Analysis of the Nonoxidative Conversion of Methane into Benzene and Hydrogen using Numerical Simulation

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Recent discoveries of new natural gas sources and advances in natural gas production made the conversion of methane a promising technique to obtain different types of fuels and fine chemicals, such as aromatics. The non-oxidative conversion of methane occurs without the presence of O_2, thus not emitting CO_x. In addition, this renewable-based technology can also lead to a reduction in organic waste generation, once biomethane may be synthesized from organic residue. One of the challenges to implanting this technology is that this reaction is thermodynamically unfavorable and it only happens in harsh conditions with temperatures above 800 K in the presence of a catalyst, nevertheless, low conversions of methane are achieved, ranging from 10 % to 15 %. High coke formation and quick catalyst deactivation are other issues this system must overcome. Many efforts were made experimentally focusing on the reaction conditions and the reactor project to reach better methane conversion. In this case, to optimize and find better conditions computational simulation software, such as AspenPlus® may help. Therefore, in this work, AspenPlus® was used to simulate the direct non-oxidative conversion of methane in a plug flow reactor with a 3 % Mo/HMCM-22 catalyst. For the simulated results, the reaction produced benzene, ethylene, hydrogen, and naphthalene with the best methane conversion of 11.7 %. In the optimization step, a methane conversion of 13.0 % was found. These results indicated that the modeling requires a more complex kinetic model to fit the experimental data.

1. Introduction

The conversion of methane into value-added chemicals and materials is gaining great attention in the last years since the world needs new sources of clean energy that are not oil dependent and the natural gas reserves (90% methane) are considered abundant (estimated at 196.9 trillion cubic meters in 2018). Therefore, it makes methane an easily available and cheap feedstock (Monster et al., 2019). In addition, at the 2015 United Nations Climate Change Conference, an international treaty on climate change called "the Paris Agreement" was negotiated by 195 countries and it aims to mitigate the emission of Greenhouse Gases and decarbonize the decarbonization of energy production. From this perspective, it is essential the development of new technologies capable of reducing environmental impacts (Teske et al., 2019).

The conversion of methane may occur by two different pathways: in an oxidative and non-oxidative environment. The first one is an indirect route in which the methane is first converted into syngas (CO and H_2) and the latter is a direct route responsible to produce hydrogen, fuels, and other olefins from methane without CO_x emissions which makes it a promising renewable technology (Zhang, 2021).

However, the direct non-oxidative conversion of methane is a strong thermodynamic unfavorable reaction due to the tetrahedral methane structure which makes the molecule very inert requiring high energy to break the C-H bonds (approximately 439 kJ/mol). Therefore, temperatures at least above 800 K are needed and even then, low yields are achieved, ranging from 10 to 15 % (Karaya and Kee, 2016). In addition, the conversion of methane is subjected to be kinetically driven to undesired products and high coke formation.

Two examples of the direct conversion of methane are the dehydroaromatization (MDA) Eq (1) and the direct production of ethylene Eq (2):

$$6CH_4 \leftrightarrow 9H_2 + C_6H_6 \qquad\qquad \Delta H^o_{298} \approx +532\frac{kJ}{mol} \ * \qquad\qquad (1)$$

$$2CH_4 \leftrightarrow H_2 + C_2H_6 \qquad\qquad \Delta H^o_{298} \approx +202 \frac{kJ}{mol} * \qquad\qquad (2)$$

* Temperature-dependent

Equations Eq (1) and (2) shows a high energy consumption for benzene and ethylene production, combined with the high formation of coke and low yields of these reactions, proves that an economical direct non-oxidative conversion of methane is a great challenge (Yadav and Upadhyayula, 2020).

To overcome this challenge different types of heterogenous metal-based catalysts were proposed in the literature, such as the molybdenum (Mo) supported in zeolites like HZSM-5, HMCM-22, HMCM-36 and HMCM-49 (Karaya and Kee, 2016, Menon et al., 2020). The catalyst must be chosen carefully to find better conditions for methane functionalization, better product selectivity, and reaction yields (Schwach et al., 2017).

Mo/HZSM-5 is a catalyst that catalyzes methane conversion through a bifunctional mechanism. First, on the surface of the catalyst, the C-H bonds are activated in the molybdenum carbide (MoC_x) site forming C_2 intermediates, and then these species are oligomerized in the Bronsted acid site producing aromatics and cyclic molecules, such as benzene, ethylene, naphthalene and, hydrogen (Zhang, 2019). The selectivity and reaction yield of the products are strongly dependent on the nature of the catalyst. Thus, some research groups showed that Mo/ZSM-5 and Mo/MCM-22 are better for benzene yields (Zhang, 2021), however, some drawbacks as the high formation of coke and quick catalyst deactivation still major issues and continue to be objects of research for the final reactor design (Han et al., 2022).

Among the reaction products, there is a great interest in hydrogen, benzene, and ethylene. In the last years, hydrogen started to become a promising alternative to fossil fuels, since it may be used as feedstock for energy supply in several types of applications and can be produced in different ways without greenhouse gas emissions, named "green hydrogen". Benzene and ethylene are mainly subproducts from oil refining and are widely used as fuel and as feedstock for plastic production, respectively. Following the principle of decarbonization of the production, the direct non-oxidative conversion of methane is a good alternative especially when biomethane (methane produced by organic waste digestion) is converted (Moritz et al., 2022; Mishra et al., 2022; Abiogás – Associação Brasileira de biogás e biometano, 2021).

With the discussion above is possible to infer that the optimization of the reactor design is a key factor in the research for an economical non-oxidative direct conversion of methane, and for this purpose, computational tools may be very useful to find better conditions. One such simulator for industrial processes is Aspen Plus®, with a wide range of applications in different fields. Among the advantages are, the possibility of modeling realistically each equipment individually or as part of a process, in addition to describing the process behavior, carrying out technical-economic analyses, and comparing different process scenarios (Ahmed, et al., 2015; Corridor et al., 2019). Therefore, this work aims to use data given by the literature to simulate the direct non-oxidative conversion of methane using the AspenPlus® software to evaluate the best conditions for the reactor design proposed.

2. Mathematical Model and Methods

2.1 Literature review

All experimental data used in this work were obtained from the literature (Gao et al. 2016). They prepared a 3 % Mo/MCM-22 catalyst using hexamethylenediamine (HMI) as a structure-directing agent and did all the characterization methods to confirm its properties. Then they filled a tubular fixed-bed reactor, 7 mm diameter, and 6 cm length, with 0.5 g (2.3 cm³) of Mo/MCM-22 and performed the experiments at atmospheric pressure. The feed was approximately W= 1.62 kg/h (9.42 mol/h) with composition of 90 % methane (CH_4) and 10 % nitrogen (N_2) ($X_{CH_4} = 0.9$ and $X_{N_w} = 0.1$). The temperature range varied from 923.15 to 1023.15 K.

2.2 Kinect model

The MDA reaction network and the reaction rates, Figure 1, and Equations 3,4, and 5 were obtained from Gao (2015) and Gao et al. (2016).
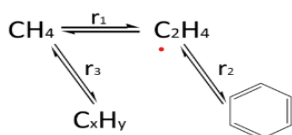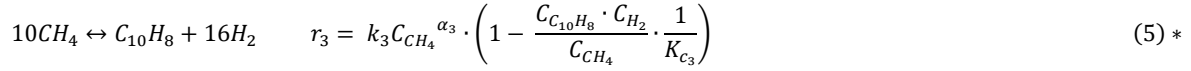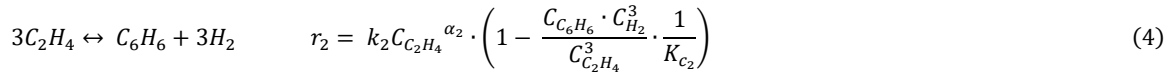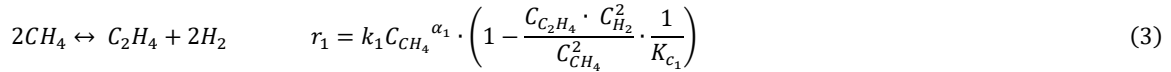

Figure 1 – Reaction network with 3 reactions

$$2CH_4 \leftrightarrow C_2H_4 + 2H_2 \qquad r_1 = k_1 C_{CH_4}{}^{\alpha_1} \cdot \left(1 - \frac{C_{C_2H_4} \cdot C_{H_2}^2}{C_{CH_4}^2} \cdot \frac{1}{K_{c_1}}\right) \qquad (3)$$

$$3C_2H_4 \leftrightarrow C_6H_6 + 3H_2 \qquad r_2 = k_2 C_{C_2H_4}{}^{\alpha_2} \cdot \left(1 - \frac{C_{C_6H_6} \cdot C_{H_2}^3}{C_{C_2H_4}^3} \cdot \frac{1}{K_{c_2}}\right) \qquad (4)$$

$$10CH_4 \leftrightarrow C_{10}H_8 + 16H_2 \qquad r_3 = k_3 C_{CH_4}{}^{\alpha_3} \cdot \left(1 - \frac{C_{C_{10}H_8} \cdot C_{H_2}}{C_{CH_4}} \cdot \frac{1}{K_{c_3}}\right) \qquad (5) *$$

*This reaction represents coke formation inside the reactor, with nothing really to do with naphthalene.

The Activation energy (E_A) was calculated by the Arrhenius equation, represented in Equation (6):

$$k(T) = k_\infty \exp(-\frac{E_A}{RT}) \qquad (6)$$

where k_∞ is the pre-exponential factor.
The parameters for each reaction were given by the authors and presented in Table 1.

Table 1 - Pre-exponential factor, activation energy, and order for the reaction network (Gao et al., 2016)

Reaction	Pre-exponential factor k_i ($\frac{m^{3(\alpha-1)}}{s \cdot mol^{\alpha-1}}$)	Activation Energy $E_{A,l}$ ($\frac{kJ}{mol}$)	Reaction order α_i
r_1	107.16	95.25	0.84
r_2	0.97	14.83	0.99
r_3	128.28	84.74	0.65

The equilibrium constants K_{ci} were calculated from the temperature-dependent free Gibbs enthalpies with Equations (7) and (8) (Yaws, 1999):

$$\Delta G_f^0 = A + B \cdot T + C \cdot T^2 \qquad (7)$$

$$K_{ci} = \exp\left[-\frac{\Delta G_{fi}^0}{R \cdot T}\right] \cdot \frac{P_i}{R \cdot T} \qquad (8)$$

with ΔG_{fi}^0 in kj/mol and T in K; A, B e C in kJ/mol, kJ/(mol.K) and kJ/(mol.K²) respectively and P_i/RT in mol/m³.
The conversion of methane was then calculated using Equation (9).

$$X_{methane} = \left(\frac{F_{methane\ in} - F_{methane\ out}}{F_{methane\ in}}\right) \cdot 100\ \% \qquad (9)$$

2.3 Numerical Simulation

Aspen Plus version 10 (36.0.0.249) software (2019) recommends the Peng-Robinson equation of state for gas-processing procedures that involve hydrocarbons and light gasses such as hydrogen, carbon monoxide, and carbon dioxide. Since in this work, the reaction system is composed of light hydrocarbons and light gasses in high temperatures, the Peng-Robison model should represent well its properties.
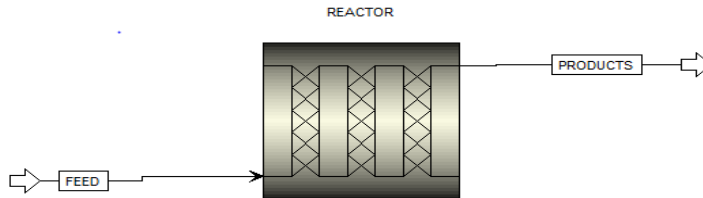The flow sheet with the Rplug reactor for the simulation is shown in Figure 2.

Figure 2 – Process simulation flowsheet in Aspen Plus software

The simulation carried out in this work was obtained using the data from Gao (2015) and Gao et al. (2016) using Aspen Plus®. To compare and verify if the model fits the experimental data the same conditions studied by those authors were applied in the simulations (that is why the flows are very small).

3. Results and discussions

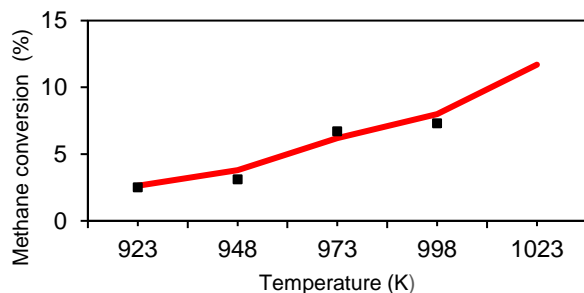Once the simulation was completed the results are shown in Figure 3 and Figure 4 a, b, and c.

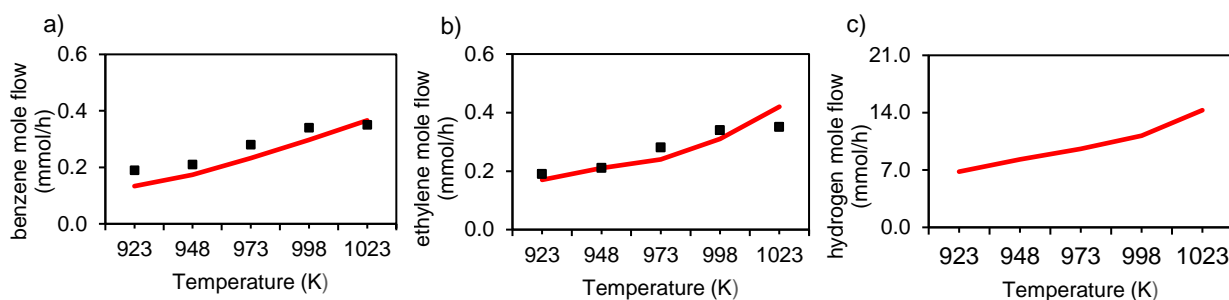*Figure 3 – Methane conversion (%) over different temperatures (K)*

Figure 4 – (⬛━━) Simulation and (■) Experimental millimolar flow (mmol/h) of the products from direct non-oxidative methane conversion a) benzene b) ethylene and c) hydrogen. Feed: 94.2 mol/h

3.1 Comparing with results from the literature

Figure 3 showed that the direct non-oxidative conversion of methane is a very endothermic reaction and as the temperature increases, the conversion also increases. According to Menon et al. (2020), the conversion of methane in temperatures ranging from 923 to 1023 K reaches its limits of around 12 %, and in this work, this parameter was below 12 %. Gao et al. (2016), in their experimental data, found a maximum methane conversion of 14.2 % in 998 K, but in equilibrium, the conversion felt to 7.3 %, while in this work, using the same conditions for feed, concentration, temperature, pressure, and catalyst, the conversion was 8.0 % a deviation of approximately 10 % for the model in AspenPlus®. These results demonstrated the potential of the model proposed and simulated to describe the experimental data, but more research must be done to optimize the system to predict accurately the methane conversion.

Figure 4 shows that low yields of products are achieved with the postulated reaction network for the direct non-oxidative conversion of methane. In terms of quantity, hydrogen was the most produced, followed by ethylene and benzene with almost the same yield. Comparing the model with the experimental data is possible to imply that both follow similar tendencies and are in the same degree even with a relative deviation in some temperatures. Figure 4 also demonstrates that better yields of products are found in higher temperatures, but in 1023 K this increase in the yield was not seen in the experimental data, probably due to the quick deactivation of the catalyst. As discussed before, when the temperature increases the conversion of methane also increases and thus the formation of the product. However, a high coke formation is observed, a phenomenon responsible for catalyst deactivation.

In the system of equations proposed in this work, the benzene conversion was smaller than ethylene, different from the works of Gao et al. (2016) and Rahman et al. (2018), which used Mo/HZSM-5 catalyst. This behavior may be due to the lateral reactions that might be occurring in the reactor and was not included in the simulation, especially the formation of ethane, but also the formation of cyclohexane, and even other aromatics. A little deviation in results may also occur with the use of different software to simulate the experimental data, which is the case of this work.

All these results imply that for this process a more complex system of reactions and better reactor optimization is needed. To reach better yields another simulation was carried out in AspenPlus® adding more 0.5 g of catalyst mass in the reactor simulated in the software.

3.2 Simulation and Optimization

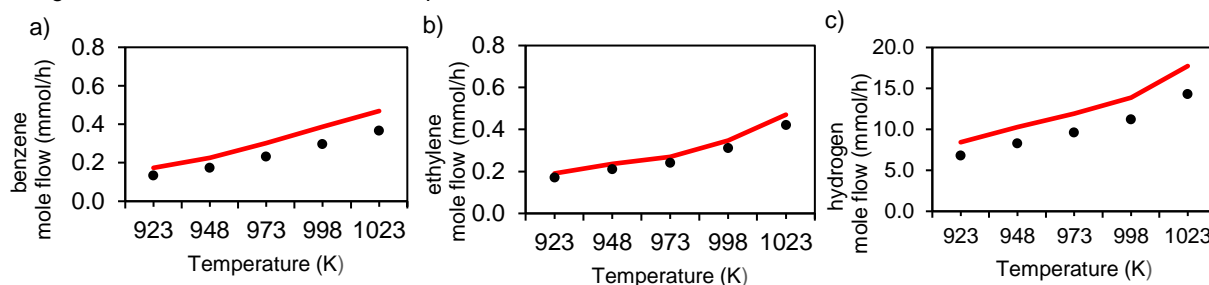Figure 5 shows the results from the optimized reactor:

Figure 5 — (▬▬) Optimized and (●) simulated millimolar flow (mmol/h) of the products from direct non-oxidative methane conversion a) benzene b) ethylene and c) hydrogen. Feed 94.2 mol/h.

The new reactor design increased the yield of benzene by almost 30 %, ethylene by 12 %, and hydrogen by 24 %, however, coke formation was the most improved. Better benzene selectivity is expected In Mo/HZSM-5 catalysts among the other products. Indeed, low yields for products were found even with more catalyst mass, and the methane conversion was meanly improved (13.0 % in the highest temperature). This means that another rector design may be necessary to reach better results, and one way to achieve this, is to couple a hydrogen permeable membrane in the reactor to shift the equilibrium of the reaction to produce more products, the same strategy used by Gao et al. (2016).

4. Conclusion

This study has demonstrated that the direct non-oxidative conversion of methane is a very endothermic reaction needing high temperatures to occur, and yet low yields are achieved. The results from the simulation that was carried out in Aspen Plus® version 10 using experimental data and reactor design from the literature, showed that the highest conversion of methane was reached at 1023 K with 11.7% of the gas converted, and also the highest yield of products. The reaction produced low yields: 0.37, 0.42, and 14.3 mmol/h of benzene, ethylene, and hydrogen respectively, due to the laboratory scale of the experiments, and even with optimization the results were poorly upgraded. The model deviation from the experimental data was around 10% at the highest temperature. These results indicated that a more complex system of reactions and kinetic model is needed to accurately fit the experimental data and a different reactor design to achieve better yields. One way to enhance the reactor design and shift the equilibrium towards the formation of the product is to add a hydrogen-permeable membrane in the system to remove the hydrogen produced and then reach higher methane conversion. It will be a part of this work as future research as well as the scale-up and technical-economic analysis of the process.

Acknowledgments

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