futuro, della mia vita.

Con questo ultimo atto di riconoscenza voglio raccogliere chiunque non sia stato esplicitamente ringraziato: così concludo questo capitolo, così ne apro uno nuovo. Grazie ancora a tutti!

