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CO₂ Methanation Under Atmospheric Pressure Conditions on a Ni catalyst: Experiments and Kinetic Modelling

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Abstract

Hydrogen storage and the associated infrastructure stand out among the major barriers towards a hydrogen based economy. One of the most promising concepts to overcome this problem is the “Power to Gas” (P2G) conversion. In a P2G installation, the surplus electricity coming from a renewable primary energy source (mostly wind and PVs) and not utilized in the electricity grid (mostly for stability reasons), is used to generate hydrogen, or potentially methane, for further use and storage in the natural gas distribution grid. In the aforementioned P2G scheme, electrolysis is utilized for hydrogen generation, while a methanation process is required for generating methane. A methanation process is a catalytically assisted physical-chemical process that generates methane from a mixture of various gases like CO, CO₂ and H₂. Producing methane using carbon dioxide as a raw material would have a two-fold positive effect: reduction of total CO₂ emissions and conversion of CO₂ to an energy vector.

In the present work, novel methanation experiments are conducted under atmospheric pressure conditions on a Nickel catalyst, in a temperature range between 250 – 500 °C, for stoichiometric (H₂/CO₂=4) and hydrogen excess (H₂/CO₂=5) feeds. All tests were performed with nitrogen dilution. Stoichiometric experiments depict a maximum CH₄ yield of ≈69% recorded at 364°C (GHSV=10000 h⁻¹), whereas hydrogen excess measurements depict increased maximum CH₄ yield (of approximately ≈82%) recorded at 364 °C. Furthermore, experiments implementing a bimetallic catalyst with nickel (Ni) and ruthenium (2%wt) (Ru) have taken place. The Ru catalytic sample resulted in a greater CH₄ yield when chemical equilibrium was still not reached (i.e., at low temperatures), highlighting the positive impact of the Ru addition on the conversion.

In the second part of the paper a basic kinetic study has also been conducted in order to simulate the aforementioned experiments. Although the implemented Xu & Froment [11] model succeeded in capturing the basic trend of the experimental CO₂ conversion “curve” for temperatures between 250 – 500 °C, discrepancies still exist.. Future work will focus on optimizing the implemented model’s kinetic and adsorption parameters according to the examined conditions.

Introduction

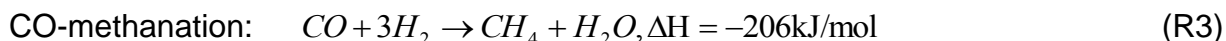
Hydrogen storage and the associated infrastructure stand out among the major barriers towards a hydrogen based economy. One of the most promising concepts to overcome this problem is the “Power to Gas” (P2G) conversion. In a P2G installation, the surplus electricity coming from a renewable primary energy source (mostly wind and PVs) and not utilized in the electricity grid (mostly for stability reasons), is used to generate hydrogen, or potentially methane, for further use and storage in the natural gas distribution grid. In the aforementioned P2G scheme, electrolysis is utilized for hydrogen generation, while a methanation process is required for generating methane. A methanation process is a catalytically assisted physical-chemical process that generates methane from a mixture of various gases like carbon monoxide (CO), carbon dioxide (CO₂) and hydrogen (H₂).

Numerous researchers have studied CO₂ methanation since Sabatier first reported the methanation of synthesis gas [1]. CO₂ methanation presents a number of benefits. An application of the process can be found in ammonia production units and hydrogen production units. CO₂ acts as a catalyst poison and methanation is used for the purification of ammonia synthesis gas [2]. CO₂ is also one of the major greenhouse gases. The utilization of CO₂ for CH₄ has a two-fold positive effect: reduction of total CO₂ emissions and conversion of CO₂ to an energy vector [3, 4]. Additionally, the methanation process produces Substitute Natural Gas (SNG) that is fully compatible with the existing pipeline network NG and relevant storage infrastructure and could be directly imported in the natural gas grid [5]. Research activities on methanation are also reported for space applications. The CO₂ produced by the astronauts in the cabin can be used to produce methane (for further use as a fuel) and water (for astronaut life-support systems) [6].

Methanation is a highly exothermic process. It takes place within a temperature range of 200-500°C and for pressure conditions ranging between 1 to 30 bar. Maximum CH₄ production can be anticipated at temperatures around 350 °C [7]. The basic reaction describing the production of methane from CO₂ and H₂ is the Sabatier reaction:



Furthermore, other reactions, such as the reverse Water Gas Shift (rWGS), the methanation of CO and the Boudouard reaction, are considered to take place during the methanation process:



It must be noted that CO₂ methanation is a thermodynamically favorable reaction, however it needs to be catalyzed in order to achieve acceptable rates and selectivities [8]. Several metal supported catalysts have been studied for the production of methane from CO₂: Ni, Ru, Pd, Pt, Rh, Mo, Re and Au [9]. Ni and Ru based catalysts are found to be the most active catalysts for methanation process. Ni supported catalysts are the most commonly used and widely studied due to their high activity and low cost. On the other hand, Ru has proved to be more active than Ni, however its high cost prevents its use as an industrial catalyst [6].

In the present work, the methanation of CO₂ is experimentally investigated in atmospheric pressure conditions by implementing two different catalytic samples of Ni (20%wt

supported on γ -Al₂O₃) and Ni (20%wt) + Ru (2%wt) (also supported on γ -Al₂O₃). The impact of temperature, space velocity (GHSV) and reacting mixture composition on the methane yield is analyzed. Furthermore, a preliminary kinetic study has also been conducted in order to simulate the aforementioned experiments.

This work can be classified under the framework of proposing a highly efficient Power-to-Gas (P2G) technology by thermally integrating high temperature electrolysis with methanation and use of CH₄ as a means of chemical storage.

2. Experimental study

In this section, the experimental methodology, as well as the obtained results of the tests conducted, is briefly described. The experimental campaign has been carried out at the DISAT (“Department of Applied Science and Technology”) labs of POLITO (Polytechnic of Turin, Italy). A laboratory-scale system was built up in order to enable control of reaction conditions and monitor products formation. The tests have been performed at atmospheric pressure, with the reacting mixture always consisting of hydrogen and carbon dioxide highly diluted with nitrogen. The impact of temperature, space velocity (GHSV) and reacting mixture composition on the methane yield has been analysed.

Figure 1 schematically presents the experimental test rig. Pressurized gas bottles were used in order to provide the reactant components. H₂, CO₂ and N₂ were properly mixed by using calibrated and computer-controlled mass flow controllers. The reactor with the catalyst was placed inside a PID-controlled oven in order to maintain a constant temperature. A thermocouple was put on the top of the catalytic bed in order to track and measure the reaction temperature, recorded by using the National Instruments Labview software. After the reaction, the gas mixture passed through a condenser and a silica water trap in order to remove the water and protect the gas analyser.

To characterize the performance of the system, the compositions of the gas before and after the reactor were measured in each experiment. A system of valves allowed the bypass of the oven-reactor section, enabling the analysis of reacting and exhaust gases through a single device. For the gas analysis a multi-channel analyser (Emerson X-Stream) with capabilities to measure CO, CO₂, CH₄, H₂ and O₂ was used. The gas analyser utilizes infrared (NDIR) sensors for CO, CO₂ and CH₄ measurement, a thermal conductivity (TCD) detector for H₂, and a paramagnetic sensor for O₂. The analyser has a web user interface allowing the sensors calibration and the data acquisition. Each measurement channel was calibrated by using bottled gases.

For each test session, the oven temperature was varied between 250 °C and 500 °C with increasing steps of 25 °C. All measurements in each experiment have been conducted after the establishment of steady-state conditions.

The following two catalyst samples were tested:

- Nickel (20%wt) supported on γ -Al₂O₃
- Nickel (20%wt) + Ruthenium (2%wt) supported on γ -Al₂O₃

Both samples were calcined at 550 °C; the spherical particles had a diameter of 0.6 mm. The two samples were prepared and provided by the European Research Institute for Catalysis (ERIC), one of the partners of the FCH-JU project “HELMETH” (see acknowledgements).

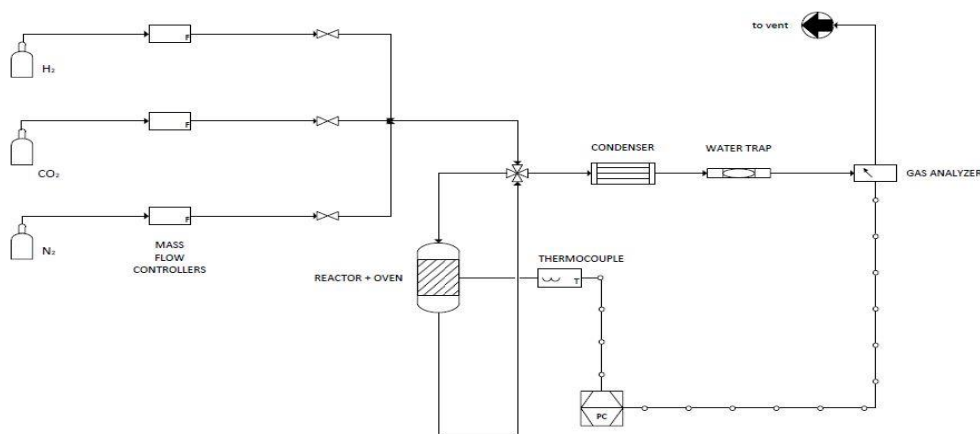


Figure 1 – Schematic of the methanation test unit

For all tests the catalyst load were fixed at a value of 600 mg: this results in a reaction volume of about 600 mm³ (both samples had a density ca. 1 g/cm³).

All samples were reduced at a temperature of 500 °C for 3 hours by passing through the bed an activating stream of 10% H₂ in N₂. Two kinds of reacting mixture were considered: a stoichiometric feed (H₂/CO₂=4) and a hydrogen excess feed (H₂/CO₂=5).

Longer residence time of the feed gases in the reaction chamber increases the CH₄ yield. Residence time is measured by a term called space velocity (GHSV), which indicates the relationship between the volumetric flow rate and the volume of the packed catalyst bed. Space velocity defines how many reactor volumes of feed can be treated per hour; it is expressed in units of h⁻¹. As space velocity increases, residence time decreases, and thus it is expected that the CH₄ yield will decrease. To test this, a series of experiments in which the total flow rates of the feed gases were varied at a constant H₂/CO₂ molar ratio and with the same catalyst bed volume were performed. Three different values of space velocity were considered: 10000 h⁻¹, 15000 h⁻¹ and 20000 h⁻¹ corresponding to volumetric flow rates of 100 ml/min, 150 ml/min and 200 ml/min, respectively.

CH₄ yield was chosen as the parameter to evaluate the catalysts performance. It can be defined as follows:

$$CH_4 \text{ Yield} = \frac{\dot{V}_{CH_4, out}}{\dot{V}_{CO_2, in}} \quad (1)$$

The charts presented in this section show CH₄ yield vs. reaction temperature (measured with thermocouples). All tests were performed with nitrogen dilution, in order to avoid a too high temperature rise within the catalyst bed due to the exothermal methanation.

In Figure 2(a) results concerning the first test session (stoichiometric) for the Ni/Al₂O₃ catalyst sample are shown. As expected, higher space velocities lead to lower methane production at a fixed temperature. The maximum CH₄ yield is shifted by varying the residence time. A maximum CH₄ yield of ≈69% was recorded at 364 °C with a volume flow of 100 ml/min (i.e., a GHSV equal to 10000 h⁻¹).

Afterwards, the operating condition with hydrogen excess (H₂/CO₂=5) was tested. Results are presented in **Fehler! Verweisquelle konnte nicht gefunden werden.2(b)**. A maximum CH₄ yield of ≈82% (higher than the stoichiometric feed case) was recorded at 364 °C with the GHSV equal to 10000 h⁻¹. In this second session the effect of the space velocity was weaker. For the stoichiometric feed the yield peak passed from ≈69% to ≈42% by doubling the space velocity, meaning a relative reduction of ≈39%. In the

hydrogen excess case the maximum CH₄ yield reduced from ≈82% to ≈69%: in this case the calculated relative reduction was ≈15%.

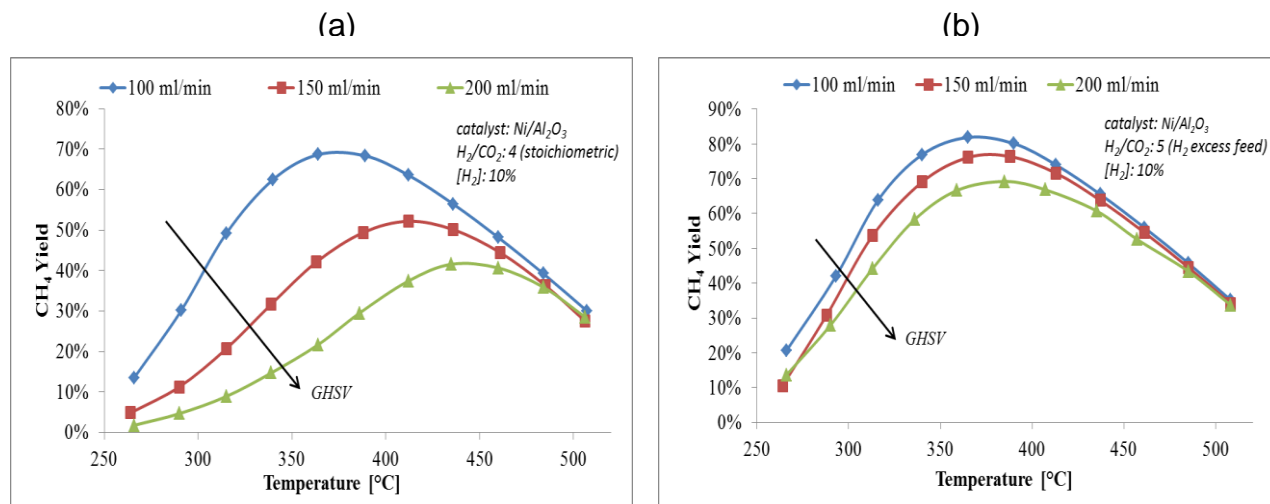


Figure 2: (a) Test results for Nickel catalyst. The reactor was fed with 10% of hydrogen in a stoichiometric ratio with carbon dioxide, (b) Test results for Nickel catalyst. Reacting mixture had the following composition: H₂:10%, CO₂:2% and N₂:88%.

The effect of the reacting mixture composition has been analysed (Figure 3). The hydrogen content in the reacting mixture was increased from 10% to 15% and then to 20%, while keeping constant both the H₂/CO₂ ratio (set equal to 5) and the space velocity (10000 h⁻¹). Focusing on results at low temperature (before the peak) the hydrogen fraction growth from 10% to 15% led to a notable yield rise, probably due to the concentration effect on kinetics. On the contrary, the further dilution decrease did not produce a significant yield increase: conversion could be constrained by diffusion phenomena. At high temperature (when equilibrium is reached) the rise of methane yield by increasing the hydrogen content is due to thermodynamics. Major concentration of H₂ and CO₂ in the inlet flow means an increase of the reacting gases partial pressure. Thus, at chemical equilibrium the methane yield rises according to the Le Chatelier's principle.

Also the bimetallic catalyst with Ni and Ru supported on Al₂O₃ spheres was tested. For this second sample, only the condition with a stoichiometric feed was considered. Results are presented in Figure 4(a). The space velocity impact was weaker as compared to the Ni catalyst tested under the same conditions (see Figure 2). CH₄ maximum yield passed from ≈76% (100 ml/min) to ≈68% (200 ml/min) with a relative decrease of ≈11%. This peak took place at a temperature of 344 °C when the volume flow was 100 ml/min and shifted to 368 °C with a doubled volume flow of 200 ml/min. However, in Figure 4(b) a comparison between Ni and Ni-Ru catalyst samples is presented. The two experimental curves refer to the same operating condition in terms of inlet mixture composition and volume flow (i.e., space velocity / residence time). The sample with Ru showed a greater methane yield when chemical equilibrium was still not reached (i.e., at low temperature), highlighting the positive impact of the Ru addition to the conversion. Moreover, for the Ni-Ru catalyst the peak CH₄ yield appears shifted towards a lower reaction temperature.

The results presented before suggest some considerations. All the curves show an initial methane yield increase followed by a subsequent drop. This happens because initially the temperature impact on the catalyst activity plays a relevant role according to the Arrhenius law. After the peak, chemical equilibrium effect becomes dominant, constraining the conversion. CO₂ hydrogenation is an exothermic reaction, then thermodynamically favoured by low temperature. Methane production was observed also at low temperature (below 300 °C) for both the catalysts. As expected, the effect of the space velocity (i.e., the

residence time) was verified for different samples and operating conditions. This effect was stronger for the nickel-based catalyst tested in stoichiometric conditions. This could be due to a not full activation of the catalyst. Probably, the 3 hours with H₂ pre-treatment is not enough to completely stabilize and fully activate the Ni/support samples. The nickel-ruthenium catalyst showed a higher methane production, confirming the benefit of the ruthenium addition. Moreover, the Ni-Ru sample reached the CH₄ yield peak (or, in other terms, the chemical equilibrium) at a lower temperature, meaning better performance in terms of activity. This is a potential benefit with reference to methanation processes taking place at low temperature, as the potential integration with pressurized high temperature electrolysis.

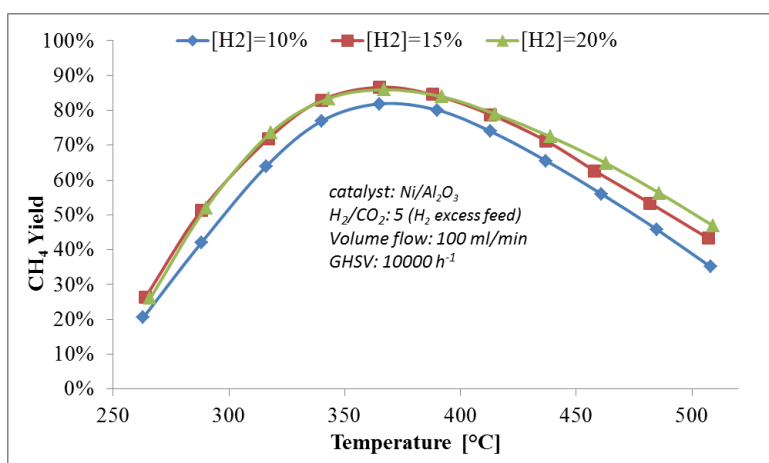


Figure 3: Nickel-based catalyst: effect of the reacting mixture composition by maintaining a constant H₂/CO₂ ratio

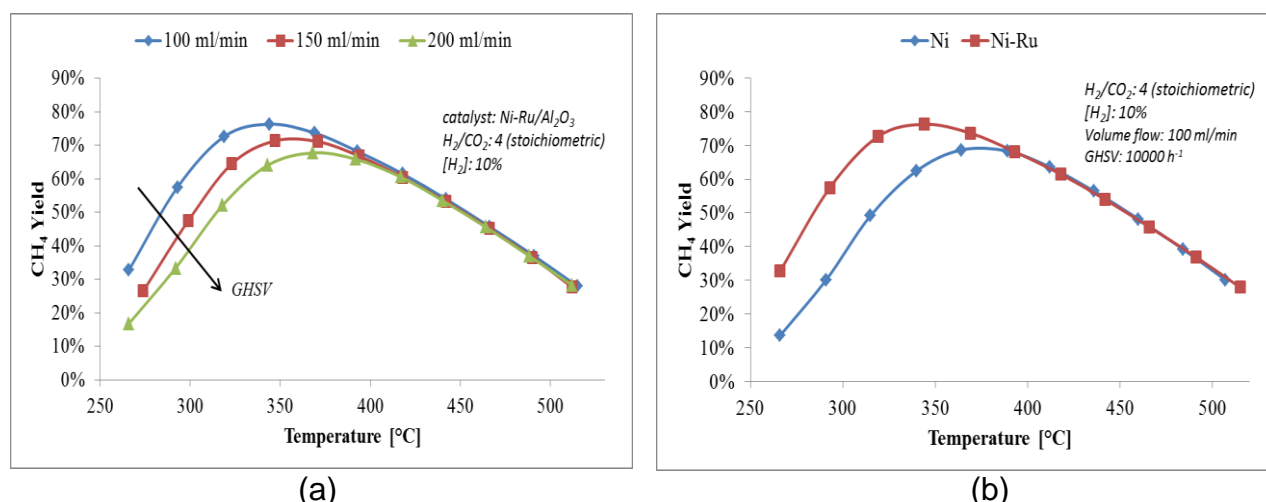


Figure 4: (a) Nickel-Ruthenium catalyst sample: effect of temperature and space velocity on the methane yield. The reactor was fed with 10% of hydrogen in a stoichiometric ratio with carbon dioxide. (b) Comparison between nickel and nickel-ruthenium catalyst.

3. Computational approach

A kinetic study has also been conducted in order to simulate the experiments presented in the previous section of the paper, focusing on the reproduction of CO₂ methanation measurements when the Ni (20% wt) is implemented. An extended literature review of the available kinetic models describing CO₂ methanation on Ni based catalysts has been initially conducted and is presented in Table 1.

Authors	Conditions			Catalyst	Reactions
	T (°C)	P (bar)	Molar ratio H ₂ /CO ₂		
Van Herwijnen <i>et al.</i> ^[10] (1972)	200-230	1	0.22-2.38% H ₂	33.6% wt NiO	Sabatier
Xu & Froment ^[11] (1989)	300-400	3-10	1/1, 1/2	Ni/MgAl ₂ O ₄	CO-methanation rWGS Sabatier
Ibraeva <i>et al.</i> ^[12] (1991)	220-270	1	Not available	NKM-4A Nickel catalyst	Sabatier
Lapidus <i>et al.</i> ^[13] (2007)	360-420	1	Not available	Ni/ANM	rWGS CO-methanation Boudouard
Hwang ^[6] (2007)	225-300	1-3	4/1 up to 5/1	Ni/Al ₂ O ₃	Sabatier
Sohrabi & Shabani ^[14] (2012)	330	≥20	35/65	3% Ni supported on Na-Y zeolite	Sabatier
Swickrath & Anderson ^[15] (2012)	225-300	1-3	4/1 up to 5/1	Ni/Al ₂ O ₃	Sabatier

Table 1: List of available kinetic models describing CO₂ methanation on Ni based catalysts

Van Herwijnen *et al.* [10] studied three models for the hydrogenation of CO₂ before selecting in the most suitable rate expression that described their experiments. In this way they examined the sensitivity of the kinetic model towards the exponent of the adsorption term. Xu and Froment [11] investigated the steam reforming of methane and the CO₂ methanation and postulated a 3-reaction scheme accompanied by the corresponding rate equations. They studied a large number of possible methanation mechanisms and concluded in a single one after thermodynamic analysis and model discrimination. Another mechanism, consisting of 9 elementary reactions for CO₂ methanation was proposed by Ibraeva *et al.* [12]. The authors considered that the surface reactions control the overall reaction rate. Lapidus *et al.* [13] investigated the CO₂ hydrogenation over copper and nickel catalyst and showed that on the nickel catalyst, contrary to the copper catalyst, CO₂ doesn't retard the CH₄ formation. They proposed a kinetic model for both catalyst cases. Hwang [6] investigated the application of a reactive separation technology, in which the catalytic methanation and CO₂ separation steps are coupled in-situ through the use of high-temperature membranes. For this purpose, he adopted a published kinetic model and recalculated the kinetic parameters using nonlinear least square fitting on his experimental data. Sohrabi and Shabani [14] worked in higher pressures (>20 bar) and formulated a mechanism based on the Langmuir-Hinshelwood theory.

It should be noted that the available CO₂ methanation kinetic models have been developed and subsequently tested for different ranges of pressure and temperature conditions. They also adopt varying number of reactions. Given that they were developed with the aim to accurately reproduce specific sets of experimental data, it is anticipated that they will not depict global applicability. However, a comparative assessment investigating their performance and potential ability to capture the basic characteristics of the present atmospheric pressure Ni- experiments, within an acceptable level of accuracy,

reveals the capabilities and limitations of each model and can be considered as an essential first step towards developing the most appropriate reaction scheme (with respective rate expressions) to fit the examined operational conditions and implemented catalysts.

Towards this direction, simulations have been performed implementing the mechanisms and their respective rate expressions aiming to reproduce the atmospheric pressure – Ni catalyst measurements. The experimental reactor of Section 2 was modelled as a Continuous Stirred Tank Reactor (CSTR) operating at isothermal and atmospheric pressure conditions. The RK-SOAVE (Redlich-Kwong-Soave) method was chosen to describe the thermodynamic properties of the methanation process. The rate equations follow the Langmuir – Hinshelwood approach (Eq. 2) thus the (available in ASPEN PLUS) LHHW (Langmuir-Hinshelwood-Hougen-Watson) model has been used for the simulations.

$$r = \frac{(\text{kinetic factor}) \cdot (\text{driving force})}{(\text{adsorption term})^{\text{exponent}}} \quad (2)$$

Figure 5 presents a comparative assessment between experiments and computational results implementing the kinetic models enlisted in Table 1 for the indicative case of the stoichiometric feed (H₂=10%vol, CO₂=2,5%vol) with an inlet volumetric flow equal to 100 ml/min (GHSV=10000 h⁻¹). Evidently, the Xu & Froment [11] model succeeds in capturing the basic trend of the experimental CH₄ yield “curve” for temperatures between 250 – 500 °C, however, some discrepancies are observed. Computational results show an improved accuracy of the model in capturing the CO₂ conversion at higher temperatures where chemical equilibrium is reached, however in lower temperatures (between 300 °C and 400 °C) where the methanation process is prominent, the model tends to underestimate CH₄ yield.

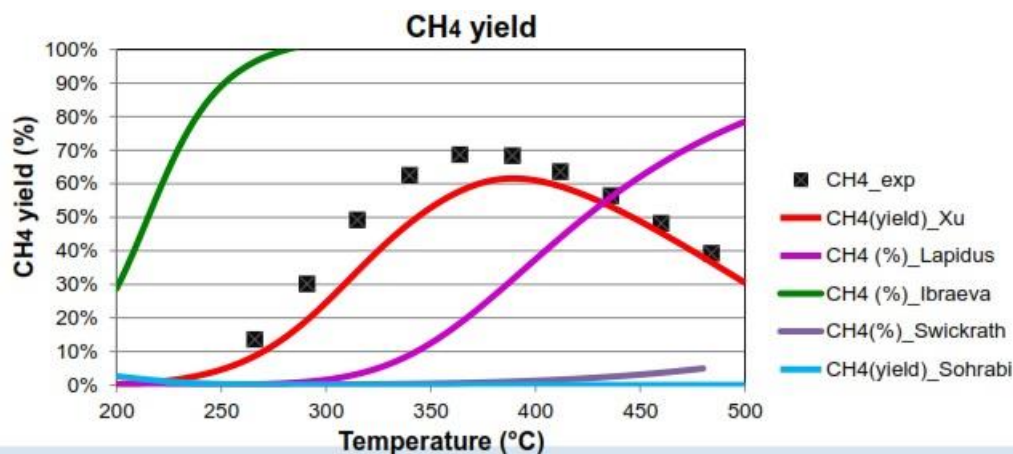


Figure 5: CO₂ conversion versus reactor temperature: Comparative assessment between experimental data and computational results implementing the kinetic models enlisted in Table 1.

The kinetic model of Xu & Froment [11] proposes a reaction scheme consisting of reactions R1 – R2 – R3 (see “Introduction”). A more detailed overview of the model’s performance for stoichiometric conditions and GHSV = 10000 h⁻¹ / GHSV = 15000 h⁻¹ is presented in Figures 6 and 7, respectively. The model succeeds in accurately predicting CO₂ conversion for the stoichiometric case at GHSV = 15000 h⁻¹ (Figure 7), however it tends to overpredict CH₄ yields particularly at temperatures between 350 – 425 °C. Discrepancies tend to become more prominent in the stoichiometric case at GHSV = 10000 h⁻¹ (Figure 6) where the implemented model underestimates both CO₂ conversion

and CH₄ yield levels. A similar trend also characterizes the model's performance for the stoichiometric case at GHSV = 20000 h⁻¹, as well as for the hydrogen excess cases.

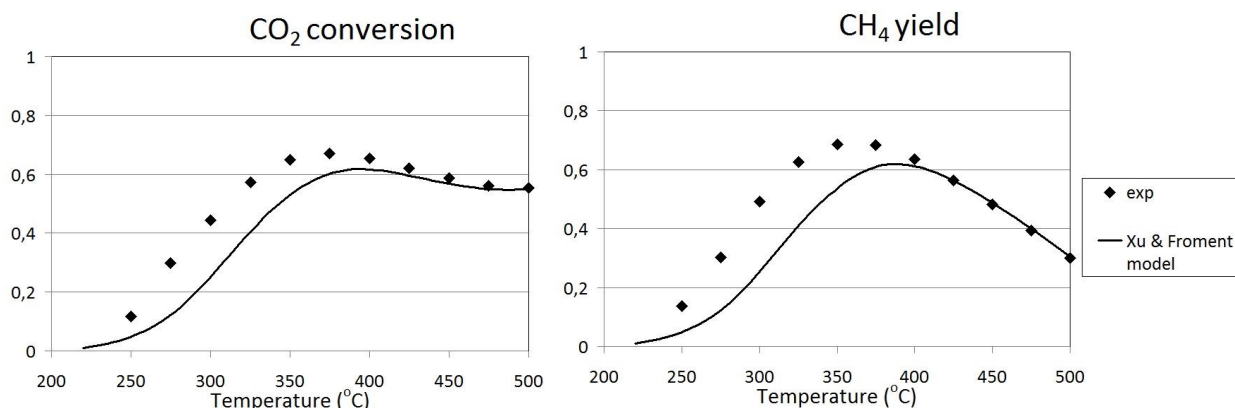


Figure 6: CO₂ conversion and CH₄ yields versus reactor temperature: Comparative assessment between experimental data and computational results implementing the Xu & Froment kinetic model: (Stoichiometric Feed, GHSV = 10000 h⁻¹)

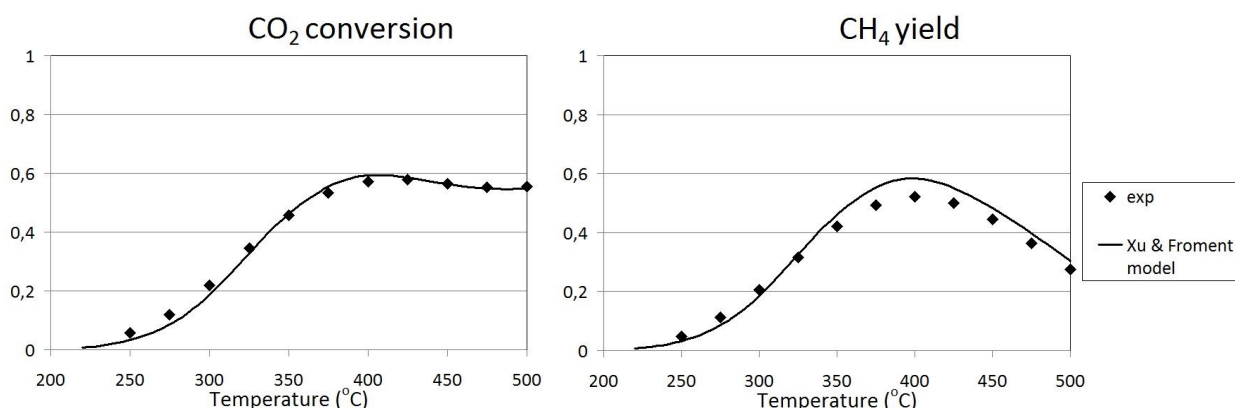


Figure 7: CO₂ conversion and CH₄ yields versus reactor temperature: Comparative assessment between experimental data and computational results implementing the Xu & Froment kinetic model: (Stoichiometric Feed, GHSV = 15000 h⁻¹)

In summary, existing kinetic models describing CO₂ methanation on Ni based catalysts, adopt varying number of reactions and perform well at the particular range of pressure and temperature for which they have been developed. Through the performed comparative assessment, the most appropriate model for the current experimental conditions was identified. Future work will focus on optimizing the implemented model's kinetic and adsorption parameters according to the examined conditions. Moreover, additional experimental and computational work will take place investigating CH₄ yields in higher pressure conditions (up to 30 bar).

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