

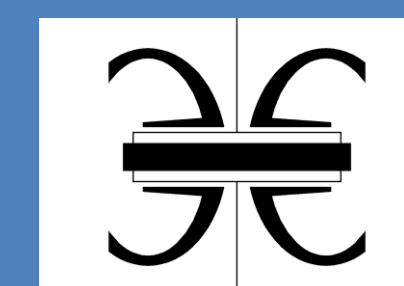


# CO<sub>2</sub> Methanation Under Atmospheric Pressure Conditions on a Ni catalyst: Experiments and Kinetic Modelling

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## Introduction

➤ **“Power to Gas” (P2G) conversion** is a promising concept which uses the surplus electricity coming from renewable energy sources to produce hydrogen, and potentially methane, for further use and storage in the natural gas distribution grid.

➤ Electrolysis is utilized for hydrogen generation and **methanation process** is required for converting hydrogen to methane.

➤ An **experimental and numerical study** on methanation is essential for the determination of the operating conditions that maximize the CH<sub>4</sub> yield.

## Scope of this Work

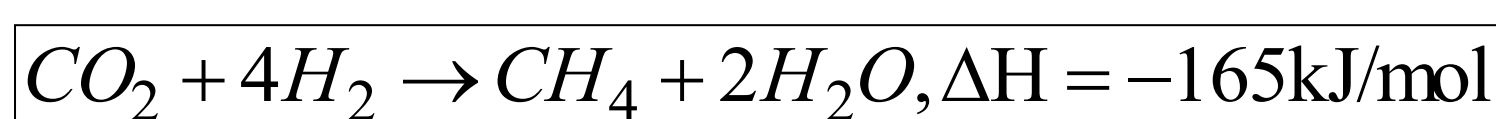
➤ In the present work, the **methanation of CO<sub>2</sub>** is experimentally investigated in **atmospheric pressure conditions** by implementing **two different catalytic samples of Ni**. The impact of **temperature**, **space velocity (GHSV)** and **reacting mixture composition** on the CH<sub>4</sub> yield is analyzed.

➤ A **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**.

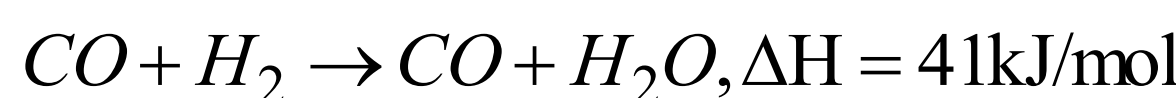
## Methanation process

Methanation is an heterogeneous catalytic process basically described by the **Sabatier reaction**:

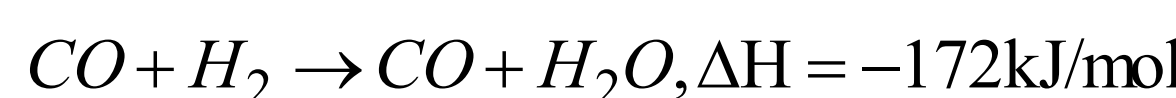


Other reactions associated with the methanation process are:

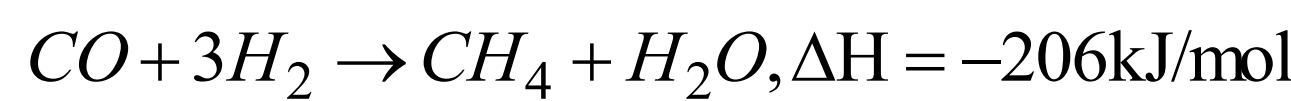
➤ Reverse Water Gas Shift (rWGS)



➤ CO-methanation



➤ Boudouard:



## Experimental study

➤ Overall, **Ni and Ru** supported catalysts are found to be the most active catalysts for the methanation process

### Experimental Setup

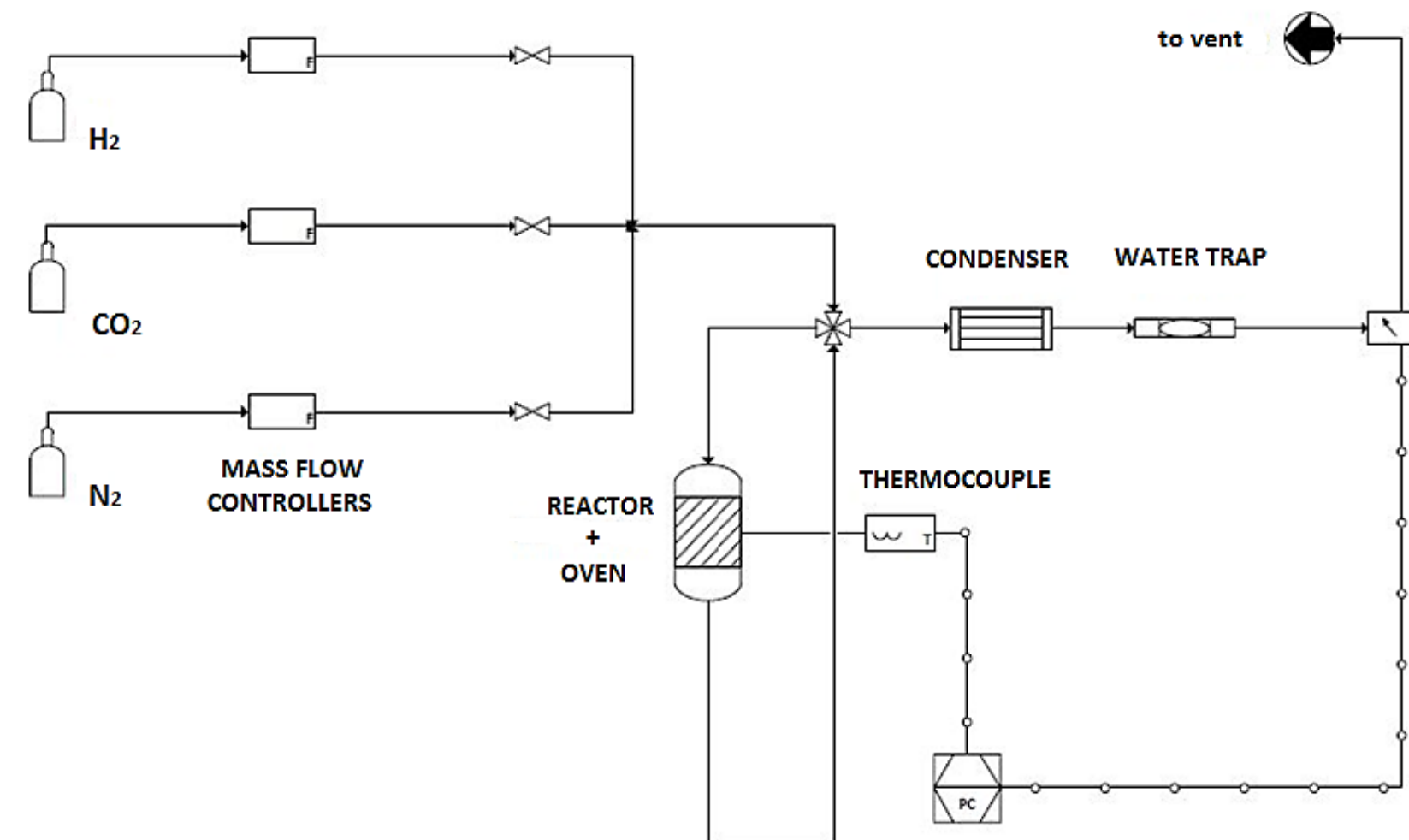


Figure 1 – Schematic of the methanation test unit

### Conditions

Oven Temperature	250 – 500° C (steps of 25° C)
Pressure	1 bar
Catalysts	Type: <ul style="list-style-type: none"><li>Nickel (20%wt) supported on γ-Al<sub>2</sub>O<sub>3</sub></li><li>Nickel (20%wt) + Ruthenium (2%wt) supported on γ-Al<sub>2</sub>O<sub>3</sub></li></ul>
	Load: 600 mg
	Particles: spherical with a 0.6 mm diameter
Feed	<ul style="list-style-type: none"><li>Stoichiometric (H<sub>2</sub>/CO<sub>2</sub>=4)</li><li>Hydrogen excess (H<sub>2</sub>/CO<sub>2</sub>=5)</li></ul>
Volumetric flow rates	<ul style="list-style-type: none"><li>100 ml/min (GHSV ≈ 10,000 h<sup>-1</sup>)</li><li>150 ml/min (GHSV ≈ 15,000 h<sup>-1</sup>)</li><li>200 ml/min (GHSV ≈ 20,000 h<sup>-1</sup>)</li></ul>

Table 1 – Experimental conditions

Both catalyst samples were reduced at a temperature of 500 °C for 3 hours by passing through the bed an activating stream of 10% H<sub>2</sub> in N<sub>2</sub>.

## Experimental Data

### Effect of space velocity

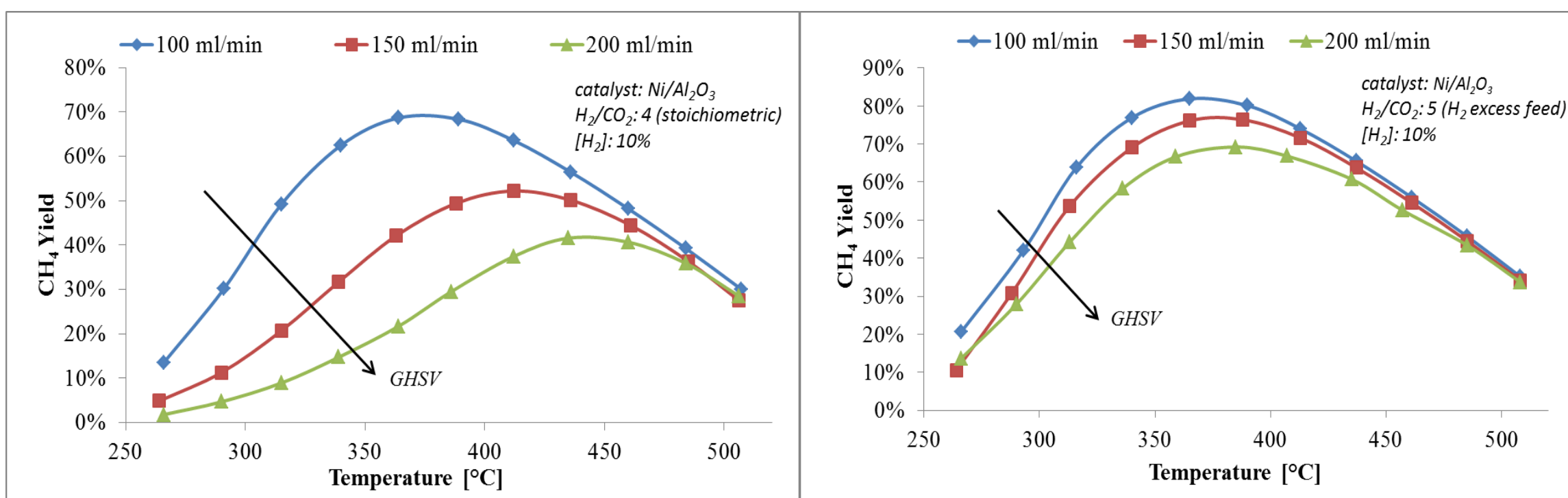


Figure 2 – Test results for Nickel catalyst. The reactor was fed with 10% of hydrogen in a stoichiometric ratio with carbon dioxide.

Figure 3 – Test results for Nickel catalyst. Reacting mixture had the following composition: H<sub>2</sub>:10%, CO<sub>2</sub>:2% and N<sub>2</sub>:88%.

➤ CH<sub>4</sub> yield reaches higher values in the **H<sub>2</sub> excess feed case** compared to the stoichiometric feed.

➤ Maximum CH<sub>4</sub> yield is recorded at about **360 °C** for both feed cases for inlet flow **100 ml/min**.

➤ **Stoichiometric case**: GHSV has a significant effect on methane production. Higher GHSV leads to lower CH<sub>4</sub> yield at a fixed temperature. The maximum CH<sub>4</sub> yield is shifted by varying the residence time.

➤ **H<sub>2</sub> excess feed**: Space velocity has a weaker effect on CH<sub>4</sub> production.

### Effect of reacting mixture composition

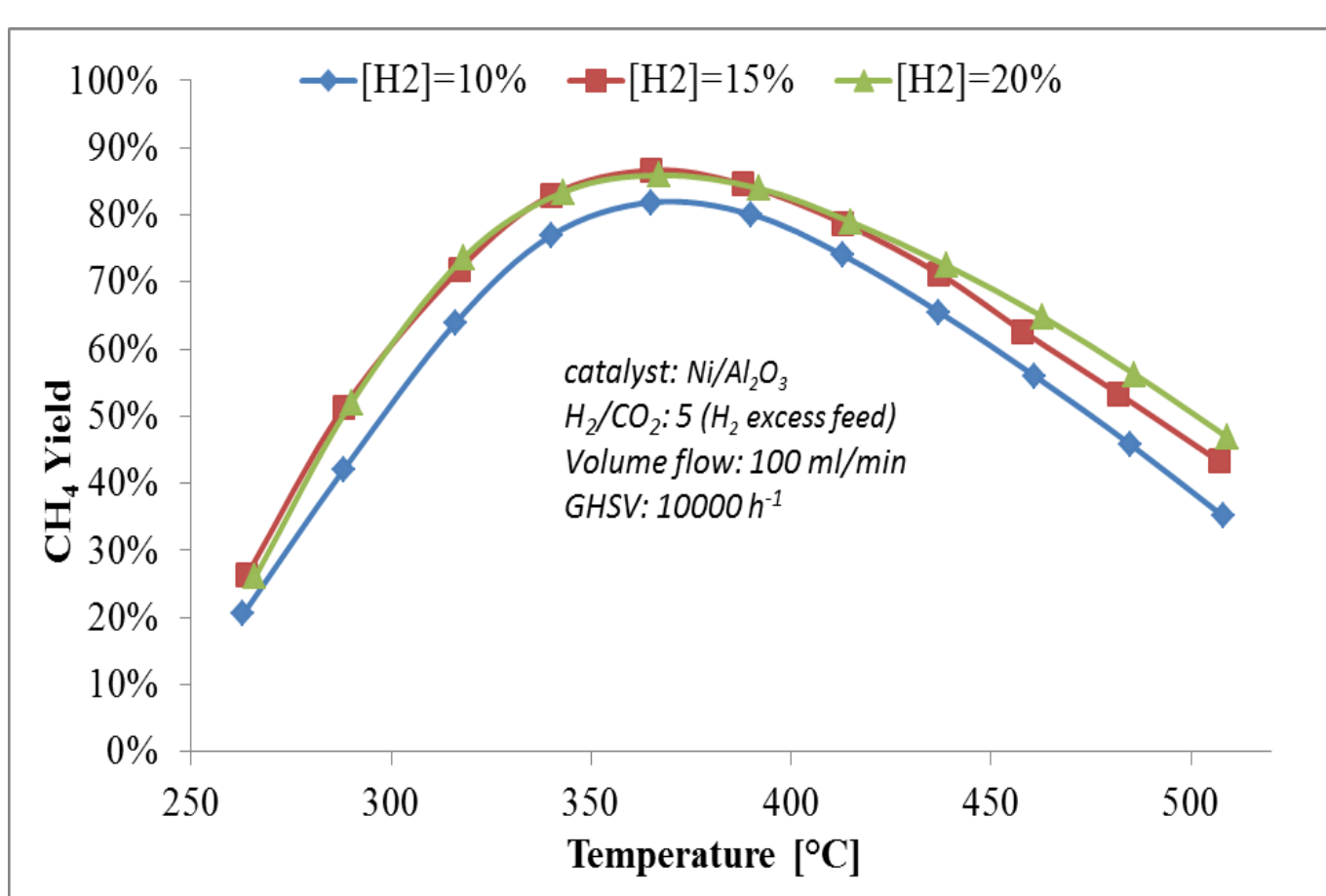


Figure 4 – Nickel-based catalyst: effect of the reacting mixture composition by maintaining a constant H<sub>2</sub>/CO<sub>2</sub> ratio

➤ **Max. CH<sub>4</sub> production at 360 °C**

➤ **T<360°C**: the first H<sub>2</sub> fraction growth leads to a notable yield rise. On the contrary, the further dilution does not produce a significant yield increase: conversion is constrained by diffusion phenomena.

➤ **T>360°C**: Equilibrium is reached and the rise of CH<sub>4</sub> yield follows the Le Chatelier's principle. Major concentration of H<sub>2</sub> and CO<sub>2</sub> in the inlet flow causes the chemical equilibrium to shift towards the methane production.

### Tests on a bimetallic catalyst Ni-Ru

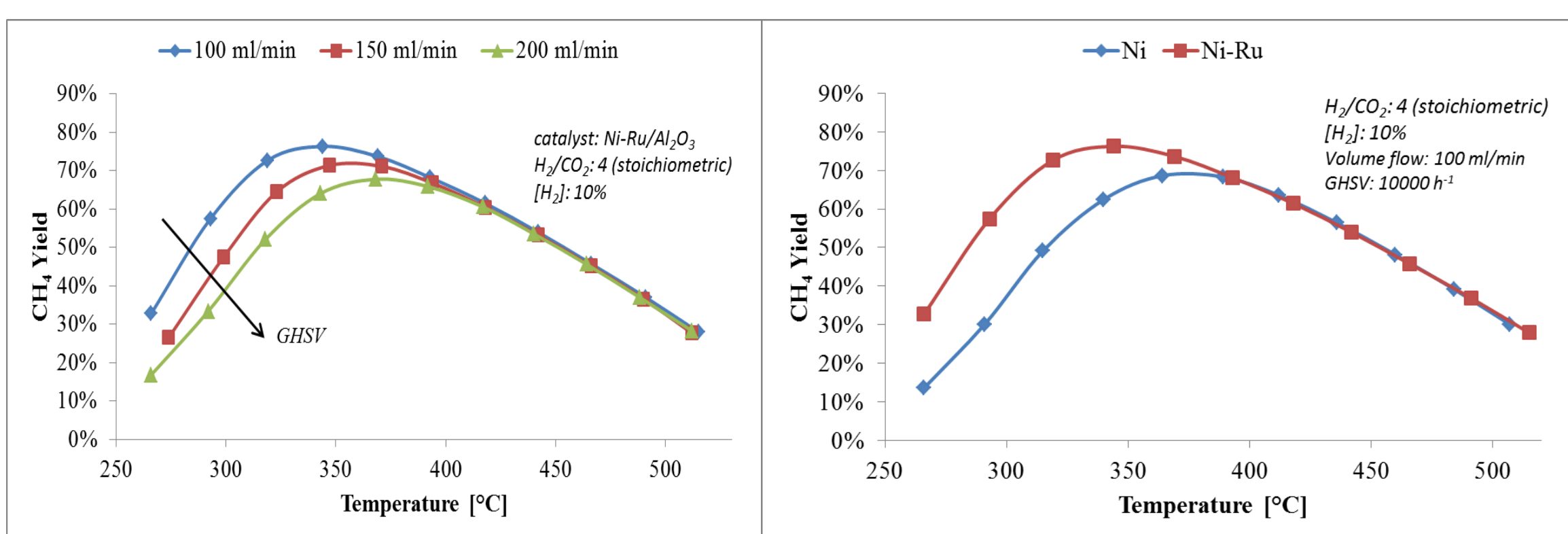


Figure 5 – Ni-Ru catalyst sample: effect of temperature and space velocity on the CH<sub>4</sub> yield.

Figure 6 – Comparison between nickel and Ni-Ru catalyst.

➤ CH<sub>4</sub> max yield decreases as the volume flow rate raises and the **CH<sub>4</sub> production peak shifts to slightly higher temperatures**.

➤ The **space velocity impact** on the reacting mixture catalysed by Ni-Ru supported on γ-Al<sub>2</sub>O<sub>3</sub> is **weaker** as compared to the Ni catalyst tested under the same conditions.

➤ For the Ni-Ru catalyst the **CH<sub>4</sub> yield peak appears shifted towards a lower reaction temperature**.

## Computational approach

### Mechanisms provided by literature

An extended literature review of the available kinetic models describing CO<sub>2</sub> methanation on Ni based catalysts has been conducted.

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

Table 2: List of available kinetic models describing CO<sub>2</sub> methanation on Ni based catalysts

### Simulation

A **comparative assessment** was realized in order to investigate the performance and potential ability of each model to capture the basic characteristics of the present Ni-experiments. Towards this direction, simulations were performed using the **ASPEN Plus software**.

- ✓ Rigorous Continuous Stirred Tank Reactor (RCSTR)
- ✓ Reaction Type: LHHW (Langmuir – Hinshelwood – Hougen - Watson)
- ✓ Thermodynamic method: RK-SOAVE (Redlich – Kwong - Soave)
- ✓ Atmospheric Pressure Conditions
- ✓ Isothermal Reactor: Temperature Range 250 – 500 °C

### Experimental vs. Computational values

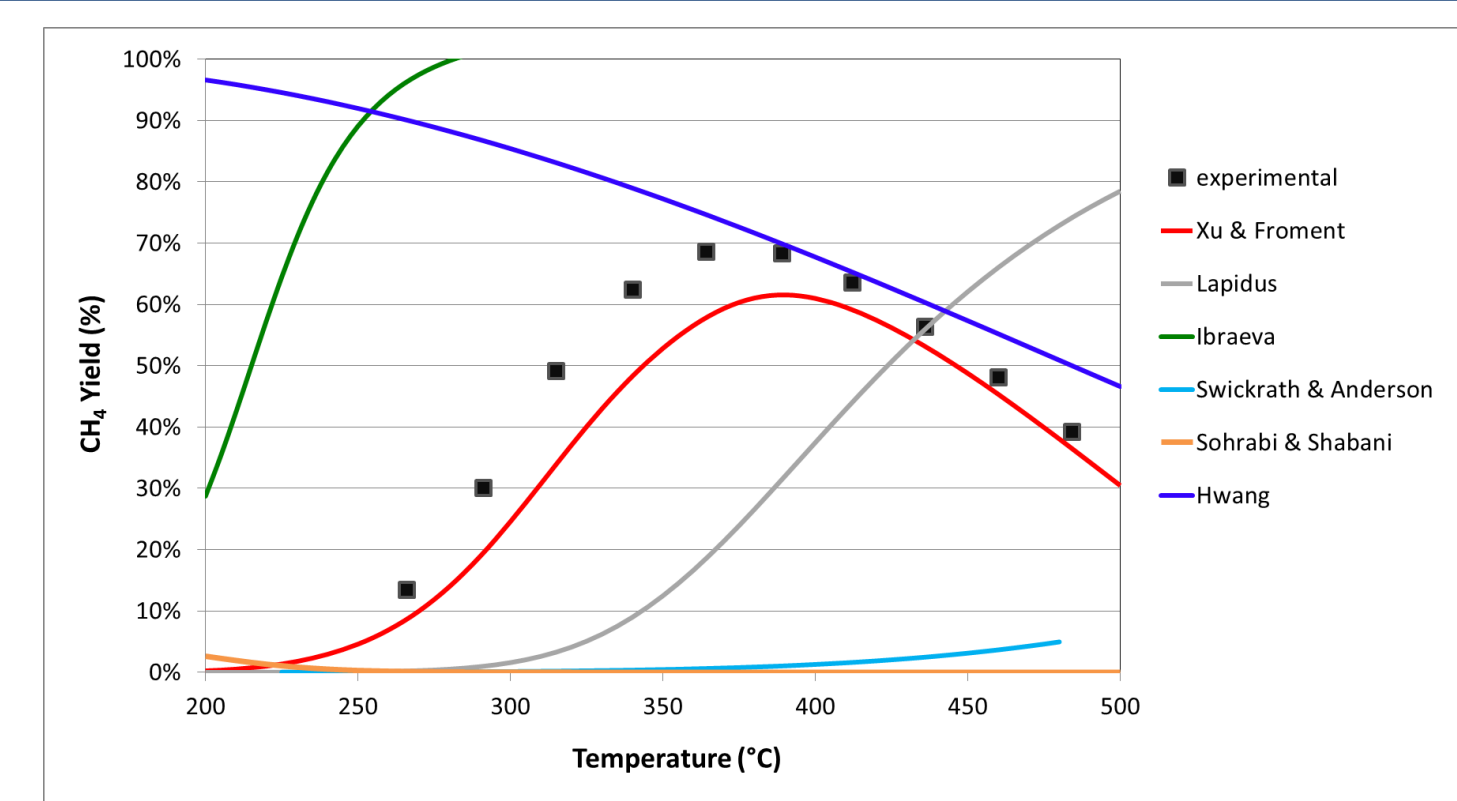


Figure 7 - CO<sub>2</sub> conversion versus reactor temperature: Comparative assessment between experimental data and computational results implementing the kinetic models enlisted in Table 2.

➤ The **Xu & Froment** model succeeds in capturing the basic trend of the experimental CH<sub>4</sub> yield “curve” for temperatures between 250 – 500 °C.

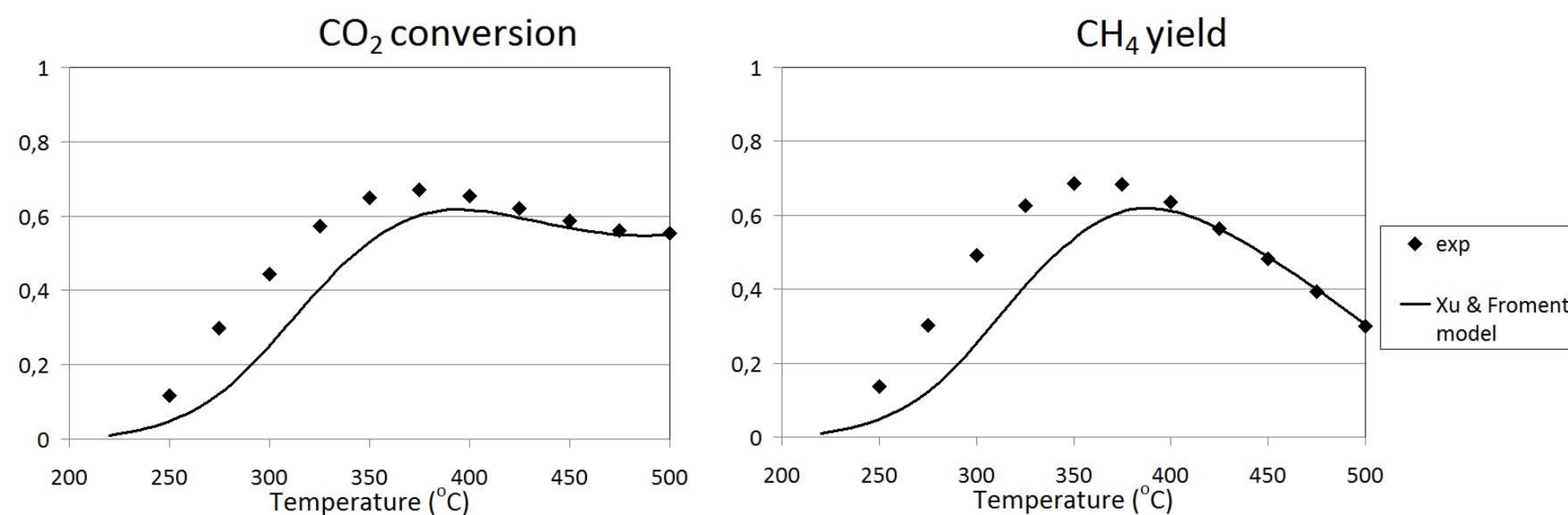


Figure 8 - CO<sub>2</sub> conversion and CH<sub>4</sub> yields versus reactor temperature: Comparative assessment between experimental data and computational results implementing the Xu & Froment kinetic model: (Stoichiometric Feed, GHSV = 10000 h<sup>-1</sup>)

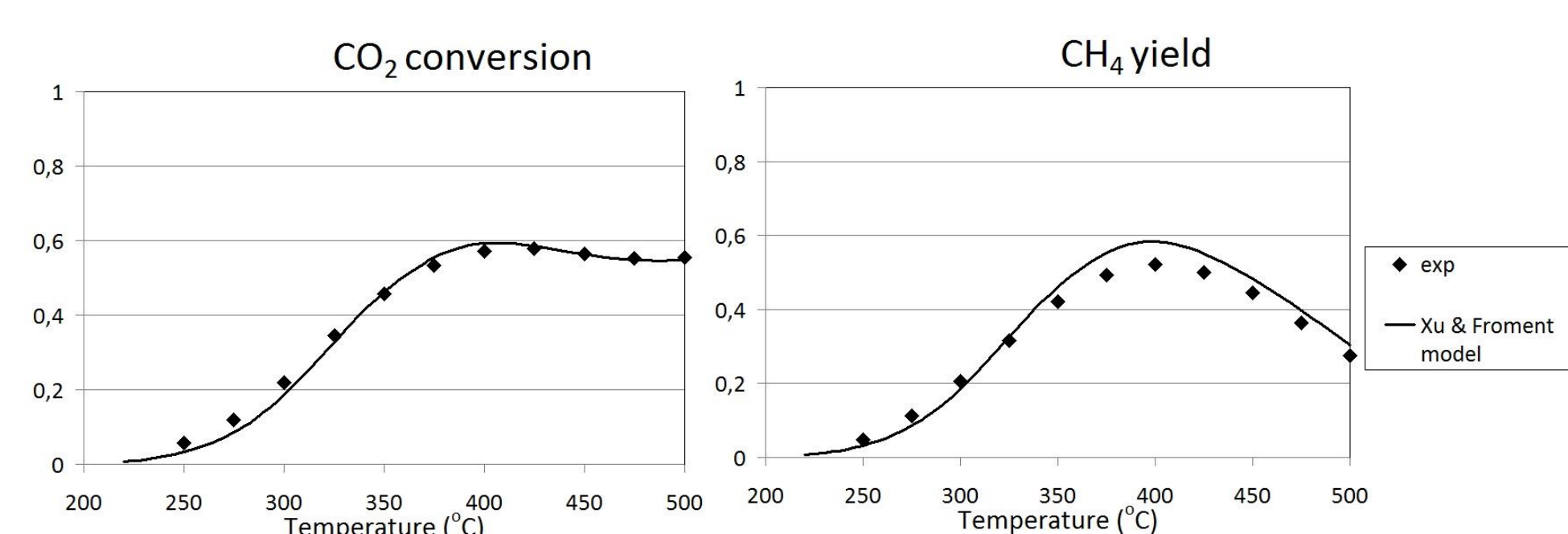


Figure 9 - CO<sub>2</sub> conversion and CH<sub>4</sub> yields versus reactor temperature: Comparative assessment between experimental data and computational results implementing the Xu & Froment kinetic model: (Stoichiometric Feed, GHSV = 15000 h<sup>-1</sup>)

➤ The computational model proposed by Xu and Froment (1989) succeeds in accurately predicting CO<sub>2</sub> conversion for the stoichiometric case at GHSV = 15000 h<sup>-1</sup>.

➤ However, it over predicts the CH<sub>4</sub> yield particularly at temperatures between 350 – 425 °C.

➤ Discrepancies become more prominent in the stoichiometric case at GHSV = 10000 h<sup>-1</sup> where the implemented model underestimates both CO<sub>2</sub> conversion and CH<sub>4</sub> yield levels.

## Discussion

➤ **Experiments:**

CH<sub>4</sub> production was observed at low temperature (below 300 °C) for both the catalysts. The effect of the space velocity (i.e., the residence time) was stronger for the Ni-based catalyst tested in stoichiometric conditions. This could be due to a not full activation of the catalyst. The Ni-Ru catalyst led to higher CH<sub>4</sub> production. The Ni-Ru sample reached the CH<sub>4</sub> yield peak at lower temperatures. This is a potential benefit with reference to methanation processes taking place at low temperature, as the potential integration with pressurized high temperature electrolysis.

➤ **Computational Results:**

The comparative assessment investigating the available mechanisms performance and potential ability to capture the basic characteristics of the present atmospheric pressure Ni- experiments, reveals the capabilities and limitations of each model and can be considered as an essential first step towards developing the most appropriate reaction scheme to fit the examined operational conditions and implemented catalysts.

□ Additional experimental and computational work will focus on investigating CH<sub>4</sub> yields in higher pressure conditions (up to 30 bar).

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