

# Synthesis of Global Reaction Routes using Thermodynamic Evaluation

Consuelo C.G. Silva<sup>a</sup>, Luiz Henrique S. Silva<sup>b</sup>, Reginaldo Guirardello<sup>c</sup>

<sup>a,b</sup> Federal University of Recôncavo Bahia – UFRB – Brazil

<sup>c</sup> School of Chemical Engineering – Unicamp, Av. Albert Einstein 500, Campinas–SP, 13083-852, Brazil  
[guira@feq.unicamp.br](mailto:guira@feq.unicamp.br)

The global demand for sustainable, energy-efficient chemical processes has accelerated innovations in methane (CH<sub>4</sub>) utilization. Methane, a versatile and abundant resource, offers dual benefits: meeting energy demands while reducing environmental impacts through advanced conversion methods. However, existing approaches often face the challenge of being endothermic, consuming substantial energy and limiting industrial feasibility. This study introduces as a goal an exothermic process design to optimize energy use, while achieving sustainability goals such as avoiding the emission of carbon dioxide. Through thermodynamic pathway evaluations, one case study, the production of urea, was identified as a viable product of CH<sub>4</sub> conversion, alongside with hydrogen generation, in an overall energetically favourable process. Rigorous simulations analyze the process feasibility, emphasizing carbon emission reductions and resource efficiency. By integrating advanced modelling tools, this work aligns with global efforts to develop green chemical technologies, highlighting its role in industrial innovation and environmental responsibility.

## 1. Introduction

Many processes aiming to use CH<sub>4</sub> without emitting CO<sub>2</sub> have the disadvantage of being endothermic, that is, they consume energy, so the motivation for this work is from the very beginning the process to use reagents and products in such a way that the overall process is exothermal or autothermal, so that it does not consume energy. The thermodynamic evaluation of a global reaction route is performed in order to determine whether the overall reaction is thermodynamically favourable or not. This step is important, because it predicts whether the process will consume energy or not. From the formation enthalpy, the enthalpy variation  $\Delta H$  of the global reaction is calculated. In addition,  $\Delta G$  provides important information regarding the spontaneity of the process or individual steps. If  $\Delta G$  is negative the reaction route is thermodynamically favourable. Therefore, the thermodynamic evaluation of a global reaction route involves the evaluation of the formation enthalpy of reagents and products, the determination of variations of enthalpy and Gibbs energy, and the interpretation of the results to determine whether the reaction route is thermodynamically favourable or not.

The thermodynamics of a global reaction route can also be evaluated by considering the variation of Gibbs energy  $\Delta G$ . The Gibbs energy is the available energy to perform work in a system and is related to variations of enthalpy and entropy. If  $\Delta G$  is negative, it means that the reaction is spontaneous and the reaction route is thermodynamically favourable. If  $\Delta G$  is positive, it means that the reaction is not spontaneous and the reaction route is thermodynamically unfavourable. As a case study, the proposed approach was applied in a thermodynamic analysis for the production of urea, which is exothermic, while avoiding the production of CO<sub>2</sub>. For thermodynamic analysis, it is considered how many reaction routes are possible for the same reagent and the same product. The data obtained was handled in graphical and numerical computational simulations with the help of the software Aspen, which is a process modelling tool used for process monitoring, optimization and simulation. Also, this particular case study (urea production) uses the CO<sub>2</sub> generated in one reaction step to produce the final product, thus preventing carbon dioxide from being released into the atmosphere. Finally, hydrogen is also produced as a by-product in this particular process.

## 2. Methodology - Linear Programming Model

This is a synthesis strategy, since the process is not known in advance, not even the products and reactants, except methane as raw material, hydrogen as a by-product and carbon dioxide is not desired as a product (maybe only as an intermediate). Also, it is desirable that the global process be exothermic.

The first step is the definition of the products and the reactants. They are not specified in advance, they will be determined from a list of possible substances that may exist or not. These substances have their enthalpies evaluated at the conditions of the feed and exit of the process (reference state), to calculate the total enthalpy variation, so that the whole process is exothermic, to avoid energy consumption. This problem can then be formulated as a linear programming model, whose resolution will define the overall process, and is given by:

$$\max_{n_i} \{n^{\text{desired product}}\} \quad (1)$$

$$\sum_{i=1}^{Np} a_{mi} \cdot n_i^{\text{products}} = \sum_{i=1}^{Nr} a_{mi} \cdot n_i^{\text{reactants}} \quad (\text{atomic balance}) \quad (2)$$

$$(-\Delta H_R^{\text{global}}) \geq \text{given value} \geq 0 \quad (3)$$

$$n_i \geq 0 \quad (4)$$

where:

$$\Delta H_R^{\text{global}}(T_0, P_0) = \sum_{i=1}^{Np} n_i^{\text{products}} \cdot \hat{h}_i(T_0, P_0) - \sum_{i=1}^{Nr} n_i^{\text{reactants}} \cdot \hat{h}_i(T_0, P_0) \quad (5)$$

and where the decision variables are  $n_i$ : if  $n_i > 0$  the substance exists in the global mass balance, while if  $n_i = 0$  the substance is not present in the global balance (it may only exist as an intermediate). One critical step is the definition of the set  $i \in \{\text{list of possible substances}\}$ .

Once the raw materials and products have been determined, a viable reaction route must be found to obtain the desired products from the raw materials. This step involves an analysis of the Gibbs energy of each intermediate reaction involved, so that each reaction has a favourable equilibrium at the temperature, pressure and composition of each reaction step in real operating conditions (since intermediate steps may use different temperatures and pressures than the reference conditions). This stage of the project can then be carried out using a commercial software, such as Aspen, to simulate the entire process with the routes considered.

## 3. Case Study - Global Route

This is just an illustrative example, since the proposed methodology is general. The following conditions were considered:

- potential raw materials: CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O

- potential products: (NH<sub>2</sub>)<sub>2</sub>CO (urea), C<sub>2</sub>H<sub>4</sub> (ethylene), C<sub>6</sub>H<sub>6</sub> (benzene), H<sub>2</sub>O, H<sub>2</sub>

Note that in this step water can be either a raw material or a product, it is not yet known.

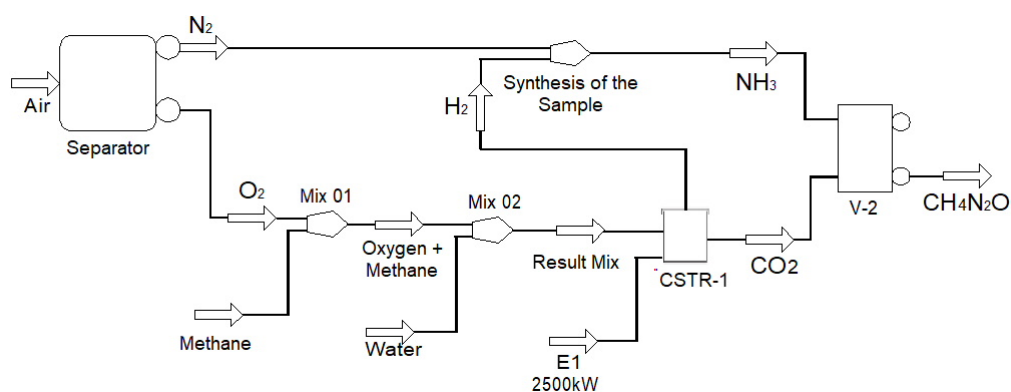
- calculation basis: 100 mol CH<sub>4</sub>

- reference conditions for the beginning and end of the overall process: 25 °C and 1 atm.

The enthalpy of formation data were obtained from the thermodynamics literature (Reid et al, 1987). The calculations were performed with an Excel spreadsheet, using Solver to find the solution of the LP model.

Using this small list of substances, the substance that leads to more hydrogen is benzene (burning part of the hydrogen for  $\Delta H^{\text{global}} > 0$ ), but the difference with urea is small. Also, urea is useful as a fertilizer. Therefore, this case study was set to the production of urea. The raw materials were CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub>O, while the products

were  $(\text{NH}_2)_2\text{CO}$  and  $\text{H}_2$ . However, this step does not provide the reaction routes from the reactants to the final products. Therefore, the next step is finding an adequate route, which in this case is well known (Figure 1):



Font: Developed by the author

Figure 1 : Process Flow Diagram

Then, after choosing a route, this study evaluates the reaction routes' thermodynamic and energetic feasibility using Aspen Plus simulations and thermodynamic analyses to optimize operating conditions and maximize efficiency. Simulations modelled reaction conditions and calculated mass-energy balances. Thermodynamic analyses determined key quantities ( $\Delta H$ ,  $\Delta S$ ,  $\Delta G$ ) to assess reaction spontaneity and favourable conditions. Integrating these results provides an approach for developing efficient, sustainable processes.

## 4. Case Studies - Routes of Reactions

### 4.1. Methane and Oxygen Reaction

This case study analyzes the chemical reaction between methane ( $\text{CH}_4$ ) and oxygen ( $\text{O}_2$ ), with the aim of evaluating the products formed, the energy involved and the associated flows. The analysis was carried out using Aspen Plus *software*. The reaction between methane and oxygen can take place via different chemical routes, depending on the conditions of temperature, pressure and the ratio between the reactants. These conditions were chosen to evaluate the behaviour of the different chemical routes, providing a basis for future adjustments. The main reactions include:

1. Complete Combustion (highly exothermic):



2. Incomplete Combustion (exothermic):



3. Partial Oxidation Reaction (slightly exothermic):



4. Solid Carbon Formation (if oxygen is extremely limited, endothermic):



The products depend on the prevailing thermodynamic conditions and chemical routes, which are: carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O), carbon monoxide (CO), hydrogen (H<sub>2</sub>), solid carbon (C). For preliminary analysis, it was considered at the feed: molar ratio 1 CH<sub>4</sub> : 2 O<sub>2</sub>, T = 25°C, P = 1 atm.

#### 4.2. Methane and Water Reaction

This case study analyzes the interaction between methane (CH<sub>4</sub>) and water (H<sub>2</sub>O), focusing on the thermodynamic analysis and feasibility of the process. The simulation, carried out in the Aspen Plus software, investigates the energy flows, the molar and volumetric fractions of the products, as well as the overall efficiency of the reactions, allowing a detailed assessment of the ideal conditions for industrial applications. The reaction between CH<sub>4</sub> and H<sub>2</sub>O follows various chemical routes, which are widely used in industrial processes, such as the production of synthesis gas (syngas) and hydrogen. The products vary according to the predominant chemical route and thermodynamic conditions. The main reactions include:

1. Methane Steam Reform (endothermic):



This is the main reaction in industrial processes for synthesis gas production (mixture of CO and H<sub>2</sub>).

2. Gas-water shift reaction (slightly exothermic):



3. Solid Carbon Formation (exothermic):



The products depend on the prevailing thermodynamic conditions and chemical routes, which are: hydrogen (H<sub>2</sub>), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O) and solid carbon (C). For preliminary analysis, it was considered at the feed: molar fractions y<sub>CH<sub>4</sub></sub> = 0.5289 and y<sub>H<sub>2</sub>O</sub> = 0.4710, T = 25°C, P = 1 atm.

#### 4.3. Converting Intermediate Products into Value Added Products

Using the results of the previous case studies, which demonstrate the thermodynamic feasibility of the reactions between methane and oxygen and methane and water, it is proposed a process to use these reactions in the production of more valued products, such as urea. This is based on the proposed approach of focusing on the synthesis of high value-added chemical compounds, integrating sustainable technologies and optimized processes. In the case of urea, it can be obtained from the reaction between ammonia (NH<sub>3</sub>) and carbon dioxide (CO<sub>2</sub>), by developing and evaluating thermodynamically viable and economically attractive routes. For example, integrating with methane reforming, using the hydrogen (H<sub>2</sub>) produced in steam reforming as raw material for the synthesis of ammonia (NH<sub>3</sub>) and evaluating the energy efficiency of the ammonia synthesis process considering the use of nitrogen from the air. For the conversion of CO<sub>2</sub> and NH<sub>3</sub> into urea, the CO<sub>2</sub> captured in the combustion and the reforming can be used to produce urea (NH<sub>2</sub>CONH<sub>2</sub>), a product used as a fertilizer and industrial additive. The final process will be found by carrying out simulations to determine the optimal conditions (temperature, pressure and molar ratios) to maximize the urea yield.

### 5. Numerical Results

The thermodynamic analysis of global reaction routes plays a fundamental role in the development of sustainable processes for utilizing methane (CH<sub>4</sub>) without emitting carbon dioxide (CO<sub>2</sub>). This study is especially relevant to overcome the limitation of many endothermic processes, which consume energy and reduce economic and environmental viability. This work focused on evaluating different reaction routes for the production of urea, as a case study, avoiding the emission of CO<sub>2</sub>, with a focus on identifying a global exothermic process. Thermodynamics was considered by calculating the enthalpy variations (ΔH) and Gibbs energy (ΔG) of the reactions. These analyses made it possible to predict the spontaneity and thermodynamic feasibility of the processes studied. The initial conditions for the reactants and the final conditions for the products in the global process were considered at the reference state of 25°C and 1 atm.

In order to achieve the proposed objectives, the Aspen software was used to carry out graphical and numerical simulations, using a conversion reactor. The input data, which included CH<sub>4</sub>, O<sub>2</sub>, and specific temperature and pressure conditions, was parameterized to evaluate the thermodynamic behaviour of different combinations of

reactants and products. The simulations carried out were fundamental in determining global enthalpy variations and identifying potentially favourable reaction routes. The work also considered the need for the reactions to be sufficiently exothermic to compensate for losses in the process, ensuring greater efficiency and sustainability. The results presented below provide an analysis of the routes evaluated, taking into account the thermodynamic criteria established and the practical feasibility of implementation of the proposed strategy.

Table 1: Case Study 1 – CH<sub>4</sub> + O<sub>2</sub>

Compound	Molar Ratio
CH <sub>4</sub>	1
O <sub>2</sub>	2

Table 2: Case Study 1 – Flows

Energy	Molar Flow	Mass Flow	ΔEnthalpy
-4646.14kW	62.35 mol/s	1kg/s	<b>-15.50 kJ/kmol</b>

As shown in Tables 1 and 2, the negative variation in enthalpy indicates that the process is exothermic, which is in agreement that the simulated reaction route meets the objective of compensating for energy losses, making the process thermodynamically favourable in terms of energy released. Also, all the reaction products are in the gas phase at the end of the process.

The increase in molar flux suggests a reaction with efficient conversion of reactants into products, since for an initial mole of CH<sub>4</sub> and 2 moles of O<sub>2</sub>, an increase in molar flow indicates the formation of several products per mole of reactant, such as CO<sub>2</sub> and H<sub>2</sub>O. On the other hand, a constant mass flow (not molar flow) just reflects the conservation of mass in the process. The conversion of CH<sub>4</sub> and O<sub>2</sub> into products maintains the same initial mass flow, with the difference concentrated in the composition of the products.

The negative enthalpy reinforces the exothermic nature of the reaction. This value reflects the release of heat in the process, contributing to the goal of minimizing the need for external energy.

Table 3: Case Study 2 – CH<sub>4</sub> + H<sub>2</sub>O

Compound	Molar Fraction Input
CH <sub>4</sub>	0.5289
H <sub>2</sub> O	0.4710

Table 4: Case Study 2 – Flows

Energy	Molar Flow	Mass Flow	ΔEnthalpy
-20699kW	117.84 mol/s	2kg/s	<b>22332.9 kJ/kmol</b>

As shown in Tables 3 and 4, this process is endothermic, which suggests that the chemical reactions between CH<sub>4</sub> and H<sub>2</sub>O involve the formation of energetic by-products. Possible answers include:

Steam reforming (endothermic):



The reforming event is endothermic, but the overall process can be exothermic due to other interactions.

Gas-water displacement reaction (exothermic):



The following observations can also be made, at the end of the overall process:

#### Product Phase

- Approximately half of the products are in the vapour phase, while the rest remain in the liquid phase.
- The presence of the liquid phase can be attributed to excess (unconverted) water or to the partial condensation of water vapour under reference conditions (25°C, 1atm) at the end of the process.
- Components in the vapour phase predominantly include H<sub>2</sub>, CO, and possibly residual CH<sub>4</sub>. In the liquid phase, water dominates.

### Physical flows

- The molar amount of products is significantly greater than the input of reactants, suggesting the formation of multiple molecules of gaseous products, such as H<sub>2</sub>.
- Volumetric expansion is associated with the production of gases, such as H<sub>2</sub>, which occupy a larger volume than liquids.

### Enthalpy variation

- A negative value indicates an exothermic system. This is in line with the energy released in secondary reactions, such as the gas-water displacement reaction.

The results are in line with advanced studies on methane reforming and CO<sub>2</sub> capture. Aasberg-Petersen et al. (2003) highlighted that autothermal reforming improves energy efficiency. Adhikari et al. (2007) demonstrated that the combination of reformers and displacement reactions improves the conversion of CO to H<sub>2</sub>.

## 6. Conclusions

This study contributes with optimized strategies for urea and H<sub>2</sub> production from methane, as a case study, while avoiding CO<sub>2</sub> release. Based on a list of possible products and raw materials, with the goal of a global process that is exothermic and produces a valuable product and hydrogen, without releasing carbon dioxide, the product chosen was urea and hydrogen, using methane, water and air (N<sub>2</sub> and O<sub>2</sub>) as reactants. The preliminary results indicated the viability of the proposal. However, this global route requires some reactions to achieve the main goal, so some of these individual reactions of the global route were studied in this work.

Analysis of the CH<sub>4</sub> + O<sub>2</sub> route indicated that it is exothermic and produces carbon dioxide, which can be used later in the production of urea. Analysis of the CH<sub>4</sub> + H<sub>2</sub>O route highlights a thermodynamically promising process for generating useful gases such as H<sub>2</sub> and CO, with strategic potential for meeting the demand for chemical and energy inputs in the transition to more sustainable technologies. The coexistence of liquid and steam phases at the end of the process reflects the presence of unconverted residual water, opening up the opportunity to optimize the process through precise control of operating variables such as temperature and pressure, as well as the introduction of more selective catalysts. In addition, partial conversion observed suggest that fine adjustments to the reaction design can significantly increase the efficiency of the process. The integration of optimized reforming and water-gas shift steps can increase H<sub>2</sub> production, consolidating the system as an attractive solution for generating clean energy and high value-added chemical inputs. In this way, this study provides a solid basis for the development of promising technologies in the use of CH<sub>4</sub>, with direct implications for environmental sustainability and the advancement of a low-carbon economy.

Other steps of reactions to produce urea have to be evaluated, such as the production of NH<sub>3</sub> and the reaction of CO<sub>2</sub> and NH<sub>3</sub>, using real process conditions (temperature and pressure at operating conditions), simulated with a software such as Aspen. It will be a part of this work as future research, as well as the scale-up and technical economic analysis of the process.

### References

- Aasberg-Petersen K., Christensen T.S., Nielsen C.S., Dybkjaer I., 2003, Recent developments in autothermal reforming and pre-reforming for synthesis gas production in GTL applications. *Fuel Processing Technology*, Amsterdam, v. 83, n. 1-3, p. 253-261.
- Adhikari S., Fernando S., Gwaltney S., 2007, A thermodynamic analysis of hydrogen production by steam reforming of glycerol. *International Journal of Hydrogen Energy*, p. 2875 – 2880.
- BOROS L.A.D., Mathematical and Thermodynamic Modeling of Solid-Liquid Equilibrium of Fatty Systems, 2005, Master's Thesis in Chemical Engineering – Unicamp – Brazil.
- Chaubey R., Sahu S., James O.O., Maity S., 2013, A review on development of industrial processes and emerging techniques for production of hydrogen from renewable and sustainable sources. *Renewable and Sustainable Energy Reviews*, Oxford, v. 23, p. 443-462.
- Edgar T.F., Himmelblau D.M., Lasdon L.S., 2001, *Optimization of Chemical Processes*, McGraw-Hill, 2<sup>nd</sup> ed., New York.
- Freitas A.C.D., Guirardello R., 2014, Thermodynamic analysis of methane reforming with CO<sub>2</sub>, CO<sub>2</sub> + H<sub>2</sub>O, CO<sub>2</sub> + O<sub>2</sub> and CO<sub>2</sub> + air for hydrogen and synthesis gas production. *Journal of CO<sub>2</sub> utilization*, p 30-38.
- Reid R.C., Prausnitz J.M., Poling B.E., 1987, *The Properties of Gases & Liquids*, 4th Edition, McGraw-Hill, New York.