AVALIAÇÃO TERMODINÂMICA DA SÍNTESE DO METANOL VIA HIDROGENAÇÃO DO DIÓXIDO DE CARBONO E DA SEPARAÇÃO LÍQUIDO-VAPOR

THERMODYNAMIC EVALUATION OF METHANOL SYNTHESIS VIA CARBON DIOXIDE HYDROGENATION AND LIQUID-VAPOR SEPARATION

EVALUACIÓN TERMODINÁMICA DE LA SÍNTESIS DE METANOL MEDIANTE HIDROGENACIÓN DE DIÓXIDO DE CARBONO Y SEPARACIÓN LÍQUIDO-VAPOR LÍQUIDO-VAPOR

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RESUMO

O metanol é um insumo amplamente utilizado na indústria química como solvente e componente para diversos produtos, enfrenta desafios em sua produção convencional, incluindo a hidrogenação de CO_2, oxidação de metano, ou gaseificação térmica de biomassa agrícola, devido à necessidade de catalisadores caros. Esse trabalho visa avaliar os parâmetros termodinâmicos da síntese de metanol a partir da hidrogenação de CO_2, através de simulação computacional. No simulador DWSIM foram avaliados os parâmetros, ou variáveis, temperatura, pressão, conversão e vazão de produto, para as condições de equilíbrio. Os resultados expressaram a dualidade do sistema reacional: (1) a reação de síntese do metanol é exotérmica e domina a conversão do CO_2 em temperaturas mais baixas; (2) reação de deslocamento gás-água, ou no inglês *Reverse Water-Gas Shift* (RWGS), é endotérmica prevalecendo em temperaturas mais elevadas e o aumento da pressão favorece a conversão do CO_2 de maneira aproximadamente linear. A síntese de metanol que visa otimizar o uso do dióxido de carbono tem despertado interesse por muitas indústrias, inclusive com a disponibilidade de hidrogênio renovável. Logo, a avaliação termodinâmica é essencial para entender o comportamento do sistema reacional de interesse. Na parte subsequente de separação líquido-vapor do sistema aquoso, a abordagem com o modelo UNIQUAC foi aplicada de forma precisa com apenas dois parâmetros de interação binária. O comportamento líquido-vapor predito nas condições de interesse, aproximadamente 230 ºC e 50 bar, demonstrou ser inadequado para a purificação do metanol apesar de não apresentar azeotropia. Por fim, a análise termodinâmica do processo permitiu descrever a dependência das condições operacionais na síntese do metanol.

Palavras-chave: Reator de Gibbs. DWSIM. Equilíbrio líquido-vapor. Simulação computacional.

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ABSTRACT

Methanol is an input widely used in the chemical industry as a solvent and component for various products, but it faces challenges in its conventional production, including CO2 hydrogenation, methane oxidation, or thermal gasification of agricultural biomass, due to the need for expensive catalysts. This work aims to evaluate the thermodynamic parameters of methanol synthesis from CO2 hydrogenation through computer simulation. In the DWSIM simulator, the parameters or variables temperature, pressure, conversion and product flow were evaluated for equilibrium conditions. The results expressed the duality of the reaction system: (1) the methanol synthesis reaction is exothermic and dominates the conversion of CO_2 at lower temperatures; (2) the Reverse Water-Gas Shift (RWGS) reaction is endothermic and prevails at higher temperatures and the increase in pressure favors the conversion of CO_2 in an approximately linear manner. The synthesis of methanol to optimize the use of carbon dioxide has aroused interest in many industries, including the availability of renewable hydrogen. Thermodynamic evaluation is therefore essential to understand the behavior of the reaction system of interest. In the subsequent liquid-vapor separation part of the aqueous system, the UNIQUAC model approach was applied accurately with only two binary interaction parameters. The liquid-vapor behavior predicted under the conditions of interest, approximately 230 ºC and 50 bar, proved to be unsuitable for methanol purification despite not showing azeotropy. Finally, the thermodynamic analysis of the process made it possible to describe the dependence of the operating conditions on methanol synthesis.

Keywords: Gibbs reactor. DWSIM. Liquid-vapor equilibrium. Computer simulation.

RESUMEN

El metanol es un insumo ampliamente utilizado en la industria química como disolvente y componente de diversos productos, pero se enfrenta a retos en su producción convencional, incluyendo la hidrogenación de CO2, la oxidación de metano o la gasificación térmica de biomasa agrícola, debido a la necesidad de costosos catalizadores. Este trabajo pretende evaluar los parámetros termodinámicos de la síntesis de metanol a partir de la hidrogenación de CO2 mediante simulación por ordenador. En el simulador DWSIM se evaluaron los parámetros o variables temperatura, presión, conversión y flujo de producto para condiciones de equilibrio. Los resultados expresaron la dualidad del sistema de reacción: (1) la reacción de síntesis de metanol es exotérmica y domina la conversión de CO_2 a temperaturas más bajas; (2) la reacción de Reverse Water-Gas Shift (RWGS) es endotérmica y prevalece a temperaturas más altas y el aumento de presión favorece la conversión de CO_2 de forma aproximadamente lineal. La síntesis de metanol para optimizar el uso del dióxido de carbono ha despertado interés en muchas industrias, incluida la disponibilidad de hidrógeno renovable. Por lo tanto, la evaluación termodinámica es esencial para comprender el comportamiento del sistema de reacción de interés. En la posterior separación líquido-vapor del sistema acuoso, se aplicó con precisión el enfoque del modelo UNIQUAC con sólo dos parámetros de interacción binaria. El comportamiento líquido-vapor previsto en las condiciones de interés, aproximadamente 230 ºC y 50 bar, resultó ser inadecuado para la purificación de metanol a pesar de no mostrar azeotropía. Finalmente, el análisis termodinámico del proceso permitió describir la dependencia de las condiciones de operación en la síntesis de metanol.

Palabras clave: Reactor Gibbs. DWSIM. Equilibrio líquido-vapor. Simulación por ordenador.

INTRODUCTION

Methanol is one of the most relevant raw materials for the chemical industry, being widely used in the synthesis of a variety of industrial and consumer products. Traditionally, its application is associated with the production of formaldehyde, acetic acid, solvents and chemical intermediates. However, in recent years, an expansion of its scope of use has been observed, particularly in the energy sector, in which methanol has become an energy vector as a primary fuel or additive in fuel mixtures, especially in contexts that require low-carbon solutions. (Schrader et al., 2009; W. Zhang et al., 2017) (Jiang et al., 2025)

Despite their versatility, conventional routes for the production and use of methanol remain highly dependent on fossil sources, demanding high energy consumption and generating potentially toxic waste, which contributes to adverse environmental impacts. In this scenario, methanol from renewable sources emerges as a technologically viable and environmentally more sustainable alternative. Among its main advantages, the clean combustion properties stand out, the feasibility of production from non-fossil sources with low climate impact with potential scalability and the ease of storage in a liquid state under ambient conditions, which makes it particularly favorable for long-distance logistics applications. Due to these characteristics, renewable methanol has been progressively recognized as an alternative energy vector with high potential for integration into low-carbon energy matrices, reconciling economic and environmental viability. (Dalena et al., 2018; Deka et al., 2022) (Verhelst et al., 2019) (Svanberg et al., 2018) (Bilgili, 2023; Korberg et al., 2021)

Methanol, as a *commodity*, has its price determined by the interaction between supply and demand in the global market, standing out as a crucial aspect to consider for the development of future national production. However, conventional methods of producing methanol, including CO2 hydrogenation (EPE, 2019) (Behr, 2014; X. Du et al., 2016) , methane oxidation, or thermal gasification of agricultural biomass, are limited by the requirement for expensive catalysts. Thus, since the 90s, there has been a significant focus on research on the production of methanol from the hydrogenation of CO2, directed to the development of new catalysts and efficiency improvements in this process. (Ott et al., 2012)

In the study, the development of a new process for the production of CO from CO_2 and CH_4 was reported. This process results in suitably pure CO, which makes it suitable for use in conventional low-pressure methanol synthesis processes using ZnO-Al_2O_3 catalysts. The experimental yield obtained was 3.07 mol of CO per mole of CH_4, substantially higher than the yield of 2 mol of CO mol per mole of CH_4 produced by the dry reforming process.

In addition, for the first time, the production of CO with 84% molar purity, with the remaining CO_2, without the need for additional dilution or separation gas, was demonstrated. Keller & Sharma (2022)

According to , the storage of chemical energy in the form of hydrogen plays a crucial role in the synthesis of alternative energy carriers such as synthetic natural gas (SNG), methanol, and dimethyl ether (DME), supplemented by a carbon source. The modeling of a new combined solid oxide electrolysis cell (SOEC) and a biomass gasification system blown with oxygen, using the Aspen Plus simulator, is described. The comparison between the reforming technologies revealed that an autothermal reformer (ATR) can be advantageous, since oxygen is already available in the electrolysis pile and the syngas produced by the ATR has a CO/CO_2 ratio, increasing the reaction rate of methanol synthesis. ATR requires significantly less energy for almost complete methane conversion, compared to Steam Reforming (SR), which requires about 35 MW. Ali et al. (2020)

The need to mitigate carbon dioxide emissions has increased interest in methanol production via CO2 hydrogenation in recent years. Although the catalysts used are still being improved, the real challenge of this technology is the production of renewable hydrogen from various energy sources, as well as the economically viable production of clean CO2 from waste gas streams. (Ott et al., 2012)

Thus, the present work aims to evaluate the thermodynamic parameters of methanol production from CO2 hydrogenation, using computational tools such as the DWSIM software to simulate methanol production. Additionally, the study of the liquid-vapor equilibrium of the methanol/water system, current derived from the synthesis reactor, was carried out using the UNIQUAC (*Universal Quasichemical Activity Coefficient*) model in the SPECS v5.63 (*Separation and Phase Equilibrium Calculations*) program, developed by the Technical University of Denmark (DTU).

METHODOLOGY

In the DWSIM simulator, a sensitivity analysis was performed to investigate the impact of the variables on carbon dioxide conversion and methanol production in equilibrium. For this, a Gibbs reactor was used, a tool available in the simulator that estimates the equilibrium conditions. The Gibbs reactor estimates equilibrium conditions based on the minimization of Gibbs' free energy among compounds from a predetermined list. The interesting thing is that it does not require the specification of any chemical reaction. In the analysis, the thermodynamic reactor was considered isothermal and isobaric, simplifying the visualization of the effect of temperature and pressure on the system in equilibrium. Figure 1 illustrates the flowchart of the methanol formation reaction process used in the DWSIM simulator. For the thermodynamic models, the Peng-Robinson equation of state was used throughout the flowchart. Figure 1 illustrates the flowchart of the reaction process of methanol formation used in the simulator.

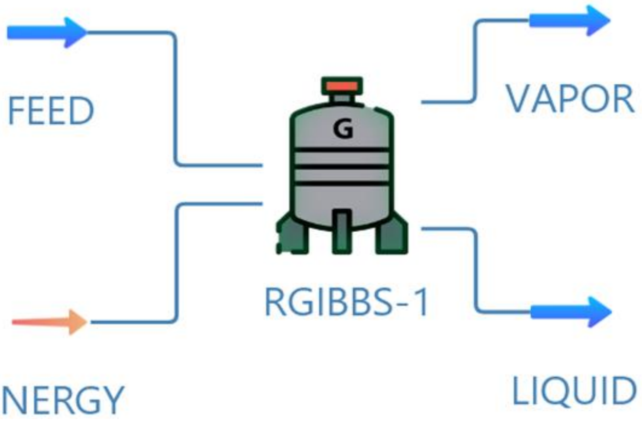


Figure 1. Gibbs reactor for evaluation of the thermodynamic parameters of methanol synthesis in the DWSIM simulator.

To describe the process mathematically, the reactions of the literature model involving carbon dioxide, methanol synthesis and the gas-water displacement reaction (RWGS) were used, Equations 1 and 2, respectively: (Froment et al., 2011)

CO2 + 3H2 CH⇌3OH + H2O ΔH_{300K} = -49.16 kJ/mol *Equation 1*

CO2 + H2CO + H ⇌ 2O ΔH_{300K} = 41.21 kJ/mol *Equation 2*

The reaction system composed of carbon dioxide (CO_2), carbon monoxide (CO), water (H2O), hydrogen (H2) and methanol (CH3OH) involves reversible reactions. These reactions reach a maximum equilibrium conversion for each combination of pressure and temperature. In this study, the operating conditions of temperature of 200 and 300 °C and pressure ranging from 50 to 100 bar, proposed by . Nieminen et al. (2019)

From the literature review, data were collected from the mixture of the methanol (1) and water (2) system at 35, 45, 50 and 65°C. Using the (McGlashan & Williamson, 1976; Yao et al., 1999) SPECS program, the ELV experimental database was used in the reparameterization of the binary interaction parameters "*aij*" of the UNIQUAC (Universal QuasiChemical) model in which it is applicable to a wide variety of liquid mixtures and uses only two adjustable parameters per binary, in addition to area and volume parameters of the pure species. Antoine's constants applied to water and methanol meet the required application temperature range in the process. For methanol, Antoine's constants reported in NIST from the data of . For the water, Antoine's constants reported by (Anderson &

Prausnitz, 1978) (Linstrom & Mallard, 2001) Ambrose et al. (1975) Moura-Neto et al. (2020).

With the thermodynamic parameters obtained, it was possible to simulate the equilibrium behavior of the methanol-water system over different temperatures. The predictive capacity of the model was validated by means of a test with experimental data from the literature at 100 °C. SPECS also made it possible to determine the thermodynamic consistency of the liquid-vapor equilibrium (ELV) data based on the deviation test. The correlation of the experimental data was performed by minimizing the objective function (F.O.), i.e., the sum of the squares of the differences between the values of total bubble pressure determined by the model and those obtained experimentally (Equation 3). (Raj Nayak & Prakash Akhouri, 2022)

$$F.O. = min. = \sum_{i=1}^{N}\left(\frac{P_i^{exp} - P_i^{calc}}{P_i^{exp}}\right)^2$$

Equation 3

The deviation test was evaluated as a function of the quality of the correlation (see Table 1), due to the fact that the UNIQUAC model satisfies the Gibbs–Duhem equation.

Table 1. ELV data quality criterion based on the deviation* and area consistency test (Smith et al., 1983) .

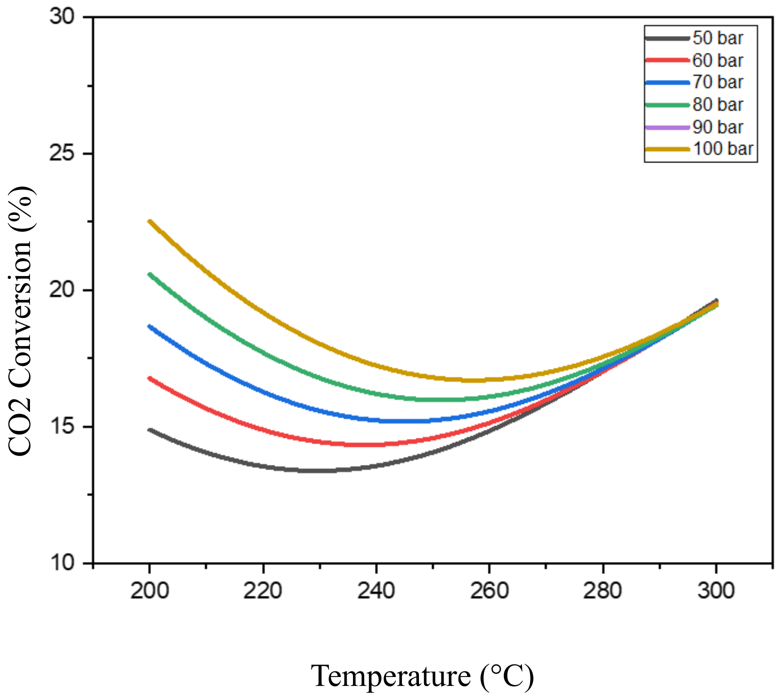
Class	**Δ *T* or Δ *P* **(%)**	**A/B**	**Definition**
One	< 0.25	0,95 – 1,00	Accurate data, suitable for any use
B	0,25 – 0,50	0,90 – 0,95	Good data, applicable for design and correlation
C	0,50 – 1,00	0,80 – 0,90	Applicable for jobs where high precision is not required
D	1,00 – 2,00	0,70 – 0,80	They can be applied, but with great caution
And	> 2.00	< 0.70	Unacceptable, it is suggested to estimate the ELV by another way

* The mean absolute deviation in y must be less than 0.01 for consistent data (Δ *y1<0.01).*
** Relative deviation.

RESULTS AND DISCUSSION

To investigate the effect of temperature, constant pressure was maintained covering the established range. Figure 2 shows how temperature variation affects the equilibrium conversion of CO_2.

Figure 2. Temperature dependence on the conversion of CO_2 at equilibrium between 50 and 100 bar.

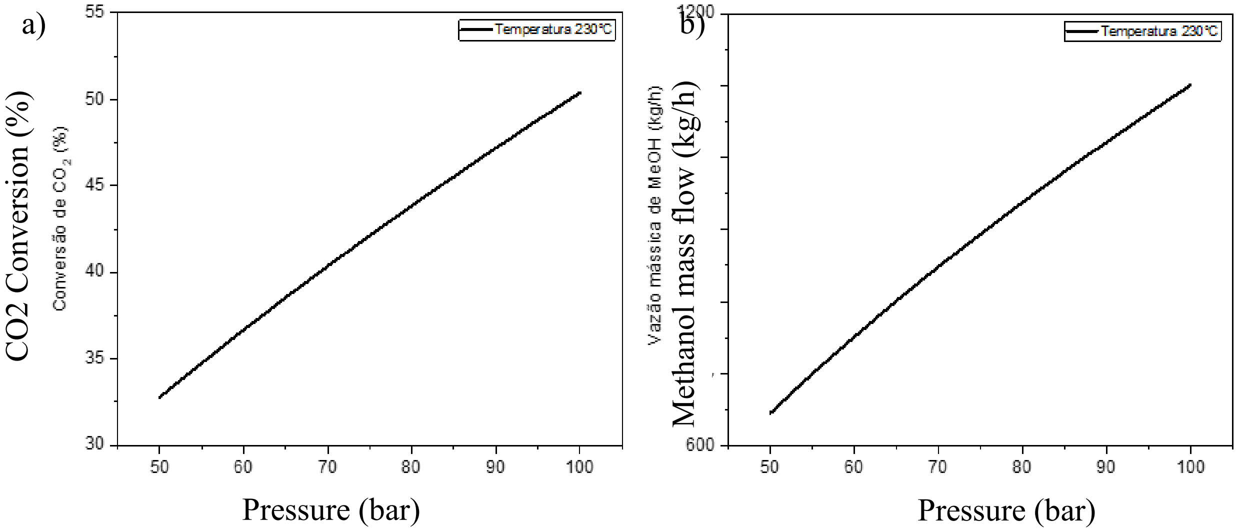


The conversion of CO_2 to methanol at equilibrium under the operating conditions of interest presents a twofold behavior as a function of temperature, as can be seen in Figure 2. Initially, with the increase in temperature, there is a reduction in CO_2 conversion, reaching a minimum value of around 230 °C.   From that point on, the conversion grows again with the increase in temperature. Such behavior is directly related to the superimposition of two competing reaction routes: the synthesis of methanol (Equation 1), of an exothermic nature, and the reverse reaction of displacement of water gas – RWGS (Equation 2), which is endothermic. While the former is thermodynamically favored at low temperatures and high pressures, the latter has a higher yield under more intense thermal conditions. This behavior was detailed because they highlight the importance of optimizing reaction conditions to maximize methanol production and minimize CO formation.   (Ren et al., 2022),

Recent studies corroborate this behavior. showed that by feeding a reactor with a mixture of CO_2/H_2 at 210 °C and 75 bar, a CO_2 conversion of 99% and a methanol yield of 98% was achieved. However, as the temperature increases beyond this point, the RWGS reaction becomes more pronounced, reducing selectivity for methanol. highlighted that, at temperatures above 260 °C, the formation of methanol occurs predominantly by hydrogenation of the CO generated by RWGS, rather than direct hydrogenation of CO_2. It is worth noting that in the simulations carried out in this work, the Gibbs equilibrium reactor does not consider the catalytic and mass transfer effects, but described the dependence on temperature in a coherent way. Yusuf & Almomani (2023) Roy et al. (2025)

The influence of pressure on the equilibrium conversion of carbon dioxide (CO_2) and methanol production was evaluated by keeping the temperature constant at 230 °C, a condition under which a significant change in the performance of the reaction system is evidenced. As illustrated in Figure 3a, an almost linear upward trend in CO_2 conversion is observed with increasing pressure in the range of 50 to 100 bar. This behavior can be rationalized based on the thermodynamics of the hydrogenation reaction of CO_2 to methanol (Equation 1), which is characterized by a decrease in the total number of gaseous moles, and is therefore favored by high pressures according to Le Chatelier's principle. This trend was confirmed by , who experimentally demonstrated that increasing pressure intensifies CO_2 conversion, especially in reoperating actors with copper-based catalysts, whose active sites have high sensitivity to system pressure conditions. (Ren et al., 2022)

Figure 3. CO2 conversion and methanol selectivity at 230 ºC: a) influence of pressure on CO_2 conversion at equilibrium; b) mass flow of methanol at the outlet as a function of pressure.

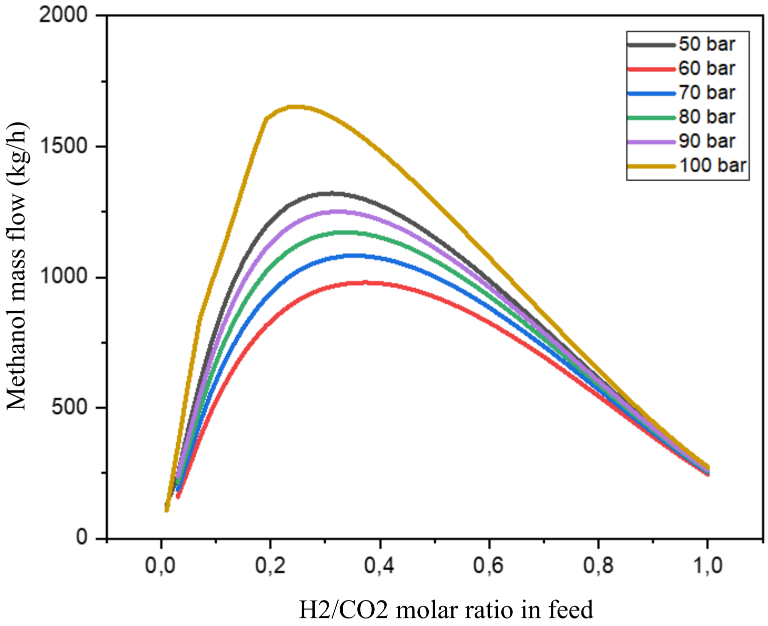


Similarly, the data represented in Figure 3b show that the increase in pressure also promotes a significant increase in the mass flow of methanol at the exit of the system, reflecting not only the increase in conversion, but also the greater selectivity of the process for methanol. The density of the reaction mixture is a relevant parameter in the optimization of carbon dioxide (CO_2) hydrogenation for methanol production, especially because it directly influences the initial steps of adsorption and activation of CO_2 in the catalytic sites.

Several advances have been reported regarding the synthesis of methanol under mild conditions, especially at temperatures below 100 °C, using homogeneous catalysts. However, for industrial-scale applications, heterogeneous catalysts prove to be more advantageous due to their higher thermal and structural stability, ease of product separation, and lower preparation complexity. In this context, the study of the density of the gaseous mixture emerges as a strategy to intensify the collisions between the CO_2 and H_2 molecules, promoting a more efficient adsorption of CO_2 on the active surface of the catalyst. This increase in the frequency of collisions contributes to greater surface cover and facilitates the subsequent activation of CO_2. (W. Du et al., 2025; Elaouzy & Zaabout, 2025; L. Zhang et al., 2023) (Xiao et al., 2025; Zhong et al., 2020)

Figure 4 shows the results of the sensitivity analysis applied to the variation of the reactor inlet composition, with emphasis on the hydrogen concentration, under operating conditions of 230 °C and pressure range between 50 and 100 bar. This approach allows to evaluate the impact of the modification of the molar ratio of the reactants on the performance of the system in the synthesis of methanol, providing subsidies for the optimization of the reaction conditions.

Figure 4. Variation of reactor input composition (H2/CO2) for the production of methanol at 230°C.



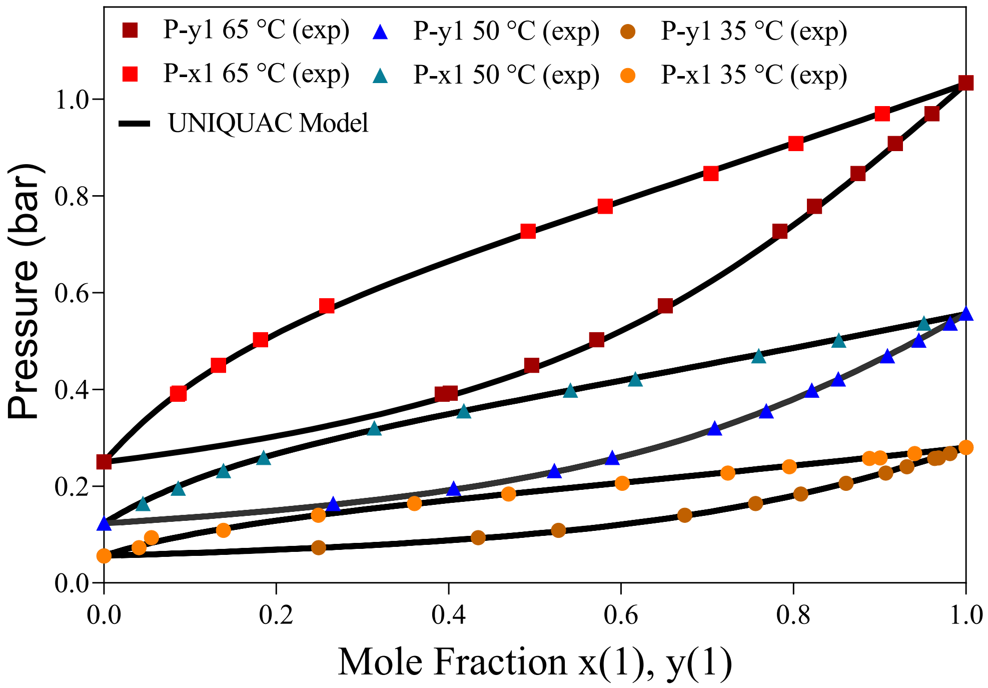
It is observed that, for the pressure ranges analyzed (50 to 100 bar), there is a parabolic behavior with a maximum point of methanol production in an intermediate region of H_2/CO_2 ratio, followed by a sharp drop with the continuous increase of the hydrogen fraction. , evidenced the sensitivity of the H_2/CO_2 ratio to operational conditions, such as temperature and pressure, from the analysis of band areas associated with electronic void positions. From a thermodynamic point of view, Le Chatelier's principle predicts that an excess of hydrogen shifts the equilibrium of the main reaction (Equation 2) towards the formation of methanol. However, when the availability of hydrogen becomes excessive, the reverse displacement reaction of the water gas (Equation 3) is also favored, competing with the formation of methanol. (Gaikwad et al., 2020)

This competition leads to the existence of an optimal feeding point, at which the conversion of CO_2 to methanol is maximized, while the formation of unwanted by-products, such as CO, is minimized. The increase in pressure, in turn, contributes to a general increase in the mass flow of methanol, which is in accordance with the nature of reactions that involve a reduction in the number of gaseous moles in the product, favored by higher pressures (Yusuf & Almomani, 2023) , i.e., Le Chatelier's principle.

Sequentially to the analysis of the effects of the H_2/CO_2 molar ratio on the efficiency of CO_2 hydrogenation, whose results indicated the existence of an optimal conversion point associated with the equilibrium between the competitive routes of methanol and RWGS formation, the thermodynamic modeling of the reaction system was carried out in order to elucidate the molecular aspects underlying the observed behavior. For this purpose, the SPECS program was used, adopting the UNIQUAC model, a model widely used in the thermodynamics of solutions to predict the behavior of non-ideal liquid mixtures. The UNIQUAC model improves the prediction of the thermodynamic behavior of non-ideal liquid mixtures by incorporating a formulation that accounts for the residual effects of molecular and combinatorial, or entropic, interactions in a flexible manner for a wide range of mixtures, containing species diverse in terms of polarity. As a result, the model enables the simultaneous description of fundamental thermodynamic properties, such as liquid-vapor equilibrium (ELV), liquid-liquid equilibrium (LLE), excess enthalpy (hE) and infinite dilution activity coefficients (γ^∞). (Weidlich & Gmehling, 1987) In this work, with the help of accurate data from mixtures of the methanol (1) + water (2) system under milder operating conditions, it was possible to predict the behavior at high pressures with Antoine's constants for wide pressure ranges.

Figure 5 presents the liquid-vapor equilibrium (ELV) diagram for the binary methanol–water system, in which the bubble pressure and dew pressure curves are represented as a function of the molar fractions of the components in the liquid (x) and vapor (y) phases, respectively. For the purpose of calibrating the thermodynamic model, isotherms extracted from the literature at temperatures of 35, 50 and 65 °C were used, which served as a basis for the construction of the database applied to the parameterization in the SPECS software. From the application of the model, calculated values of pressure and molar fractions were obtained in the two phases, with the help of the corresponding activity coefficients. These results were then compared with the available experimental data, in order to evaluate the fidelity of the fit and the ability of the model to accurately describe the equilibrium behavior of the system in the range of thermodynamic conditions analyzed.

Figure 5. P-xy diagram of the binary system methanol (1) + water (2) obtained at temperatures of 35 (McGlashan & Williamson (1976) ●), 50 (▲) and 65 (■) °C used for the parameterization of the UNIQUAC model (–).

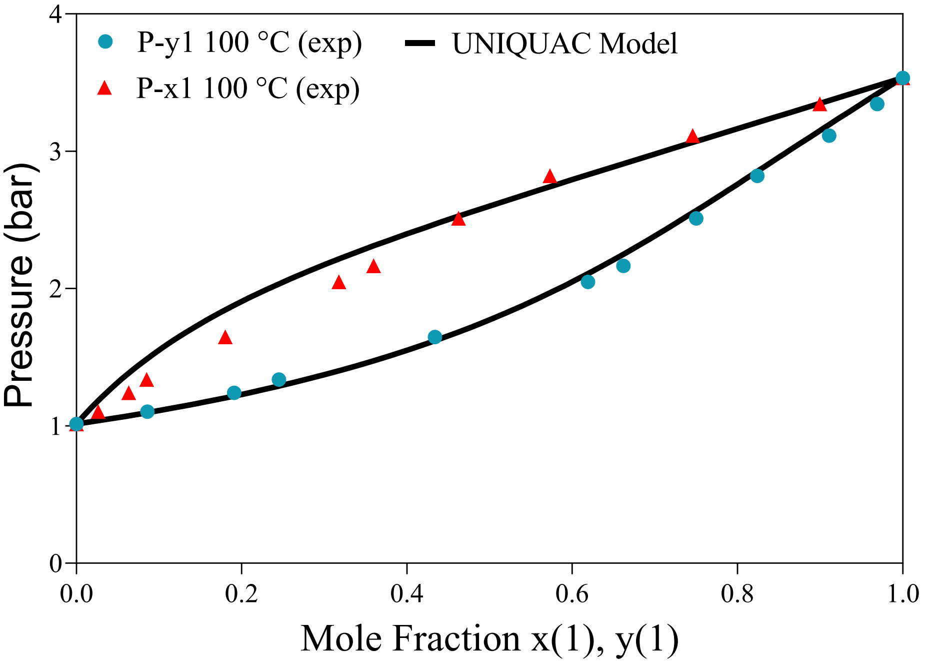


*x1-E and y1-E refer to the experimental data.

The UNIQUAC thermodynamic model in the computational environment of the SPECS software was applied to estimate the binary interaction parameters based on the minimization of the total pressure of the system, see Equation 3. The estimated aij interaction coefficients were -188.692 K for the pair water (1) – methanol (2) and 301.444 K for methanol (1) – water (2). As discussed by , these parameters represent the asymmetry in the molecular interactions between the components and can be applied in predicting liquid-vapor equilibrium under more severe operating conditions. Abrams & Prausnitz (1975)

Based on the parameters adjusted in the SPECS software environment, simulations of the liquid-vapor equilibrium were conducted for the binary methanol-water system, in order to evaluate the accuracy of the parameterized model. Initially, the isotherm at 100 °C was selected as a reference for validation, since there are experimental data available in the literature for this condition. From this, the molar fractions of methanol in the liquid and vapor phases were determined, as well as the respective equilibrium pressures, allowing the construction of the corresponding P–xy diagram, illustrated in Figure 6. The typical behavior of a system with moderate non-ideality is observed, evidenced by the deviation between the equilibrium curves. Such distancing reflects the presence of differential interactions between the components in the mixture, which are adequately captured by the UNIQUAC model, as discussed earlier. The upper curve () represents the bubble pressure, indicating the point at which the liquid phase begins vaporization for a given composition, while the lower curve () represents the dew pressure, corresponding to the condition at which the vapor phase condensation begins. The good agreement between the experimental and calculated data reinforces the robustness of the applied model and its ability to describe, with a high degree of accuracy, the phase equilibrium of the system studied, even under high pressures. The results obtained corroborate previous studies that used thermodynamic models in process engineering contexts aimed at the production of alternative fuels. The literature demonstrates that this approach provides consistent results in the prediction of phase equilibria in multicomponent systems with non-ideal behavior – – (Ye et al., 2011).

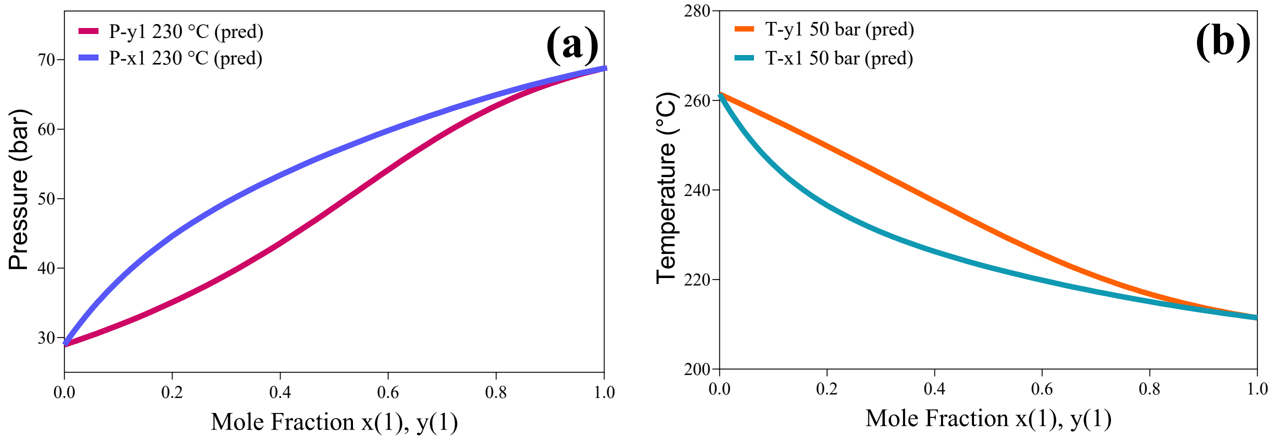
Figure 6. P-xy isothermal diagram of the binary system methanol (1) + water (2) obtained at 100 °C, where y1 (Raj Nayak & Prakash Akhouri (2022) ▲) and x1 (●) are used for the validation of the UNIQUAC model (–).



*x1-E and y1-E refer to the experimental data. x1-C and y1-C, in turn, those calculated by UNIQUAC.

After the parameterization stage, the thermodynamic behavior of the system was predicted under the operating conditions previously identified as critical. The temperature of 230 °C was selected based on a sensitivity analysis performed in the DWSIM simulator, which indicated this point as the condition of minimum conversion into methanol obtained, established to enable the separation of the product. The simulation at this temperature allowed the generation of the P–x–y isothermal diagram, shown in Figure 7a, showing a liquid-vapor equilibrium range between 30 and 70 bar, without the presence of an azeotropic point. Simultaneously, the simulation of the isobaric behavior at 50 bar (Figure 7b) was performed, a value also identified by the sensitivity analysis as the lowest outlet pressure of the Gibbs reactor. The results reinforce the relevance of studying intensified process scenarios, since high temperature and pressure conditions directly impact the thermodynamics of equilibrium and subsequent purification strategies and process and product costs.

Figure 7. Liquid-vapor equilibrium diagrams of the binary system calculated by the UNIQUAC model (**–**): (a) P-xy isothermal diagram obtained at 230 °C, representing the pressure variation as a function of the molar composition in the liquid and vapor phases; b) T-xy isobaric diagram at 50 bar.



* x1-C and y1-C calculated through the prediction of the data parameterized by UNIQUAC.

From the simulations under the conditions of 230 °C and 50 bar, a molar fraction of methanol close to 0.7 in the reactor output current was observed. This high concentration, combined with high pressure, opens up opportunities for energy integration into the system. Considering the possibility of taking advantage of the pressure gradient, a controlled depressurization stage would be possible, capable of recovering energy in the form of mechanical work, such as for turbine drives. Another strategic possibility is the integration of a subsequent separation step, such as a distillation column operating at reduced pressures, by increasing the relative volatility difference between the components under such conditions. As presented by , the reduction of the operating pressure in systems with a high degree of molecular association, such as the methanol-water mixture, can lead to greater efficiency in separation and purification, especially when preceded by a controlled depressurization that contributes to the partial recovery of the expansion energy of the fluid. Seader et al. (2011)

The evaluation of thermodynamic consistency was conducted based on the analysis of the quality of the correlation between the modeled data and the reference values. In this context, the mean percentage deviation of pressure (∆P) according to each temperature range of 35, 45, 50 and 65 °C presented mean values of 1.79, 0.16, 0.52 and 0.37 %, respectively. This evidences the high accuracy of both the experimental data reported in the literature and the parameterization of the thermodynamic model employed. Additionally, the mean absolute deviation in the mole fraction of the vapor phase (∆y) remained below 0.01, reinforcing the reliability of the fit and the validity of the model to represent the liquid-vapor equilibrium of the system under study. Based on the criteria proposed by for classifying the quality of ELV data, as presented in Table 1, the results obtained fall into the categories between A and D, corresponding to data that can be used with thermodynamic consistency. (Smith et al., 1983)

CONCLUSION

Product synthesis routes that aim to reduce the use of carbon dioxide have aroused the interest of many industries. Thus, evaluating the thermodynamic parameters is essential to understand the behavior of a system of interest, such as the products of CO2 hydrogenation (methanol and water), expressing the great importance for the elaboration of process projects or the implementation of industrial plants.

The advantage of the UNIQUAC model is its extreme simplicity, with only two binary interaction parameters, given the wide range of application in phase equilibrium. The experimental data of ELV evaluated proved to be accurate and consistent, with relative deviations of around 1.79 to 0.16 %, classifying the quality criterion between A and D (see Table 1). Thus, the calculated UNIQUAC "aij" interaction parameters are of great importance for the prediction of thermodynamic and phase equilibrium properties, enabling a process optimization by means of simulations that can be performed for a wide range of temperature and pressure of interest.

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