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Nyári, Judit; Izbassarov, Daulet; Toldy, Árpád I.; Vuorinen, Ville; Santasalo-Aarnio, Annukka

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Choice of the kinetic model significantly affects the outcome of techno-economic assessments of CO₂-based methanol synthesis

Judit Nyári^{*}, Daulet Izbassarov, Árpád I. Toldy, Ville Vuorinen, Annukka Santasalo-Aarnio

Research Group of Energy Conversion, Department of Mechanical Engineering, Aalto University, FI-00076 Espoo, Finland

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ABSTRACT

Keywords: Methanol synthesis Hydrogenation Aspen Plus Process modeling Kinetic modeling Techno-economic assessment Carbon dioxide hydrogenation to methanol is a cornerstone of the CO2 utilization toolkit, and its comparison to fossil-based methanol through techno-economic assessments (TEAs) has helped establish barriers to its commercial feasibility. TEAs are often performed in process simulation software that relies on kinetic models (KMs). The choice of KM could influence the outcome of the TEA, however, their effect has not been quantified earlier. This study quantifies this effect through TEAs performed using three different KMs in Aspen PlusTM. Three KMs are selected for comparison: two of them are commonly used in TEAs while also a third, a recently published model, will be studied herein. The models are first validated in Aspen PlusTM and then compared in a series of sensitivity analyses in a one-pass reactor. Finally, a TEA study is conducted for a large-scale methanol plant to investigate the effects of the KM choice. It was found that the choice of the kinetic model significantly influences the results of TEAs as it can result in a 10% difference in the levelized cost of methanol. This can be mainly attributed to differences in one-pass yield. As CO₂ utilization approaches economic viability, understanding such uncertainties will be crucial for successful project planning. Hence, these results suggest that extending a TEA's sensitivity analysis to cover the KM's contribution could increase confidence in the robustness of the TEA.

1. Introduction

According to the most recent report by The Intergovernmental Panel on Climate Change, climate change due to anthropogenic emissions will continue to have a severe negative impact across all sectors and regions unless urgent climate-resilient development is implemented [1]. In 2021, the global CO₂ emissions from energy combustion and industrial processes reached a record high at 36.3 gigatonnes [2]. Shifting from fossil feedstocks to renewable sources in electricity production contributes to reducing these emissions. However, due to the intermittency of these sources, energy storage will become critical for maintaining the stability of energy systems. Long-term storage of renewable electricity is possible through power-to-X (P2X) processes where X stands for a variety of products including hydrogen, ammonia, and hydrocarbons. Carbon dioxide hydrogenation, a branch of P2X where CO2 is also used as a feedstock, is considered one of the key tools proposed to mitigate CO₂ emissions and increase renewable electricity storage [3]. One of the most important products produced this way is methanol which is both a significant raw material for the chemical industry and fuel, especially in the marine industry [4]. Fossil-free production of methanol could electrify many sectors where direct electrification is currently not possible [5].

Methanol is one of the most traded chemicals globally with more than 80 million tonnes in demand [4]. Its use in traditional chemical applications accounts for slightly more than half of its demand, including the production of olefins, while the other half is used in energy-related applications [4]. Its use in fuel applications, especially as a marine fuel is growing due to its clean-burning properties and more stringent emission regulations [6,7]. Currently, more than 65% of the global demand is produced by steam reforming of methane from natural gas feedstock. Other feedstocks for the production of synthesis gas include coal and different biomass sources [8]. Its production without the synthesis gas step directly from captured carbon dioxide and green hydrogen is gaining interest due to its greenhouse gas mitigation and renewable electricity storage potential [9,10]. Moreover, stepping away from fossil fuels that are often based on imports and instead turning to

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Abbreviations: CAPEX, capital expenses; CW, cooling water; GHSV, gas hourly space velocity; HI, heat integration; KM, kinetic model; KPI, key performance indicator; LCoM, levelized cost of methanol; LHHW, Langmuir-Hinshelwood-Hougen-Watson; LHV, lower heating value; OPEX, operational expenses; P2X, power-to-X; RWGS, reverse water–gas shift; TEA, techno-economic assessment; VB, Vanden Bussche and Froment; VD, Van-Dal and Bouallou.

^{*} Corresponding author.

E-mail address: judit.nyari@aalto.fi (J. Nyári).

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feedstocks that can be locally produced can lead to more geopolitical and energy independence for several regions [11].

Kinetic modeling of low-pressure methanol synthesis has been studied since the 1970s according to Bozzano and Manenti [12]. Most early kinetic models (KMs) attributed the formation of methanol solely from carbon monoxide (Eq. (1)). Even then, some researchers considered whether the hydrogenation of carbon dioxide (Eq. (2)) also plays a role during the process. Since the late-80's the idea that methanol is solely synthesized from carbon monoxide has been abandoned and instead either only the hydrogenation of carbon dioxide [13-15] is considered or hydrogenation of both carbon dioxide and monoxide [16–18]. Moreover, in the mid-80's the reverse water–gas shift (RWGS) reaction (Eq. (3)) was included in the reaction mechanism by Villa et al. [19], however, still solely for CO hydrogenation. The first model accounting for both the RWGS and CO₂ hydrogenation reactions was given by Dybkjær [20]. They proposed a Langmuir-Hinshelwood-type model where H₂ and H₂O compete for the same active site, while CO₂ and CO compete for a second active site. The first KM considering all three reactions (Eqs. (1)-(3)) was developed by Graaf et al. [16]. After more than 50 years, questions concerning the origin of the carbon atom in the methanol molecule and the formation pathway in methanol synthesis are still actively studied [12,21,22].

$$CO + 2H_2 \rightleftharpoons CH_3 OH, \ \Delta H_{298 \ K} = -90.2 \ kJ/mol$$
(1)

 $CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O, \ \Delta H_{298 \ K} = -48.8 \ kJ/mol$ (2)

$$CO_2 + H_2 \rightleftharpoons CO + H_2O, \ \Delta H_{298 \ K} = +41.3 \ kJ/mol$$
 (3)

Besides catalyst studies [23,24,25,26,15,14], kinetic modeling is heavily used in techno-economic assessment (TEA) studies [27-32] due to the increased interest in CO2 utilization and P2X processes. TEA can be a useful decision-making tool for investment and development activities for a variety of stakeholders depending on its scope and goal [33]. In TEA of P2X processes process simulation software, such as Aspen Plus, is often applied as this software provides detailed mass and energy balance of the process in question, and have built-in economic and energy analysis tools. However, even though there is a large number of KMs available, in these TEA studies KMs based on either the model by Graaf et al. [16] (Graaf) or the model by Vanden Bussche and Froment [13] (VB) is utilized. Moreover, reasons behind selecting a certain model in TEAs are usually not provided, but rather followed by tradition. A possible reason for the overwhelming use [31,34,35,36,37,38,39] of VB's KM could be attributed to its detailed description of its implementation to Aspen Plus by Van-Dal and Bouallou [30]. Moreover, Van-Dal and Bouallou [30] not only presented a detailed implementation of the model but also readjusted the activation energies based on Mignard and Pritchard [40] to expand the model up to 7.5MPa. The other widely used KM is the one developed by Graaf et al. [16]. This model is either used as the original one developed in 1988, but since 2016, when Kiss et al. [29] published Graaf's model with updated parameters from An et al. [41] and Lim et al. [18], it has been adopted in a large number of studies [42,43,44,27,45]. This is most probably attributable to Kiss et al. [29]'s detailed description of implementing the model in Aspen Plus.

Comparison studies of KMs for process modeling are scarce. Asif et al. [46] compared the most commonly used Graaf and VB KMs for their TEA study, both already adjusted by Kiss and Van-Dal, respectively. They have decided to use the model by Graaf as it had higher methanol yield under the same process conditions compared to the one by VB. However, they did not compare TEA results considering both of the models.

Studies that compare KMs are based on catalyst studies or at least with access to experimental results [14,15,23]. In the case of technoeconomic studies, the scope does not include the investigation of the KMs but instead uses already established ones. Slotboom et al. [14] compared 5 kinetic models (Villa et al. [19], Graaf et al. [16], Vanden Bussche and Froment [13], Seidel et al. [47], Ma et al. [48]) by re-fitting them and developed a 6-parameter kinetic model, which is valid for pressures ranging between 20 and 70 bara, and temperatures between 450 and 530 K. When comparing the KMs of Graaf and VB based on fit and predictive power, both models perform well within their set range of operating conditions, but their predictions become unreliable outside of these. As for being a predictive model Seidel's model [47] proved to be the best, while Villa's [19] and Ma's [48] model were the least accurate. They concluded that models that do not include the RWGS reaction, such as Ma's, or are solely considering CO for hydrogenation, such as Villa's, do not represent methanol synthesis correctly. Based on good fit and predictive properties, low variance and crosscorrelation, and statistically good prediction their own six parameter model was selected as the best model.

What is common in most of the listed catalyst comparison literature is that they develop a new KM [14,15] or a new fit for an existing KM [23] based on experimental data and compare it to the already existing ones to identify which is the best model to describe the phenomena of methanol synthesis. In process modeling and TEA studies oftentimes there is no access to such experimental results. Therefore, the development of a new or the adjustment of an existing KM is out of the scope of these studies. This often results in the direct application of a KM found in the literature. In this paper, three different KMs from the literature are compared to establish their impact on the outcome of TEAs and the process modeling of full-scale CO2-based methanol plants. Here, the main objective is to quantify the sensitivity of the TEA estimate on the chosen KM. In the present study-three different KMs are explored: (1) the Graaf model [16] as presented by Kiss et al. [29], (2) the VB model [13] as presented by Van-Dal and Bouallou [30], and (3) the Slotboom model [14]. This paper also investigates whether a more recent KM, such as the Slotboom model should be used over the traditional, already proven KMs for TEA studies in the future. These questions are especially interesting as Nestler et al. [15] wrote that state-of-the-art catalysts of the same nominal composition have significantly higher activities and it is recommended that KMs developed on these newer catalysts are favored.

2. Methodology

In this paper, three KMs are compared for TEA purposes in Aspen Plus. Two of the KMs are the most commonly used models in process simulation and TEA studies, the Graaf model as presented by Kiss et al. [29] (Kiss model hereafter), and the VB model as presented by Van-Dal and Bouallou [30] (VD model hereafter). These common models are compared with a recently published KM by Slotboom et al. [14]. These three models have been selected due to being either commonly used or recently developed and claimed to be superior. Moreover, all the considered models are developed for commercial Cu-based catalysts and consider either only CO_2 hydrogenation or the hydrogenation of both CO and CO_2 including the RWGS reaction. RWGS is included as it is too important to be neglected in the reaction system for methanol synthesis, while models considering CO as the sole source of carbon cannot be used as universal ones [14]. The selected KMs with their respective literature source and parameter source are shown in Table 1.

The process conditions of temperature and pressure of the selected models are shown in Fig. 1. The range of traditional, syngas-based methanol synthesis is within 473–573 K and 5–10 MPa. The models do not cover the upper-pressure limit of the operating range, especially the Kiss model is rather limited. However, as Kiss et al. [29] studied the sensitivity of their model on a range of 473–573 K and 0.1–10 MPa it is considered a valid model for these ranges in this paper as well.

The VD model has a very wide range where it predicts with high accuracy [12]. It is originally based on the model developed by Vanden Bussche and Froment [13] in 1996 over a commercial $Cu/ZnO/Al_2O_3$ catalyst from ICI. This model considers only the CO_2 hydrogenation and the RWGS reactions during methanol synthesis. The original model is valid between 453 K and 553 K, and from 1.5 to 5.1MPa. The model considers the equilibrium constants given by Graaf et al. [49]. Moreover,

Table 1

Reaction rates of the considered kinetic models.





Fig. 1. Comparison of the pressure and temperature ranges of the selected kinetic models [14,29,30], and the one-pass reactor and full-scale methanol plant designs.

the model was developed in an adiabatic tubular reactor. The model's pressure range was broadened by Mignard and Pritchard [40] to 7.5MPa and then rearranged and implemented in Aspen Plus by Van-Dal and Bouallou [30]. The original experimental model from Vanden Bussche and Froment [13] considered both CO and CO_2 in the feed to emulate traditional synthesis gas-based methanol synthesis.

The model presented by Kiss et al. [29] is based on the model by Graaf et al. [16] developed in 1988 over a commercial catalyst from Haldor Topsoe. This KM considers all three aforementioned reactions for methanol synthesis and uses the same equilibrium constants as Graaf et al. [49]. The original model is valid between 483.5 and 516.7 K, and between 1.5 and 5 MPa. This model was updated by Kiss et al. [29] in 2016 with experimental results based on lab-scale Cu/ZnO/Al₂O₃/ZrO₂ catalyst from Lim et al. [18] for the equilibrium constants, and An et al.

[41] for the activation energies, rate constants and adsorption equilibrium constants developed on lab-scale fibrous Cu/Zn/Al/Zr catalyst. With these newer constants, however, the range of model validity has not increased. The work of Graaf et al. [16] considered a wide range of feed ratios including H₂ : $CO_2 = 0.885 : 0.115$, while the work of Lim et al. [18] and An et al. [41] considered also the stoichiometric feed of H₂ and CO₂ without CO. Kiss et al. [29] published their work with a detailed description of the implementation and sensitivity analyses of the model. Kiss et al. [29] considered the feed in ratio of pure H₂ and CO₂ from the stoichiometric value up to 12 during their simulations.

Slotboom et al. [14]'s model is the most recent KM for commercial $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst. The model is similar to the VD model, as it does not consider CO hydrogenation. The main difference between the two models is the number of active sites considered.

While in the VD model only one active site is considered, this one applies three active sites. The range of the Slotboom model is between 450 K and 530 K, and between 2 and 7 MPa in terms of pressure. They considered a wide range of feed during their experiments including the stoichiometric ratio of H_2 and CO_2 . The equilibrium constants for the model are taken from Graaf and Winkelman [50]. Therefore, this model can be considered to pose a state-of-the-art description of surface chemistry as well as a broad operational range.

Slotboom et al. [14] wrote that "comparing KMs after being re-fitted is fair manner". However, in the case of TEA, the scope of the study does not allow for such considerations, and the authors usually just use a KM that has been proven to be working in the modeling environment. Therefore, in our research, the KMs will not be compared by refitting them, and they will be implemented in Aspen Plus the way they have been published. The only reformulation applied to the KMs is the conversion of units and equations to formats that can be directly implemented in the chosen software, Aspen Plus. Note that the current work does not intend to select a "best" KM or decide on the superiority or inferiority of one KM compared to the others, it merely investigates the difference their selection might have on TEAs and quantifies the sensitivity of KM selection on their predictions.

First, the KMs are converted from their original format to the one compatible with Aspen Plus. Here, the rearranged models and the underlying parameters are presented. Then, the model validations are given against the original results, which are followed by a series of sensitivity analyses. The sensitivity analyses are carried out to investigate how the models work under different reactor conditions, such as pressure, temperature, and reactor type. Finally, the models are implemented to a full-scale CO₂-based methanol plant such as the one published by Nyári et al. [27] to study the possible differences in TEA results.

2.1. Implementation and validation of the selected kinetic models in Aspen Plus

The rearranged KM and parameters published by Kiss et al. [29] are not presented here in detail as the respective Aspen Plus model has been already validated and discussed in our earlier publications [51,52]. Here, only the models of Van-Dal and Bouallou [30] and Slotboom et al. [14] are presented and validated. Each KM is modeled in Aspen Plus v11 with a plug flow reactor as the tubular reactor. The underlying plug flow reactor model assumes one ingoing stream for the reactants, and one out-going stream for the products. The selected equation of state is the Soave modification of the Redlich-Kwong equation [53] (RK-SOAVE in Aspen Plus) due to the high pressure in the reactor and the reactants and products present. Each model is validated against the reference reactor conditions (size, process conditions) of the original article, i.e. adiabatic reactor for the VD model and isothermal reactor for the Slotboom model.

Aspen Plus is quite specific with how Langmuir-Hinshelwood-Hougen-Watson (LHHW) type reactions can be input to its interface, especially with regard to units. The general LHHW expression in Aspen Plus with its units when the rate basis is the weight of the catalyst is given in Eq. (4).

$$r = \frac{(\text{kinetic factor}) \cdot (\text{driving force})}{(\text{adsorption term})} \left[\frac{\text{kmol}}{\text{sec} \cdot \text{kg}_{\text{cat}}} \right]$$
(4)

The formula of the kinetic factor depends on whether a reference temperature has been specified for the KM or not. If such temperature has been defined, the kinetic factor is the following:

kinetic factor (T₀ specified) =
$$k \left(\frac{T}{T_0}\right)^n \exp\left[\left(\frac{-E_a}{RT}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$
 (5)

where k is the pre-exponential factor, T is the absolute temperature, T_0 is the reference temperature, n is the temperature exponent, E_a is the activation energy, and R is the gas law constant.

In the selected KMs no reference temperature was specified, therefore, the simplified kinetic factor can be expressed as in Eq. (6):

kinetic factor (no T₀) = kTⁿexp
$$\left(\frac{-E_a}{RT}\right)$$
 (6)

which is the multiplication of a pre-exponential factor and an Arrhenius term. In some rearranged KMs the kinetic force is not expressed separately, as is the case for the VD and Slotboom models.

The driving force (Eq. (7)) has to be expressed in two terms for the difference in the concentrations of the compounds on the reactant side (Term 1) and the product side (Term 2):

driving force expression =
$$k_1 \left(\prod C_i^{v_i} \right) - k_2 \left(\prod C_j^{v_j} \right)$$
 (7)

where k_1 and k_2 are the driving force constants for Term 1, the reactant side, and Term 2, the product side, respectively, C is the component concentration, and v is the term exponent for each component. The component concentration can be selected from a wide range and its unit is predefined by AP. Here, either fugacity or partial pressure is used, and the predefined SI unit for them is pascal.

The adsorption term (Eq. (8)) is given as:

adsorption term =
$$\left\{\sum K_i \left(\prod C_j^{v_j}\right)\right\}^m$$
 (8)

where K is the adsorption term constant, C is the component concentration, v is the term exponent for each component, and m is the adsorption term exponent. The adsorption expression is dimensionless as the unit of K is the inverse of the corresponding concentration component.

Moreover, Aspen Plus uses the Arrhenius term (Eq. (9)) as the input format of the kinetic rate parts. Therefore, each constant, k_i and K_i , needs to be expressed as an Arrhenius term for Aspen Plus in the correct units.

Arrhenius term :
$$\ln(K) = A + \frac{B}{T}$$
 (9)

where K means each driving force and adsorption term constant. A and B are the Arrhenius-term constants, and T is the absolute temperature.

The results of the KM implementations are compared against the results of the original KM presented in the respective study. As the original results are mostly published only graphically, these figures are digitized using the online tool, WebPlotDigitizer 4.5. Some of the differences between the results of the implemented and the original models might arise from how the data was captured from the original figures, but these differences were found to be minimal during validation.

The KMs of Nestler et al. [15], Kubota et al. [54], Lim et al. [18], Park et al. [17] were also implemented in Aspen Plus. However, validation results obtained based on the given KM parameters and process conditions compared to the published experimental or simulated results were found to be out of the 20% error range. It is suspected that these KMs result in systems of equations that are beyond the capabilities of Aspen Plus' solver. Therefore, considering the requirement that KMs for TEAs must be readily implemented in TEA software, these KMs were not included in this paper.

2.1.1. Validation of the rearranged kinetic model of Vanden Bussche as presented by Van-Dal

Validation of the VD model (Eqs. (10) and (11)) was constructed against the results presented in the Appendix A of Van-Dal and Bouallou [30]. Values for the KM parameters, reproduced here in Table 2, catalyst characteristics, process conditions, adiabatic reactor sizing and reactant flow were taken from the Appendix of their publication.

$$r_{CH_3OH} = \frac{k_1 P_{\rm CO_2} P_{\rm H_2} - k_6 P_{\rm H_2O} P_{\rm CH_3OH} P_{\rm H_2}^{-2}}{\left(1 + K_2 P_{\rm H_2O} P_{\rm H_2}^{-1} + K_3 P_{\rm H_2}^{0.5} + K_4 P_{\rm H_2O}\right)^3} \left[\frac{kmol}{sec \cdot kg_{cat}}\right],\tag{10}$$

Table 2

Parameters of the rearranged Vanden Bussche and Froment [13] kinetic model as presented by Van-Dal and Bouallou [30].

Parameter	A _i	\mathbf{B}_i	Unit
k ₁	-29.87	4811.2	Pa ⁻²
K ₂	8.147	0	_
K ₃	-6.452	2068.4	Pa ^{-0.5}
K ₄	-34.95	14928.9	Pa^{-1}
k ₅	4.804	-11797.5	Pa^{-1}
k ₆	17.55	-2249.8	_
k7	0.131	-7023.5	Pa ⁻¹

$$r_{RWGS} = \frac{k_5 P_{\rm CO_2} - k_7 P_{\rm H_2O} P_{\rm CO} P_{\rm H_2}^{-1}}{1 + K_2 P_{\rm H_2O} P_{\rm H_2}^{-1} + K_3 P_{\rm H_2}^{0.5} + K_4 P_{\rm H_2O}} \left[\frac{kmol}{\sec \cdot kg_{cat}}\right]$$
(11)

where P_i is the partial pressure of the respective species in Pa, and k_i and K_i are constants in units according to Table 2.

In the VD model, there is no separate kinetic factor for the reaction rates, therefore, the pre-exponential factor in Eq. (5), k, is given as 1. The driving force expressions for the reaction rates are given in Table 3. The adsorption term (Eq. (12)) is the same for both reaction rates, except for the adsorption term exponent which is 3 for the CO₂ hydrogenation (Eq. (10)) and 1 for the RWGS reaction (Eq. (11)).

adsorption term (VD model) =
$$\left(1 + K_2 P_{H_2 O} P_{H_2}^{-1} + K_3 P_{H_2}^{0.5} + K_4 P_{H_2 O}\right)^m [-]$$
(12)

The simulation results are compared graphically in Fig. 2 against Van-Dal and Bouallou [30]'s results. As can be seen in Fig. 2, the model implementation to Aspen Plus matches the original results perfectly across the reactor length for all the components. Unfortunately, Van-Dal and Bouallou [30] only published results at one given process temperature and pressure, therefore, any divergence from these conditions is unknown to the model. However, as the model fits exceptionally well, it is applied in the further parts of this article.

2.1.2. Validation of the rearranged kinetic model of Slotboom

The Slotboom model looks similar to the VD model in the sense that it also considers only two reactions, the CO_2 hydrogenation, and the RWGS reactions. Moreover, the rearranged model also lacks a specific kinetic factor, therefore, the pre-exponential factor is also given as 1. The rearranged model is presented in Eqs. (13) and (14) with parameters in Table 4.

$$r_{\rm CO_2} = \frac{k_{\rm CO_2} f_{\rm H_2} - K_{\rm I} f_{\rm H_1 oH} f_{\rm H_2} of_{\rm H_2}^{-1}}{\left(f_{\rm H_2}^{0.5} k_{\rm H_2} + f_{\rm H_2 o} k_{\rm H_2 O/9} + f_{\rm CH_3 OH}\right)^2} \left[\frac{kmol}{sec \cdot kg_{\rm cat}}\right],\tag{13}$$

$$r_{RWGS} = \frac{k_{\rm RWGS} f_{\rm CO_2} f_{\rm H_2}^{0.5} - K_2 f_{\rm CO} f_{\rm H_2} o f_{\rm H_2}^{-0.5}}{f_{\rm H_2}^{0.5} k_{\rm H_2} + f_{\rm H_2} o k_{\rm H_2} o / g + f_{\rm CH_3 OH}} \left[\frac{kmol}{sec \cdot kg_{\rm cat}}\right].$$
 (14)

where f_i is the fugacity of the respective species in Pa, and k_i and K_i are constants in units according to Table 4.

The driving force expressions of Term 1 and Term 2 with their respective units are given in Table 5. The adsorption term (Eq. (15)) is the same for both reaction rates, except for the adsorption term exponent, m, which is 2 for the CO₂ hydrogenation (Eq. (13)) and 1 for the RWGS reaction (Eq. (14)).

Table 3

Driving force expressions of the rearranged Vanden Bussche and Froment [13] kinetic model as presented by Van-Dal and Bouallou [30].

Reaction	Term 1 expression	Unit	Term 2 expression	Unit
r _{CH3OH}	$\mathbf{k_1} \boldsymbol{P_{\mathrm{CO}_2}} \boldsymbol{P_{\mathrm{H}_2}}$	_	$k_6 P_{H_2O} P_{CH_3OH} P_{H_2}^{-2}$	-
r _{RWGS}	$k_5 P_{CO_2}$	-	$k_7 P_{H_2O} P_{CO} P_{H_2}^{-1}$	-

adsorption term (Slotboom model) =
$$\left(f_{\rm H_2}^{0.5}k_{\rm H_2} + f_{\rm H_2O}k_{\rm H_2O/9} + f_{\rm CH_3OH}\right)^m [Pa^m]$$

(15)

The isothermal reactor size was taken from Slotboom et al. [14] Section 3.2, while process conditions were selected according to Section 3.3 in the same publication for fixed pressure at 4MPa. The validation of the rearranged and the original model is based on CO_2 conversion (Eq. (16)) and methanol selectivity (Eq. (17)).

$$Y_{\rm CO_2} = 1 - \frac{y_{\rm CO_2,out}}{y_{\rm CO_2,in}} \times \frac{\dot{V}_{\rm out}}{\dot{V}_{\rm in}}$$
(16)

$$K_{\rm CH_3OH} = 1 - \frac{y_{\rm CO,out} \times \frac{\dot{V}_{\rm out}}{\dot{V}_{\rm in}}}{y_{\rm CO_2,in} - y_{\rm CO_2,out} \times \frac{\dot{V}_{\rm out}}{\dot{V}_{\rm in}}}$$
(17)

where y_{CO_2}, y_{CO} are molar fractions of CO_2 and CO respectively, \dot{V} denotes molar flow rate. Subscripts in and out denote inlet and outlet of the reactor.

As can be seen from Fig. 3 the rearranged model fits well with the original experimental results. The implemented model is within 4% compared to the original experimental results. In general, it seems that the implemented model overestimates the CO_2 conversion, while the methanol selectivity is underestimated, except at higher temperatures. As the CO_2 conversion and the methanol selectivity of the experimental results and the rearranged model only differ slightly, it is suitable for further applications in Aspen Plus.

2.2. Kinetic models in one-pass reactor design

Once the KMs are validated they can be compared in a series of sensitivity analyses. Furthermore, both isothermal and adiabatic reactors are considered as both the original VB model and its updated version by Van-Dal were developed for an adiabatic case, while the other KMs were defined for an isothermal reactor. The considered parameters are pressure and inlet temperature. The ratio of reactants is not considered, as even though a higher ratio of H₂ : CO₂ results in a higher methanol yield [29], the increased consumption of H₂ is not beneficial financially. Therefore, only the stoichiometric ratio of H₂: CO₂ is considered. Moreover, only CO₂ is considered in the feed, no CO is fed to the one-pass reactor to deeper understand the predominant phenomenon in future P2X scenarios of methanol synthesis. The KMs are compared in a plug-flow reactor in Aspen Plus, the sizing of which is based on the experimental setup presented by Park et al. [17]. The base case is defined as T = 523 K, p = 5MPa and GHSV = 8000ml/g_{cat}h. The sensitivity analyses are carried out in the range of 453-573 K for inlet temperature and 1.5–7MPa for pressure as shown in Fig. 1. Note that in order to cover the range of operating parameters studied, all KMs had to be extrapolated outside their original experimental ranges.

The KMs are compared based on CO_2 conversion as given in (Eq. (18)) and CH_3OH yield (Eq. (19)):

$$X_{\rm CO_2} = \frac{n_{\rm CO_2,in} - n_{\rm CO_2,out}}{n_{\rm CO_2,in}}$$
(18)

$$Y_{\rm CH_3OH} = \frac{n_{\rm CH_3OH,out}}{n_{\rm CO_2,in}}$$
(19)

where n_{CO_2} , n_{CH_3OH} are molar flow rates of CO_2 and CH_3OH , respectively. Subscripts in and out denote inlet and outlet of the reactor.

Based on our background numerical sensitivity assessment [51] it is expected that each KM would have increasing methanol yield and CO_2 conversion with increasing pressure. Regarding temperature sensitivity, each KM is expected to have the highest methanol yield around the base temperature. Regarding isothermal versus adiabatic process conditions, higher methanol yield and CO_2 conversion are expected for the isothermal case than for the adiabatic one [29,41,51].



Fig. 2. Comparison of the implemented VD model in Aspen Plus and original data from Van-Dal and Bouallou [30]. Process conditions: p = 5MPa, T = 493.15 K, mass flow $= 2.8 \cdot 10^{-5}$ kg/s, $CO/H_2/CO_2/Ar = 4/82/3/11$ mol%.

Table 4Parameters of the rearranged Slotboom et al. [14] kinetic model.

Parameter	A _i	B _i	Unit
k _{CO2}	22.7266	-19966.3219	Pa^{-1}
k _{RWGS}	38.09791455	-24500.84195	Pa ^{-0.5}
K ₁	70.9140	-27539.2709	Pa ¹
K ₂	34.15974961	-20204.29372	Pa ^{-0.5}
k _{H2O/9}	5.850863408	0	_
k _{H2}	4.839451482	0	Pa ^{0.5}

 Table 5

 Driving force expressions of the rearranged Slotboom et al. [14] kinetic model.

Reaction	Term 1 expression	Unit	Term 2 expression	Unit
r _{CO2} r _{RWGS}	$k_{CO_2} f_{CO_2} f_{H_2}^2 \ k_{RWGS} f_{CO_2} f_{H_2}^{0.5}$	Pa ² Pa ¹	$K_1 f_{CH_3OH} f_{H_2O} f_{H_2}^{-1} \ K_2 f_{CO} f_{H_2O} f_{H_2}^{-0.5}$	Pa² Pa¹

2.3. Kinetic models in full-scale methanol plant design

Finally, the KMs are used in the modeling of a full-scale methanol plant where hydrogen from renewable electricity and captured carbon dioxide is considered as the feedstock. The parameters and process conditions of the considered tubular reactor are based on the most common values found in the literature [55].

In Aspen Plus, RK-SOAVE and NRTL with Henry components were selected as property methods. RK-SOAVE was used for high-pressure blocks, while NRTL with Henry components was selected for the low-pressure blocks such as the distillation units [29]. According to the authors' knowledge, there is no available data in the literature for the sizing and outputs of commercial-scale, CO₂-based methanol plants, therefore, data of a syngas-based reactor was selected [55]. Simulation of the reactor sizing and setup is based on the quasi-isothermal reactor model described by Chen et al. [55]. The model is selected as it illustrates a Lurgi-type reactor which is one of the most common types of reactors for syngas-based methanol synthesis [56].

The model of the full-scale plant can be seen in Fig. 4, where pure hydrogen (H2FEED) and pure $CO_2(CO2FEED)$ are fed to the system at



Fig. 3. Comparison of the implemented Slotboom kinetic model in Aspen Plus and original experimental data from Slotboom et al. [14]. Process conditions: p = 4MPa, gas hourly space velocity (GHSV) = 3000 h⁻¹, inlet. CO₂/H₂ = 25/75 mol%



Fig. 4. Process flowsheet of full-scale methanol plant in Aspen Plus.

70°C, 69.7 bar, and 18°C, 1.8 bar, respectively. CO2 is pressurized to 69.7 bar in a 4 -stage compressor with intercooling (COMPR). The pressurized feedstock is mixed with the re-pressurized and recycled nonreacted gases in MIX1. Then, the mix is heated in HX1 to 236° C and fed to an isothermal multi-tubular reactor (REACTOR) filled with catalyst. The products are separated after cooling (HX2) to 63°C in an adiabatic flash separator (SEP1) to liquids and non-reacted gases. The non-reacted gases are recycled to the reactor after purging 0.5wt% (SPLIT) and pressurized to 69.7 bar (COMPR2). On the liquid side, some of the remaining gases are further separated in another separator (SEP2), and then the raw methanol is expanded to 1.5 bar in VALVE1. The raw methanol is fed into a one-column distillation block (DISTILL) where water and the gases are removed to achieve fuel-grade methanol. The final methanol is then expanded to 1 bar (VALVE4) and cooled down to 20°C in HX3. All the purged and separated gas streams are expanded to 1 bar (VALVE2, VALVE3, VALVE5), mixed (MIX2), and combusted with air in an adiabatic reactor (COMBUST) as they contain some hydrogen and methanol as well. Considerations for the blocks and feed streams are listed in Tables 6 and 7.

All full-scale plants were created with the same parameters, except for the "Bottoms rate" in the distillation column, and the mass flow of air for the combustion. Both were regulated by a calculator block, where the "Bottoms rate" was equal to the molar flow rate of water of the in-going stream (S8), while the mass flow of air was set to achieve 6 mol% oxygen content in the fluegas stream (COLDGAS). Deactivation of the catalyst was only considered within the economic assumptions in Section 2.4. The plants have constant methanol output throughout their lifetime, as determined by the KMs.

Comparison of technical parameters includes the efficiency comparison based on the lower heating values of hydrogen feed and methanol product (Eq. (20)), methanol output, cooling and heating duties, feedstock and electricity consumption.

$$\eta = \frac{\dot{m}_{\rm H_2, feed} \times LHV_{\rm H_2}}{\dot{m}_{\rm CH_3 OH, prod} \times LHV_{\rm CH_3 OH}}$$
(20)

where $\dot{m}_{\rm H_2,feed}$, $\dot{m}_{\rm CH_3OH, prod}$, are mass flow rates of H₂ into the plant in stream H2FEED and CH₃OH leaving the plant in stream METHANOL respectively. LHV stands for lower heating values for H₂ and CH₃OH defined as 33.3kWh/kg and 5.54kWh/kg, respectively.

Furthermore, the conversion of CO₂ (Eq. (21)), H_2 (Eq. (22)) and methanol yield (Eq. (23)) for the whole plant without the combustion are compared:

$$X_{\rm CO_2, plant} = \frac{n_{\rm CO_2, feed} - n_{\rm CO_2, purge}}{n_{\rm CO_2, feed}}$$
(21)

Table 6	
Parameters of the main blocks used in Aspen Plus	.

Block name	Block type	Parameter	Value	Unit	Notes
COMPR	MCompr	Number of stages Discharge pressure from last stage	4 69.7	bar	Equal pressure ratio
		Outlet temperature of intercooling	40	°C	Same after each stage
DISTILL	RadFrac	Number of stages	21		
		Reflux ratio	1.5	mole basis	
		Bottoms rate	*	kmol∕ hr	*Depends on KM
		Feed stage	16		Above-stage
		Condenser pressure	1.5	bar	
		Condenser temperature	69	°C	
REACTOR	RPlug	Number of tubes	950		
	Ū	Length	7	meter	
		Diameter	0.04	meter	
		Pressure drop	Ergun		
		Bed voidage	0.285		
		Particle density	1190	kg/m ³	
		Particle diameter	5.4	mm	

Table 7

Parameters of feed streams used in Aspen Plus.

Stream name	Parameter	Value	Unit	Notes
CO2FEED	Mass flow	10,980	kg/hr	Pure CO ₂
	Pressure	1.8	bar	
	Temperature	18	°C	
H2FEED	Mass flow	1510	kg/hr	Pure H ₂
	Pressure	69.7	bar	
	Temperature	70	°C	
AIR	Mass flow	*	kg/hr	*Mass flow depends on KM
	Pressure	1	bar	-
	Temperature	20	°C	

$$X_{\rm H_2, plant} = \frac{n_{\rm H_2, feed} - n_{\rm H_2, purge}}{n_{\rm H_2, feed}}$$
(22)

$$Y_{\rm CH_3OH, plant} = \frac{n_{\rm CH_3OH, prod}}{n_{\rm CO_2, feed}}$$
(23)

where n_{CO_2} , n_{H_2} , n_{CH_3OH} are molar flow rates of CO_2 , H_2 and CH_3OH respectively. Subscript *feed* means the feed into the plant in streams CO2FEED and H2FEED for CO_2 and H_2 , respectively, while purge means the sum of non-reacted, purged CO_2 and H_2 in streams PURGE2, BOT-TOM and METHANOL.

After the development of each plant heat integration is carried out in Aspen Energy Analyzer. While it is expected that the models vary in required and available heat duties, for the integration similar considerations are taken into account. These considerations are made with rather large flexibility so the different models can be integrated successfully. The main idea is not to fulfill all heating requirements within the plant, but rather to consolidate the same design assumptions. Therefore, cooling water with a temperature between 10 and 15° C is considered for cooling utility and low- and high-pressure steam for hot utility. In all cases, the process streams can be split into a maximum of two. If there are more integration designs available, then the main target is to utilize the available heat from the combustion within the plant, then minimum hot utility, followed by the minimum cold utility, and finally minimum capital expenses for the heat exchangers.

2.4. Economics of full-scale methanol plant design

The economic performance of the plants is compared by calculating the levelized cost of methanol (LCoM) (Eq. (24)) under similar simplified assumptions as described in our earlier publication [27].

$$LCoM = \frac{\text{Total Life Cycle Cost}}{\text{Total Lifetime Methanol Production}}$$
$$= \frac{\sum_{t=1}^{n+d} \frac{CAPEX/d}{(1+r)^{t-0.5}} + \sum_{t=1}^{n} \frac{OPEX}{(1+r)^{t-0.5}}}{\sum_{t=1}^{n} \frac{M_{t}}{(1+r)^{t-0.5}}}$$
(24)

where *n* is the operating lifetime in years, *d* is the design and construction time in years, *r* is the discount rate which is the rate of return used to discount future cash flows back to their present value, M_t is the annual methanol produced, CAPEX is the capital expenses, and OPEX is the annual operational expenses.

A detailed description of how the relationship between the purchased equipment cost taken from Aspen Plus, CAPEX, fixed OPEX and what is included in OPEX and CAPEX is discussed in Nyári et al. [27]. Here, the Chemical Engineering Plant Cost Index was updated for the preliminary December 2021 value as given by Maxwell [57]. All the cost parameters that depend on resizing were calculated accordingly and with the selected model results. While models are available for the consideration of catalyst deactivation [58,59], in this study it is only taken into account in a limited fashion (i.e. the catalyst needs to be changed and repurposed once every-three years). The summary of economic assumptions including the lifetime and utility and feedstock costs is given in Table 8.

3. Results and discussion

3.1. Sensitivity analysis of kinetic models in one-pass reactor design

Comparison results of the KMs in a one-pass reactor based on the operating conditions and reactor sizes specified in Section 2.2 are presented in Fig. 5. The Slotboom and the Kiss models predict higher yield in an isothermal reactor compared to the adiabatic one. Regarding the VD model, the adiabatic model predicts a slightly higher methanol yield for the same pressure. As expected, all the models behave rather similarly when temperature and pressure change. For changes in pressure, Table 8

Economic assumptions.				
Parameter	Value	Unit		
Design and construction time	3	years		
Operating lifetime	20	years		
Annual operational time	8300	hours		
Discount rate	7	%		
Electricity cost	40	€/MWh		
CO ₂ cost	50	€/ tonne		
H ₂ cost	3000	€/ tonne		
Steam cost	15	€/MWh ³		
Cooling water cost	0.05	€/m ³		

each model predicts higher yield and conversion with increased pressure. On the other hand, predictions for changes in temperature in an adiabatic reactor differ considerably between the models. The Slotboom model predicts the highest yield values at the lowest investigated temperature, and then the yield decreases steadily, while the conversion becomes constant. The Kiss model also peaks in the lower temperature region and then performs similarly to the Slotboom one. The VD model has a methanol yield peak at around 510 K, while the conversion continues to increase. Regarding the behavior in the isothermal reactor at varying temperatures, each model predicts a yield peak at a different temperature. The Slotboom model peaks at the lowest temperature at around 500 K, then the Kiss model at around 515 K, and finally the VD model at 530 K. The increasing CO_2 conversion at higher temperatures with decreasing methanol yield is explained by Le Châtelier's principle for the RWGS and CO_2 hydrogenation reactions.

The CO_2 hydrogenation reaction prefers lower temperatures, while the RWGS prefers higher temperatures. Therefore, at lower temperatures, more methanol is produced from the CO_2 , and at higher temperatures, an increase in CO is seen. Consequently, methanol yield does not increase further despite the increasing CO_2 conversion. Overall, the Slotboom model predicts the highest methanol yield and CO_2 conversion for both types of reactor and across different temperatures and pressures, except at very low pressures in the adiabatic reactor where the VD model predicts the highest yield.

The main results for adiabatic and isothermal reactors agree with our earlier findings presented in Izbassarov et al. [51] where only the Kiss model was considered.

These findings are relevant for future simulation studies, as each model clearly has its optimal range of process conditions, therefore, any sensitivity study is highly affected by which KM is used to describe methanol formation.

3.2. Results of full-scale methanol plant techno-economic assessment

Table 9 contains the key performance indicators (KPIs) of the developed methanol synthesis plants. As expected from Section 3.1, the Slotboom model predicts the highest methanol output, with predicted outputs that are 1% and 4.6% higher compared to the models by Kiss and VD, respectively. The methanol purity achieved was the same for all models due to the Calculator block described earlier. As the result of its higher one-pass methanol yield, the Slotboom KM predicts better values for all KPIs listed in Table 9. The Slotboom model shows the highest methanol output along with the lowest utility and feedstock consumption. The VD model has the lowest methanol output and the highest consumption out of the three KMs. The low one-pass methanol yield for the VD KM results in high recycle flow, which shows in the high recycleto-feed ratio, which is more than 2.5 times higher than of the Slotboom KM. This high recycle rate results in significantly higher electricity usage originating from COMPR2. Moreover, the cooling and heating duties of the VD model are increased due to the high mass flow across the heat exchangers before (HX1) and after (HX2) the reactor. Additionally, as most of the hydrogen is converted to methanol product, the Slotboom model has the lowest available heat from the combustion of the non-



Fig. 5. Comparison of kinetic models in one-pass adiabatic (top row) and isothermal (bottom row) reactors at different pressures (left column) and inlet temperatures (right column).

reacted and purged gases. The Kiss model predictions differ slightly from the Slotboom model, in most KPIs by less than 1%.

Heat integration of the plants was successful with constraints defined earlier. The Kiss and Slotboom model needed only high-pressure steam, while the VD model also required low-pressure steam. Each integration model utilizes the heat available from the combustion of the purged and non-reacted gases. As can be seen from Table 9, the VD model has the highest utility requirement for both cooling and heating, which is mostly due to the significantly larger flows in the process streams. While after heat integration all the models consume a comparable amount of steam, the amount of cooling water is significantly higher for the VD model. This can be explained that while there are available hot streams within the plants, cooling utility is always needed from outside of the plant [31,27]. Therefore, for the VD model the significantly larger cooling duty compared to the other two models remains also after the integration. While the VD model's cooling utility decreases by 48% after heat integration, for the Kiss and Slotboom model it is 51 and 53%, respectively. At the same time, as there is a significantly larger amount of heat available from the combustion of the purged gases in the VD model, this heat is used to decrease the heating utility. Therefore, heat integration decreases the heating duty by 54% for the VD model, and only by 43% for the Kiss and Slotboom models.

Based on the KPIs the Slotboom model is expected to have the lowest LCoM, as the highest share of costs arises from the variable OPEX, specifically from the consumption of hydrogen [27]. As the Slotboom model consumes the least utilities and feedstock while producing the most methanol out of the three selected KMs, economic calculations for this plant are expected to be the most beneficial.

Fig. 6 shows the final results of the economic assessment of the developed methanol plants. The LCoM results are within the limits of

published results for similar plants [60]. Under the given economic assumptions the methanol plant using the Slotboom model predicts the lowest LCOM while the Kiss and the VD model predict 3% and 10% higher values, respectively. Fig. 6 also shows how the forecasted LCOM compares to the current, April 2022 trading price of methanol by its largest producer, Methanex [61]. This current Methanex price is the highest recorded price, and it has been increasing since mid-2020. Clearly, for all cases, the predicted LCOM is significantly higher than the current price, and the largest share of cost parameters is due to the cost of green hydrogen.

CAPEX for the VD model is higher than for the Kiss and Slotboom model mainly due to the increased size of the compressor on the recycle stream. The considerably larger mass flow of the recycle stream of the VD KM also manifests in the higher share of electricity cost. In Fig. 7 the share of OPEX is further investigated. The annual OPEX is around 47 million EUR for each model. The fixed OPEX is the same for each plant, as that is independent of the consumption and production values. The share of hydrogen and CO2 cost for all models is roughly the same, around 80% and 10%, respectively, of the annual total OPEX (Fig. 7 (A)). However, when the OPEX without hydrogen cost (Fig. 7 (B)) is examined the difference between the models becomes evident. While the VD model has lower steam consumption and associated costs, all other utility costs are higher compared to the other two models. The significantly larger share of electricity cost with the VD model is due to the higher mass flow rate in the recycle stream. Meanwhile, the Kiss and Slotboom models have almost the same cost distribution.

Overall, based on these results it can be said that the selection of KM clearly affects the outcome of process modeling-based TEA studies indeed influences the outcome. As the differences are significant with the LCoM differing by 10%, this disparity could further increase if other

Table 9

Comparison of key performance indicators of the methanol synthesis plant for the selected three kinetic models. Values in the table concerning heat use the same convention as Aspen Plus (negative: heat released by the system; positive: heat absorbed by the system).

Parameter	Unit	Kiss model	VD model	Slotboom model
Mothenal output	leg /br	7410.75	7150.67	7499.00
Methanol purity	Kg/III	/412./5	/139.0/	/400.00
Efficiency	Weight %	99.7	79.7	99.7
CO. conversion	%0 04	07.09	76.00	02.30
U ₂ conversion	%0 04	97.96	90.29	96.30
Mathanal viold	%0 04	97.09	95.61	96.21
Descuele to food	70 	92.73	89.30 7.67	93.07
ratio	11101/11101	3.4/	/.0/	2.89
Heat generated in reactor	MW	-4.08	-3.99	-4.10
Heat generated from combustion	MW	-3.28	-4.79	-2.86
Heat duty of reboiler	MW	6.66	6.52	6.68
Total heating duty (before HI ¹)	MW	13.54	18.04	12.72
Total cooling duty ² (before HI)	MW	-23.45	-29.66	-22.63
CO ₂ usage	tonne CO ₂ / tonne methanol	1.48	1.53	1.47
H ₂ usage	tonne H ₂ /tonne methanol	0.20	0.21	0.20
Electricity usage	kWh/tonne methanol	150.60	474.44	139.90
Steam usage (after HI)	tonne steam/ tonne methanol	2.19	2.00	2.03
Cooling water	tonne CW ³ /	267.64	371.61	241.96
Total heating duty (after HI)	MW	7.67	8.22	7.29
Total cooling duty (after HI)	MW	-11.57	-15.52	-10.71

1 HI – heat integration.

2 Without the hot gas cooling (HX4).

3 CW – cooling water.

process conditions and plant output scale is chosen [6]. Therefore, KMs should be carefully selected and it should be recognized that their selection will affect both the technical and economic KPIs. Even though the intention of our research was not to determine a "best" model it is worth noting that the KM developed on a state-of-the-art catalyst demonstrated the best KPIs. Therefore, our suggestion is to apply the most recent KM from the literature if there is no in-house experimental data available. This approach should be valid and applied to other TEA studies as well that are based on process modeling. However, the introduction of novel catalyst compositions will require the generation of experimental data and the development of catalyst-specific KMs. For P2X processes such as Fischer-Tropsch synthesis, ammonia synthesis, and methanation which are all based on catalytic reactions the most recent KM should be applied. This would ensure that the TEAs are comparable and up-to-date both with scientific and industrial data leading to more reliable investment decisions regarding P2X technologies.

4. Conclusions

Climate-friendly production of fuels and feedstocks for the chemical and petrochemical industries is one of the focus points of the energy transition. Methanol synthesis from captured CO_2 and hydrogen from renewable electricity as CO_2 mitigation and renewable energy storage has been widely studied through techno-economic assessment (TEA) studies in the last decade. As these studies are often developed in process modeling software, such as Aspen Plus, it is necessary to investigate how the selection of the kinetic model (KM) describing the methanol formation in the reactor could affect the outcome of these studies. In this article, three KMs, two of which are widely used in the TEA literature (Kiss model and VD model) and one that was recently published (Slotboom model), were implemented and then validated in Aspen Plus. The models were studied using one-pass sensitivity analysis for pressure and temperature, which proved that there is a significant difference in how the models predict methanol yield and CO₂ conversion. It was shown that each model has its optimum point, which would affect further studies based on them.

Then, a large-scale methanol plant was developed in Aspen Plus as the basis of the TEA studies, and the three KMs were implemented in its reactor to study their effect. The application of different KMs results in differing feedstock and utility usages, especially when the newest, Slotboom model is compared with the older VD model. The Kiss model behaves similarly to the Slotboom model. The levelized cost of methanol for all models was between 800 and 900€/ tonne, and there was a 10% cost difference between the lowest and highest costs. This is a significant disparity, considering that the plant to which the KMs are applied is developed precisely the same way in every instance. All the discrepancies can be traced back to the differences in one-pass methanol yield and CO_2 conversion amongst the models. The VD model predicted a significantly lower yield which resulted in a higher recycle rate and increased utility and feedstock utilization.

As CO_2 utilization approaches economic viability, understanding such uncertainties will be crucial for successful project planning, because a 10% difference in levelized cost could lead to an incorrect assessment of a given project's feasibility. Hence, these results suggest that extending a TEA's sensitivity analysis to cover the KM's contribution could increase confidence in the robustness of the TEA. This, in turn, will lead to faster and more robust investment decisions for the energy transition.

Finally, it must be noted that the goal of this article was not to declare a "best" model, but rather to highlight the potential discrepancies arising from selecting one model over the other which, in turn, can lead to an inaccurate assessment of the economic viability of a project. Therefore, when conducting a TEA, the options for KM use are the following, in order of decreasing confidence: 1) preferably lab experiments on the given catalyst and raw materials should be conducted and a KM should be fitted to the data; 2) in lieu of directly relevant experimental corroboration of a KM used in a TEA study, the comparison of TEAs performed with multiple KMs can give an estimate of the TEA's uncertainty; 3) if only one KM is used, a more recent one should be selected, as it is more likely to represent the current commercial state-ofthe-art for a given catalyst composition, and could predict yield and conversion with higher accuracy. Furthermore, KMs must be published in the literature in a well-described manner with all units, constants, and other parameters provided to ensure that they can be implemented and validated for further adoption in process modeling and TEA studies. These conclusions and recommendations apply to processes beyond CO2 - based methanol production, and their adaptation is highly encouraged for the entire TEA community.

CRediT authorship contribution statement

Judit Nyári: Conceptualization, Methodology, Software, Validation, Investigation, Writing – original draft, Visualization, Formal analysis. Daulet Izbassarov: Conceptualization, Methodology, Writing – review & editing. Árpád I. Toldy: Conceptualization, Methodology, Writing – original draft. Ville Vuorinen: Writing – review & editing. Annukka Santasalo-Aarnio: Conceptualization, Writing – review & editing, Funding acquisition, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence



Fig. 6. Comparison of levelized cost of methanol from the developed methanol plant using the studied kinetic models with the proportion of cost parameters, including the April 2022 methanol price by Methanex.



Fig. 7. Comparison of annual operational expenses of the developed methanol plant using the studied kinetic models (A) total OPEX, (B) OPEX without hydrogen cost.

the work reported in this paper.

Data availability

No data was used for the research described in the article.

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