

Novel efficient process for methanol synthesis by CO₂ hydrogenation

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1 **Novel efficient process for methanol synthesis by CO₂ hydrogenation**

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11 **Keywords**

12 CO₂ hydrogenation, low-pressure process, Cu/Zn catalyst, H₂ stripping, energy efficiency

13 **Highlights**

- 14 • Efficient process for methanol synthesis by hydrogenation of carbon dioxide
- 15 • Stripping of products with wet hydrogen for double positive effect
- 16 • Minimum consumption of raw materials, and limited use of electricity and steam

17 **Abstract**

18 Methanol is an alternative fuel that offers a convenient solution for efficient energy storage.
19 Complementary to carbon capture activities, significant effort is devoted to the development
20 of technologies for methanol synthesis by hydrogenation of carbon dioxide. While CO₂ is
21 available from plenty of sources, cheap sources of H₂ are less frequently found. An additional
22 source of hydrogen at industrial scale is the wet hydrogen by-product of chlorine production.
23 This study is the first to propose an efficient process for methanol synthesis by CO₂ hydro-
24 genation using wet hydrogen by-product from chlor-alkali production. A key feature of this
25 novel process is the use of a stripping unit where the wet hydrogen flows in counter-current
26 mode with the condensed methanol-water mixture resulting from the high-pressure low-
27 temperature separator after the reaction. This operation has a double positive effect, as it
28 removes the CO/CO₂ from the methanol-water mixture thus allowing a complete recycle of
29 CO₂ and avoiding its presence in the product, while also removing the water from the wet
30 hydrogen thus avoiding the negative impact of adding water on the equilibrium conversion –
31 with consumption figures of 550 kWh electricity and 0.48-1.16 ton steam per ton methanol.
32
33
34

1 **1. Introduction**

2 Methanol is a viable alternative energy source, offering a convenient solution for the efficient
3 energy storage on a large scale, while playing an important role in economy and sustainability
4 by converting the CO₂ waste from industry into a valuable product (Olah et al., 2009). At
5 industrial scale, methanol is produced from synthesis gas (CO/CO₂/H₂) using various catalysts
6 based on CuO/ZnO/Al₂O₃. Complementary to carbon capture and sequestration (CCS), much
7 effort is being put on the development of technologies for methanol production from carbon
8 dioxide. Several review papers published during the past decade cover this topic very well.
9 Liu et al. (2003) reviewed the progress in the catalyst innovation, optimization of the reaction
10 conditions, reaction mechanism, and catalyst performance in CO and CO₂ hydrogenation to
11 methanol, highlighting the key issues of catalyst improvement and areas of priority in R&D.
12 Centi and Perathoner (2009) analyzed the possibilities of converting CO₂ to fuels, noting that
13 the requisites for this objective are: minimization of the consumption of hydrogen (sources),
14 production of fuels that can be easily stored and transported, and the use of renewable energy
15 sources. Their review included CO₂ reverse water-gas shift (WGS) and hydrogenation to
16 hydrocarbons, alcohols, dimethyl ether or formic acid, as well as the reaction to synthesis gas;
17 photo- and electrochemical/catalytic conversion; and thermo-chemical conversion.
18 Kondratenko et al. (2013) discussed the heterogeneously catalyzed hydrogenation, as well as
19 the photocatalytic and electrocatalytic conversion of CO₂ to hydrocarbons or oxygenates,
20 along with the design of electrodes to improve their performance and the recent developments
21 of the application of ionic liquids as electrolytes and of microorganisms as co-catalysts.
22 Saeidi et al. (2014) focused on hydrocarbon and methanol synthesis as methods to convert
23 CO₂ to value-added products. The reaction mechanisms as well as the effects of catalyst,
24 reactor type and operating conditions on product efficiency enhancement of each process
25 were reviewed. Also a brief overview on the reactor types and configurations was provided.
26 Yan et al. (2014) concentrated on the recent advances in designing efficient catalysts for the
27 hydrogenation of CO₂ to fuels, e.g. CO₂ hydrogenation to methanol, CO₂ conversion to CO
28 via reverse WGS reaction and production of hydrocarbons through Fischer-Tropsch synthesis.
29 Jadhav et al. (2014) tackled various aspects on the CO₂ hydrogenation reaction system such
30 as: thermodynamics, innovations in catalysts, influences of reaction variables, overall catalyst
31 performance, reaction mechanism and kinetics, and recent technological advances.
32 While plenty of CO₂ is available from CCS activities, flue gas or as by-product in various
33 processes (e.g. bioethanol production), the sources of hydrogen are more limited but feature
34 processes such as steam methane reforming, coal gasification, partial oxidation of light oil

1 residues, dry reforming, water electrolysis, sulfur-iodine or copper chloride processes (Jadhav
2 et al., 2014). Another major industrial source is the chlor-alkali process, where H₂ is formed
3 as by-product of the salt electrolysis. Based on stoichiometry, 1 ton of chlorine leads to 28 kg
4 hydrogen that can be further converted into 149 kg methanol, using 205 kg CO₂.

5 This article is the first to propose an efficient process for the CO₂ conversion to methanol
6 using wet hydrogen (saturated with water) from brine electrolysis, in a catalytic process based
7 on highly active Cu/Zn/Al/Zr fibrous catalyst (Kiss et al., 2013). For convenience, the results
8 are provided for a 100 ktpy methanol plant, rigorously simulated in Aspen Plus and including
9 experimental data previously reported in literature (An et al., 2009).

11 **2. Problem statement**

12 Methanol synthesis requires efficient chemical processes and inexpensive raw materials.
13 Converting carbon dioxide to methanol by hydrogenation is considered to be a great industrial
14 opportunity (Olah et al., 2009). While cheap CO₂ is available from many sources, the options
15 for low-cost hydrogen are rather limited. An interesting option is the use of wet hydrogen
16 available as by-product in the chlor-alkali production. The issue is that the direct use of water
17 saturated hydrogen stream has a strong negative impact on the chemical equilibrium. To solve
18 this issue, an efficient process is proposed that includes a key feature – namely the use of
19 stripper that has a double positive effect as it removes the CO₂ from the methanol-water
20 mixture produced and avoids the presence of CO/CO₂ in the products, while also removing
21 the water from the wet hydrogen feed initially saturated with water. The efficiency of the
22 process is thus increased, leading to low consumption figures.

24 **3. Process simulation**

25 This section presents the main results for a plant producing 100 ktpy methanol, by CO₂
26 hydrogenation using a highly active Cu/Zn/Al/Zr fibrous catalyst (An et al., 2009).

28 **3.1 Property model**

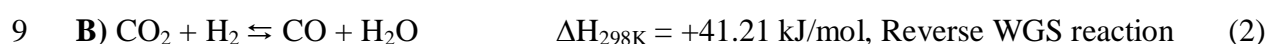
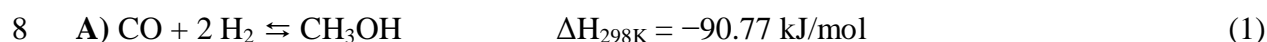
29 The complete process was rigorously simulated in Aspen Plus using the RK-Soave property
30 model which is most suitable for these components (H₂, CO, CO₂, H₂O, and CH₃OH) and
31 conditions (pressure up to 50 bar and temperature up to 250 °C). The non-random two-liquid
32 (NRTL) model was used complementary to the RK-Soave property model, for modeling the
33 distillation section operating at low pressure and in which no hydrogen is present. This is in
34 line with literature recommendations for such systems (Kiss, 2013; Dimian et al., 2014). Note

1 that all the binary interaction parameters related to the property models RK-Soave and NRTL
2 are available in the pure components databank of the Aspen Plus process simulator.

3

4 **3.2 Chemical reactions**

5 The pathways for methanol formation from CO₂/CO and H₂ on a metallic Cu catalyst are
6 given in Kondratenko et al. (2013). The actual chemistry of CO₂ hydrogenation involves three
7 main equilibrium reactions (A, B and C) leading to methanol and water (Fiedler et al., 2005):



11 The CO₂ conversion to CO (reaction B) is endothermic hence the temperature increase is
12 favorable to the equilibrium. However, the CO and CO₂ conversions to methanol (reactions A
13 and C) are exothermic hence the temperature increase has a negative impact on equilibrium.
14 Thus, higher methanol yields are obtained at lower temperatures and higher pressures. This
15 effect is clearly illustrated in Figure 1 showing the effect of temperature on equilibrium.

16 Note that in a process having all three components (CO₂, CO, and H₂) in the feed, the mole
17 fractions have to be adjusted such that the optimal stoichiometric number (SN) is equal to 2.
18 A higher value (SN > 2) indicates that there is an excess of H₂ in the feed gas, while a lower
19 value (SN < 2) means that there is an excess of carbon. When only CO₂ and H₂ are present in
20 the feed, a H₂:CO₂ ratio of 3:1 ensures that SN=2. The SN number is calculated as follows:

21
$$SN = \frac{y_{\text{H}_2} - y_{\text{CO}_2}}{y_{\text{CO}} + y_{\text{CO}_2}}$$
 (4)

22

23 **3.3 Chemical equilibrium**

24 The values for the equilibrium constants (K_A , K_B and K_C) were reported by Lim et al. (2009),
25 using $R=8.314 \text{ J/mol.K}$ and K_i . Note that the study of Lim et al. (2009) used the experimental
26 data from Graaf et al. (1986), so basically it is the same data but provided in an explicit model
27 which provides a consistent framework for process simulations in Aspen Plus.

28 The comparison between the data from literature (Lim et al. 2009) and the equilibrium
29 constant values evaluated within Aspen Plus using the equilibrium reactor showed an
30 excellent agreement. Note that in Aspen Plus, the equilibrium constants are evaluated based

1 upon fugacity in [atm]. A conversion was made to [Pa] based correlations as those will be
 2 required to express the driving force term of the kinetic rate equations.

$$3 \quad \ln K_A = \frac{9.8438 \times 10^4}{RT} - 29.07 \rightarrow K_A = 2.3717 \times 10^{-13} \exp\left(\frac{9.8438 \times 10^4}{RT}\right) [\text{atm}^{-2}]$$

$$4 \quad \ln K_A = -52.096 + \frac{11840}{T} \quad \text{with } K_A [\text{Pa}^{-2}] \quad (5)$$

$$5 \quad \ln K_B = \frac{-4.3939 \times 10^4}{RT} + 5.639 \rightarrow K_B = 2.8118 \times 10^2 \exp\left(\frac{-4.3939 \times 10^4}{RT}\right) [-]$$

$$6 \quad \ln K_B = 5.639 + \frac{-5285}{T} \quad \text{with } K_B [-] \quad (6)$$

$$7 \quad K_C = K_A \times K_B \rightarrow K_C = 6.6688 \times 10^{-11} \exp\left(\frac{5.4499 \times 10^4}{RT}\right) [\text{atm}^{-2}]$$

$$8 \quad \ln K_C = -46.457 + \frac{6555}{T} \quad \text{with } K_C [\text{Pa}^{-2}] \quad (7)$$

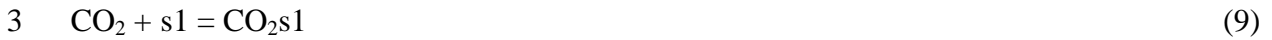
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10 **3.4 Catalyst and kinetics**

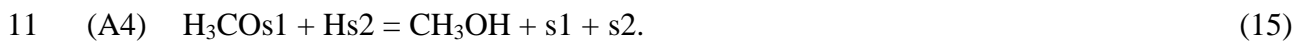
11 Many catalysts are available for CO₂ hydrogenation, based on Cu/Zn formulations (Yan et al.,
 12 2014). Also most of the commercial catalysts available from several catalyst manufacturers
 13 (e.g. Katalko from Johnson-Matthey, MegaMax from Clariant) have high performance. In this
 14 work, the kinetic model A3B2C3 – which was shown to be the best kinetic model out of the
 15 48 models tested by Graaf et al. (1988) – combined with kinetic data from An et al. (2009)
 16 was implemented in Aspen Plus. Note that other adequate kinetic models are also available in
 17 the literature (Bos et al. 1989; Vanden Bussche and Froment 1996; Coteron and Hayhurst,
 18 1994; and numerous publications from Haldor Topsoe).

19 The experimental data from An et al. (2009) validates the model of Graaf et al (1988) and it
 20 was obtained for a fibrous Cu/Zn/Al/Zr catalyst that was designed especially for the
 21 hydrogenation of CO₂. Note that the Langmuir-Hinshelwood kinetic model assumes two
 22 different active sites. CO and CO₂ adsorb competitively on the so called s1-sites, while H₂
 23 and H₂O are adsorbed competitively on the s2-sites. According to Graaf et al. (1988) the
 24 adsorption of methanol is assumed to be negligible, while H₂ is believed to adsorb
 25 dissociatively – hence the use of λ_H term. Nonetheless, it is rather straightforward to derive
 26 alternative kinetic rate expressions that are based on the molecular adsorption of H₂. The
 27 elementary reactions are described as follows (Graaf et al., 1988):

28

1 *Adsorption equilibria*

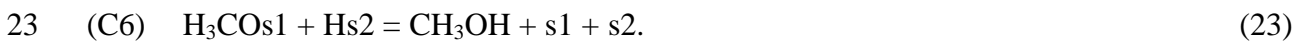
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7 *Reaction (A)*

12

13 *Reaction (B)*

16

17 *Reaction (C)*

24 In case of the best model concluded by Graaf et al. (1988) the rate controlling steps for each
 25 overall reaction A, B and C are A3, B2, and C3 respectively – hence the notation A3B2C3.

26

27 The corresponding rate equations for the kinetic model A3B2C3 are:

$$28 \quad r_{CH_3OH,A3} = k_A \frac{K_{CO} \left[f_{CO} f_{H_2}^{3/2} - f_{CH_3OH} / (K_A \sqrt{f_{H_2}}) \right]}{\left(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} \right) \left[\sqrt{f_{H_2}} + (K_{H_2O} / \sqrt{K_H}) f_{H_2O} \right]} \quad (24)$$

$$29 \quad r_{CO,B2} = r_{H_2O,B2} = k_B \frac{K_{CO_2} \left[f_{CO_2} f_{H_2} - f_{H_2O} f_{CO} / K_B \right]}{\left(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} \right) \left[\sqrt{f_{H_2}} + (K_{H_2O} / \sqrt{K_H}) f_{H_2O} \right]} \quad (25)$$

$$1 \quad r_{CH_3OH,C3} = r_{H_2O,C3} = k_C \frac{K_{CO_2} \left[f_{CO_2} f_{H_2}^{3/2} - f_{H_2O} f_{CH_3OH} / (f_{H_2}^{3/2} K_C) \right]}{\left(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} \right) \left[\sqrt{f_{H_2}} + (K_{H_2O} / \sqrt{K_H}) f_{H_2O} \right]} \quad (26)$$

2 For example, the origin of $r_{CH_3OH,A3}$ is explained hereafter.

$$3 \quad r_{A3+} = k_{A3+} \theta_{H_2CO} \lambda_H \quad (27)$$

$$4 \quad K_{A1} = \frac{\theta_{HCO}}{\theta_{CO}} \cdot \frac{\lambda_e}{\lambda_H} = \frac{\theta_{HCO}}{\theta_{CO}} \cdot \frac{1}{\sqrt{K_H f_{H_2}}} \quad \text{and} \quad K_{A2} = \frac{\theta_{H_2CO}}{\theta_{HCO}} \cdot \frac{\lambda_e}{\lambda_H} = \frac{\theta_{H_2CO}}{\theta_{HCO}} \cdot \frac{1}{\sqrt{K_H f_{H_2}}} \quad (28)$$

5 Therefore:

$$6 \quad \theta_{H_2CO} = K_{A1} K_{A2} \left(\frac{\lambda_H}{\lambda_e} \right)^2 \theta_{CO} = K_{A1} K_{A2} K_H f_{H_2} \theta_{CO} \quad (29)$$

$$7 \quad r_{A3+} = k_{A3+} K_{A1} K_{A2} K_H f_{H_2} \theta_{CO} \lambda_H \quad (30)$$

$$8 \quad r_{A3+} = k_{A3+} K_{A1} K_{A2} \frac{K_{CO} f_{CO} (K_H f_{H_2})^{3/2}}{\left(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} \right) \left(1 + \sqrt{K_H f_{H_2}} + K_{H_2O} f_{H_2O} \right)} \quad (31)$$

9 The equilibrium constant of the overall reaction (A) is used to define the driving force term:

$$10 \quad K_A = \frac{f_{CH_3OH}}{f_{CO} f_{H_2}^2} \rightarrow \text{Driving force} = f_{CO} f_{H_2}^{3/2} - f_{CH_3OH} / (K_A \sqrt{f_{H_2}}) \quad (32)$$

11 As a result it follows that:

$$12 \quad r_A = r_{A3+} - r_{A3-} = k_{A3+} K_{A1} K_{A2} \frac{K_{CO} K_H^{3/2} \left(f_{CO} f_{H_2}^{3/2} - f_{CH_3OH} / (K_A \sqrt{f_{H_2}}) \right)}{\left(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} \right) \left(1 + \sqrt{K_H f_{H_2}} + K_{H_2O} f_{H_2O} \right)} \quad (33)$$

13 According to Graaf et al. (1988) it holds:

$$14 \quad 1 \ll \sqrt{K_H f_{H_2}} + K_{H_2O} f_{H_2O} \quad (34)$$

15 Thus:

$$16 \quad r_A = k_{A3+} K_{A1} K_{A2} \frac{K_{CO} K_H \left(f_{CO} f_{H_2}^{3/2} - f_{CH_3OH} / (K_A \sqrt{f_{H_2}}) \right)}{\left(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} \right) \left(\sqrt{f_{H_2}} + (K_{H_2O} / \sqrt{K_H}) f_{H_2O} \right)} \quad (35)$$

17 Comparing this with the result presented by Eq. 43 in Graaf et al. (1988), it is concluded that:

$$18 \quad k_A = k_{A3+} K_{A1} K_{A2} K_H \quad (36)$$

19 The origin of the other terms ($r_{CO,B2}$ and $r_{CH_3OH,C3}$) can be explained in a similar way.

20 The generalized rate expression to be used in Aspen Plus is given by:

$$21 \quad r = \frac{(\text{kinetic factor})(\text{driving force expression})}{(\text{adsorption term})} \quad (37)$$

22 When a reference temperature T_o is not specified, the kinetic factor in Aspen is expressed by a

1 pre-exponential factor and an Arrhenius term: $kinetic\ factor = kT^n \exp(-E_a / RT)$. All the
 2 required input data for the kinetic factor are included in Table 1 (An et al., 2009). Note that
 3 the units for the pre-exponential constant depend on the units of the driving force term and the
 4 adsorption term. Therefore the units are not the same for all of the reactions.

5 The driving force expressions are as follows:

$$6 \text{ Reaction A: } K_{CO} f_{CO} f_{H_2}^{3/2} - \frac{K_{CO}}{K_A} f_{CH_3OH} f_{H_2}^{-1/2} [Pa^{3/2}] \quad (38)$$

$$7 \text{ Reaction B: } K_{CO_2} f_{CO_2} f_{H_2} - \frac{K_{CO_2}}{K_B} f_{H_2O} f_{CO} [Pa] \quad (39)$$

$$8 \text{ Reaction C: } K_{CO_2} f_{CO_2} f_{H_2}^{3/2} - \frac{K_{CO_2}}{K_C} f_{H_2O} f_{CH_3OH} f_{H_2}^{-3/2} [Pa^{3/2}] \quad (40)$$

9 Note that in Aspen Plus, the driving force is expressed in a generalized form:

$$10 K_1 \left(\prod c_i^{v_i} \right) - K_2 \left(\prod c_j^{v_j} \right) \quad (41)$$

11 When selecting the vapor phase as the reactive phase, and neglecting the difference between
 12 partial pressure and fugacity (i.e. assuming ideal gas), the partial pressures are used for the
 13 concentration. The resulting values for K_1 and K_2 are given in Table 2. In Aspen Plus, K_1 and
 14 K_2 are expressed in a logarithmic form, so the resulting input parameters are given in Table 3.

$$15 \ln(K) = A + \frac{B}{T} \quad (42)$$

16 The adsorption term is the same for all reactions. The expression applied in Aspen Plus is:

$$17 \left(\sum K_i \left[\prod c_j^{v_j} \right] \right)^m \quad (43)$$

18 Configuring Aspen Plus requires re-writing the adsorption term in the kinetic expression,
 19 which is the same for all three reactions (Graaf et al., 1988):

$$20 \left(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} \right) \left(f_{H_2}^{1/2} + \left[K_{H_2O} / \sqrt{K_H} \right] f_{H_2O} \right) [bar^{1/2}] = \quad (44)$$

$$21 \frac{\sqrt{f_{H_2}} + \frac{K_{H_2O}}{\sqrt{K_H}} f_{H_2O} + K_{CO} f_{CO} \sqrt{f_{H_2}} + \frac{K_{CO} K_{H_2O}}{\sqrt{K_H}} f_{CO} f_{H_2O} + K_{CO_2} f_{CO_2} \sqrt{f_{H_2}} + \frac{K_{CO_2} K_{H_2O}}{\sqrt{K_H}} f_{CO_2} f_{H_2O}}{\sqrt{f_{H_2}} + \frac{K_{H_2O}}{\sqrt{K_H}} f_{H_2O} + K_{CO} f_{CO} \sqrt{f_{H_2}} + \frac{K_{CO} K_{H_2O}}{\sqrt{K_H}} f_{CO} f_{H_2O} + K_{CO_2} f_{CO_2} \sqrt{f_{H_2}} + \frac{K_{CO_2} K_{H_2O}}{\sqrt{K_H}} f_{CO_2} f_{H_2O}}$$

22 Both the numerator and the denominator of the kinetic rate equation are divided by $\sqrt{K_H}$ in
 23 order to reduce the number of variables since this allows lumping together K_H and K_{H_2O} .

24 Although the result is that the adsorption term is not dimensionless anymore, the result is
 25 mathematically the same for the reaction rate expression. This expression is the sum of 6
 26 terms with the exponent $m=1$. The combined K_i factors for each term are specified in Table 4.

27 The adsorption constants are a function of temperature:

$$K_i = a_i \exp(b_i / RT) \quad (45)$$

Note that in Aspen Plus, K is expressed in a logarithmic form – for convenience, the resulting input parameters are also provided in Table 4.

$$\ln(K) = A + \frac{B}{T} \quad (46)$$

Finally, the LHHW-kinetics was configured in Aspen Plus and tested with a plug flow reactor (PFR) against equilibrium and kinetics data from literature (An et al., 2009). An excess of catalyst was applied in order to reach the chemical equilibrium in the PFR. The comparison between the experimental and simulated data (illustrated in Table 5) shows a good agreement with less than 5% error around the operating process conditions, thus indicating a correctly implementation of the kinetics. No model parameters were calculated and no changes were made to the kinetic data from An et al. (2009) and the equilibrium data from Lim et al. (2009) – based on the detailed model of Graaf et al. (1986). These were only translated from the implicit form to the explicit input format required by the process simulator Aspen Plus.

14

4. Results and discussion

4.1.1 Sensitivity analysis

Within Aspen Plus, the CO₂ converter was simulated by a plug-flow reactor (PFR) using the Soave-Redlich-Kwong EOS and NRTL with Henry components as property models. The amount of catalyst considered in the reactor corresponds to a gas hourly space velocity of GHSV=5.9 m³/kg_{cat}h. Due to the geometrical design of the multi-tubular reactor, the gas velocity does not exceed 1.5 m/s. The following parameters were varied in the specified range: $T=200-300^{\circ}\text{C}$, $p=1-100$ bar, reactants ratio $R=\text{H}_2:\text{CO}_2=3-12$, and catalyst loadings within the range $\text{GHSV}=0.1-10^5$ m³/kg_{cat}h. The following figures show the main results of the sensitivity analysis, in terms of methanol and CO yield as a function of temperature (Figure 2 and Figure 3), pressure (Figure 4) and catalyst loading (Figure 5), at different reactants ratios. Due to the kinetic limitations at lower temperatures versus equilibrium limitations at higher temperatures, an optimal operating region exists and this depends on the reactants ratio. The effect of pressure on the MeOH and CO yields is straightforward. The formation of methanol is clearly favored at higher pressures due to the fact that CO₂ and CO hydrogenation reactions proceed with a decrease of the total number of moles. Consequently, as more CO is converted to methanol at higher pressures, the CO yield decreases when the pressure is increased. Figure 5 shows that at 200°C the reaction is kinetically limited, as an increase in catalyst loading leads to an increase in methanol yield. Therefore, it makes sense to increase the catalytic

1 activity at lower temperatures in order to improve the yield. However, at higher temperatures
2 (>250°C) the reaction is equilibrium limited when a sufficient amount of catalyst is used
3 (GHSV<10 m³/kg_{cat}h), hence any further increase of the catalyst loading has no effect at all.
4 Furthermore, Figure 6 shows the theoretical effect of water content in the reactor feed – more
5 water leads to decreased performance as the presence of water has a detrimental effect on the
6 equilibrium. However, it should be noted that in this new process the humidity (water content)
7 of the hydrogen feed is not an actual variable, since the fresh feed stream is assumed to be
8 saturated with water at ambient conditions hence this is the worst case scenario.

10 **4.1.2 Process description**

11 The classic low-pressure methanol process follows the generic scheme shown in Figure 7
12 (Fiedler et al., 2005) – which is a typical reaction-separation-recycle system (Kiss, 2010; Kiss
13 et al., 2007). Basically, the reactants are brought to the required temperature and pressure then
14 fed together (matching the stoichiometric number $SN=2$) to a reactor operated at 200-300°C
15 and 50-100 bar. Due to the chemical equilibrium limitations, the conversion is incomplete so
16 the reactor outlet will comprise of products (methanol and water) as well as unconverted
17 reactants (CO_x and hydrogen). This gaseous mixture is cooled and flashed to separate the
18 condensable products from the non-condensable reactants, which are recycled. The condensed
19 components are then separated in two steps, typically by a direct distillation sequence, into
20 lights (dissolved CO_x and minor light impurities), methanol and a water stream.

21 In this work, a plant capacity of 100 ktpy methanol is considered. Figure 8 presents the
22 proposed process flowsheet, while the complete mass and energy balance is provided in Table
23 6. Compared to the classic low-pressure methanol process reported (Fiedler et al., 2005) there
24 are several key differences, described hereafter. The fresh CO₂ feed stream is mixed with the
25 recycle gas stream and fed to the feed-effluent-heat-exchanger (FEHE) without decompression
26 and heating. This leads to a lower gas flowrate to the recycle compressor (COMP2) and thus
27 reduced requirements of electricity.

28 Note that using classic process synthesis heuristics we have also evaluated alternative process
29 configurations that aimed to take advantage of having separate hydrogen and CO₂ feed
30 streams (e.g. higher flexibility and methanol yield, lower energy requirements). However, no
31 significant improvement was observed by feeding the reactants as mixed or pure components
32 all at once or added along the catalytic reactor. The main reason is that the reactor outlet is in
33 all cases close to the equilibrium hence implicitly limited. Consequently, the strategy of
34 feeding the reactants has no effect on a reactor reaching 100% of the equilibrium conversion.

1 The best alternative strategy was to feed the mixed reactants along the reactor working at
2 lower end temperature, and to strip out the dissolved CO₂ from the methanol using the fresh
3 feed of hydrogen that is then mixed with the CO₂ and the recycle stream. This strategy leads
4 to the highest methanol yield and the lowest energy requirements per ton product. As shown
5 later, this strategy is especially beneficial when wet fresh hydrogen is used, since the addition
6 of wet fresh hydrogen does not only result in the stripping and recycling of CO₂ and CO from
7 the produced methanol, but to removal of the water from the fresh hydrogen as well, thus
8 leading to even bigger improvements in CO₂ conversion per pass and energy reduction.

9 The fresh wet hydrogen feed from chlorine production by salt electrolysis is pressurized to 45
10 bar in a primary multi-stage compressor (COMP1). The hydrogen compressor (COMP1) was
11 optimized (e.g. reducing the intermediate cooling temperature to less than 170 °C) to take
12 advantage of the compression curve, and therefore further reduce the compression duty. The
13 resulting gas mixture is heated up in a feed-effluent heat-exchanger (FEHE) by the reactor
14 outlet stream, and then fed to a multi-tubular plug-flow reactor (PFR) operated isothermally at
15 50 bar and 250°C. The heat of reaction generated in the reactor can be used to generate high
16 pressure steam. The multi-tubular catalytic reactor has the following characteristics: 12 m
17 length, 810 tubes of 0.06 m diameter, and a loading of 865 kg catalyst (Cu/Zn/Al/Zr). More
18 catalyst could be added, but the improvements on the conversion are not significant since the
19 operation under these conditions is practically equilibrium limited. A bed voidage (defined as
20 the fraction of the reactor volume not occupied by catalyst) of 0.98 was used in simulations.
21 This means that the fibrous Cu/Zn/Al/Zr catalyst reported in An et al. (2009) is taken on a
22 support and that 0.02 volume fraction (based on reactor) of active catalyst material is used.

23 The reactor outlet stream is cooled down in the FEHE unit and an additional COOLER, then
24 being eventually flashed in a separator (SEP) to split methanol and water (liquid) from the
25 non-condensable gas components (CO, CO₂ and H₂) that are recycled. The recycle stream is
26 then purged (optionally, up to 1.5%) and mixed with the fresh CO₂ feed stream and sent to the
27 second compressor (COMP2). The liquid stream of the flash is sent to a stripping column
28 (STRIPPER) where the compressed wet hydrogen stream from COMP1 is fed in counter-current
29 mode. This has a double positive effect, as it dries the hydrogen feed thus removing water
30 from the reactor feed, and it removes the light ends (mainly CO₂ but CO as well) which are
31 completely recycled thus significantly improving the consumption figures. The liquid bottom
32 stream of the stripper is sent to a distillation column (DC) that separates water as bottom
33 product and methanol as high purity top distillate. It is worth noting that by using the stripper
34 unit, the liquid outlet (containing methanol-water) is obtained at higher temperature – the

1 consequence of using a warmer feed stream to the DC unit being a reduced reboiler duty. Note
2 that the separation of the methanol-water stream is carried out in a single distillation column
3 using a partial condenser – able to deliver a vapor distillate (lights), high purity liquid
4 distillate (methanol) and bottom product (water). Consequently, one distillation column
5 (including reboiler and condenser) of the conventional direct sequence is spared. A dividing-
6 wall column can be also considered as an alternative for this ternary separation (Kiss, 2013),
7 in order to further reduce the (minor) methanol loss in the lights stream.

9 **4.1.3 Consumption figures**

10 For convenience, Table 7 gives the key parameters and consumption figures for this process.
11 Remarkable, a large part of the total reboiler duty (about 60%) can be covered by the thermal
12 energy produced in the reactor, by generating high pressure steam usable in the reboiler. It is
13 also worth noting that the consumption of raw materials is extremely close to the minimum
14 stoichiometric value, while the use of utilities (steam and electricity) is also very low. The
15 patent of Kiss et al. (2013) includes several comparative examples showing that at various
16 operating conditions this novel process using hydrogen stripping of products allows 15-20%
17 energy savings and 5-8% more methanol product as compared to the conventional process.
18 For convenience, Table 8 shows a comparison between two cases not limited by equilibrium
19 (without and with stripper) as described in the patent of Kiss et al. (2013) which provide more
20 details about these cases and covers more possible process configurations. The advantages of
21 using a stripping unit are clearly illustrated by the lower consumption figures, higher resource
22 efficiency, as well as higher conversion of the raw materials.

24 **5. Conclusions**

25 The methanol synthesis by carbon dioxide hydrogenation is feasible in the new efficient
26 process proposed here. A key feature of this novel process is the use of a stripping unit where
27 the wet hydrogen (saturated with water) flows in counter-current with the condensed mixture
28 methanol-water resulting from the flash separation after reaction. This operation has a double
29 positive effect, as it removes CO_x from the methanol-water mixture thus allowing a complete
30 recycle of CO₂, while also removing the water from the wet hydrogen (initially saturated with
31 water) thus avoiding the negative impact on the reaction equilibrium conversion.

32 As a result, the consumption figures indicate a limited use of utilities (550 kWh/ton methanol,
33 and 0.48-1.16 ton steam per ton methanol) while the use of the raw materials is minimal, as
34 both reactants are recovered and recycled hence completely converted in the overall process –

1 being limited by the stoichiometry only. While all the carbon from the CO₂ feed ends up in
 2 the methanol product, the hydrogen valorization is less efficient since only two thirds of
 3 hydrogen is converted to methanol product, the rest being converted to the water by-product.

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5 **Notation**6 *A* pre-exponential factor7 *c* concentration (mol/kg)8 *f* fugacity (bar)9 *GHSV* gas hourly space velocity (m³/kg_{cat}h)10 *k* reaction rate constant11 *K_R* equilibrium constant of reaction *R*12 *K_i* adsorption constant of component *i* (1/bar)13 *m* number of parameters (-)14 *p* pressure (bar)15 *R* gas constant = 8.314 (J/molK)16 *W* weight of catalyst (kg)17 *y_i* gas mol fraction of component *i* (-)

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19 Greek symbols

20 ΔH enthalpy change (kJ/mol)21 ΔS entropy change (kJ/molK)22 θ_{CO} Langmuir adsorption term CO23 θ_{CO_2} Langmuir adsorption term CO₂24 θ_i fractional occupation of s1-sites with species *i*25 λ_j fractional occupation of s2-sites with species *j*26 λ_H Langmuir adsorption term for dissociated hydrogen

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28 Subscripts

29 *i* component *i* (e.g. CO, CO₂, H₂, CH₃OH, H₂O)

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31 Abbreviations

32 *SN* Stoichiometric number33 *WGS* Water-gas shift reaction

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1 **Tables**

2

3 **Table 1.** Kinetic factor for reactions A, B and C (based on data from An et al., 2009) – the
 4 units used are [Pa] for fugacity and [mol/g_{catalyst}.s] = [kmol/kg_{catalyst}.s] for reaction rate

Reaction	k	n	E _a [J/mol.K]
A	$4.0638 \cdot 10^{-6}$ [kmol./kg _{cat} .s.Pa]	0	11695
B	$9.0421 \cdot 10^8$ [kmol./kg _{cat} .s.Pa ^{1/2}]	0	112860
C	$1.5188 \cdot 10^{-33}$ [kmol./kg _{cat} .s.Pa]	0	266010

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9 **Table 2.** Constants for driving force (adsorption data from An et al., 2009; and chemical
 10 equilibrium data from Lim et al., 2009).

Reaction	Expression K ₁	K ₁	Expression K ₂	K ₂
A	K _{CO} [Pa ⁻¹]	$8.3965 \cdot 10^{-11} \exp(118270/RT)$	K _{CO} /K _A [Pa]	$3.5408 \cdot 10^{12} \exp(19832/RT)$
B	K _{CO2} [Pa ⁻¹]	$1.7214 \cdot 10^{-10} \exp(81287/RT)$	K _{CO2} /K _B [Pa ⁻¹]	$6.1221 \cdot 10^{-13} \exp(125226/RT)$
C	K _{CO2} [Pa ⁻¹]	$1.7214 \cdot 10^{-10} \exp(81287/RT)$	K _{CO2} /K _C [Pa]	$2.5813 \cdot 10^{10} \exp(26788/RT)$

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16 **Table 3.** Constants for driving force (from An et al., 2009) using the format for Aspen Plus

Reaction	K ₁		K ₂	
	A	B	A	B
A	-23.20	14225	28.895	2385
B	-22.48	9777	-28.12	15062
C	-22.48	9777	23.974	3222

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Table 4. K_i factors for adsorption term (terms 2, 3, 5 from An et al., 2009; rest is explicitly derived by calculation)

Term	Expression	a_i	b_i	$\prod c_j^{v_j}$
1	1	$a_1=1$	$b_1=0$	$\sqrt{f_{H_2}}$
2	$\frac{K_{H_2O}}{\sqrt{K_H}}$	$a_2=4.3676 \cdot 10^{-12}$	$b_2=1.1508 \cdot 10^5$	f_{H_2O}
3	K_{CO}	$a_3=8.3965 \cdot 10^{-11}$	$b_3=1.1827 \cdot 10^5$	$f_{CO} \sqrt{f_{H_2}}$
4	$\frac{K_{CO} K_{H_2O}}{\sqrt{K_H}}$	$a_4=a_2 \cdot a_3$ $a_4=3.6673 \cdot 10^{-22}$	$b_4=b_2+b_3=2.3335 \cdot 10^5$	$f_{CO} f_{H_2O}$
5	K_{CO_2}	$a_5=1.7214 \cdot 10^{-10}$	$b_5=8.1287 \cdot 10^4$	$f_{CO_2} \sqrt{f_{H_2}}$
6	$\frac{K_{CO_2} K_{H_2O}}{\sqrt{K_H}}$	$a_6=a_2 \cdot a_5$ $a_6=7.5184 \cdot 10^{-22}$	$b_6=b_2+b_5=1.9727 \cdot 10^5$	$f_{CO_2} f_{H_2O}$

Term	Expression	$A_i=\ln(a_i)$	$B_i=b_i/R$	$\prod c_j^{v_j}$
1	1	0	0	$\sqrt{f_{H_2}}$
2	$\frac{K_{H_2O}}{\sqrt{K_H}}$	-26.1568	13842	f_{H_2O}
3	K_{CO}	-23.2006	14225	$f_{CO} \sqrt{f_{H_2}}$
4	$\frac{K_{CO} K_{H_2O}}{\sqrt{K_H}}$	-49.3574	28067	$f_{CO} f_{H_2O}$
5	K_{CO_2}	-22.4827	9777	$f_{CO_2} \sqrt{f_{H_2}}$
6	$\frac{K_{CO_2} K_{H_2O}}{\sqrt{K_H}}$	-48.6395	23619	$f_{CO_2} f_{H_2O}$

Table 5. Comparison of experimental data from An et al. (2009) with the results of the Aspen Plus calculations using LHHW kinetics

SV=6000 ml/g_{cat}.h T [K]	CO₂ conversion		Methanol yield based on CO₂ feed	
	<i>Experimental data¹</i>	<i>Aspen Plus calculations</i>	<i>Experimental data¹</i>	<i>Aspen Plus calculations</i>
483	0.170	0.1244	0.110	0.1152
503	0.225	0.1957	0.155	0.1597
523	0.255	0.2398	0.178	0.1530
543	0.250	0.2404	0.140	0.1058

T=523 K SV [ml/g_{cat}.h]	CO₂ conversion		Methanol yield based on CO₂ feed	
	<i>Experimental data²</i>	<i>Aspen Plus calculations</i>	<i>Experimental data²</i>	<i>Aspen Plus calculations</i>
1000	0.262	0.2428	0.193	0.1548
2000	0.260	0.2428	0.191	0.1548
4000	0.256	0.2421	0.180	0.1544
6000	0.250	0.2398	0.166	0.1530
8000	0.243	0.2362	0.153	0.1509
10000	0.230	0.2321	0.134	0.1485

¹ Experimental data taken from Figure 2 reported in An et al. (2009)

² Experimental data taken from Figure 4 reported in An et al. (2009)

1 **Table 6.** Mass and energy balance of the proposed process for methanol synthesis

	F-2	F-3	F-3H	F-4	F-5	F-6T	F-7	F-8	F-8STRIP	F-9	F-CO2
Temperature C	42.1	28.2	225.0	93.9	31.0	30.0	30.0	30.0	92.2	87.6	20.0
Pressure bar	50	50	50	50	50	45	45	45	45.2	5.066	100
Vapor Frac	1	0.999	1	0.956	0.900	1	1	0	0	0.001	0
Mole Flow kmol/hr	8649.99	9041.05	9041.05	8259.03	8259.03	8650.00	8649.99	819.06	799.03	799.03	391.06
Mass Flow kg/hr	104793.54	122002.69	122002.69	122002.69	122002.69	104793.65	104793.54	21104.88	19867.90	19867.90	17209.15
Volume Flow cum/hr	4608.29	4572.55	7644.01	4878.20	3822.70	4907.32	4907.32	24.62	25.79	31.68	22.05
Enthalpy Gcal/hr	-185.29	-223.12	-208.89	-226.94	-235.48	-186.07	-186.07	-52.50	-49.30	-49.30	-37.83
Mass Flow kg/hr											
CO	7492.57	7492.57	7492.57	7492.57	7492.57	7492.57	7492.57	2.11	0.00	0.00	0.00
CO2	82810.65	100018.93	100018.93	82810.73	82810.73	82810.73	82810.65	1344.24	0.00	0.00	17208.28
H2	13011.73	13011.73	13011.73	10647.05	10647.05	13011.74	13011.73	1.30	1.45	1.45	0.00
H2O	3.94	4.80	4.80	7048.93	7048.93	3.94	3.94	7045.40	7337.72	7337.72	0.86
CH3OH	1474.66	1474.66	1474.66	14003.40	14003.40	1474.66	1474.66	12711.83	12528.74	12528.74	0.00
Mass Frac CO	0.0715	0.0614	0.0614	0.0614	0.0614	0.0715	0.0715	0.0001	0.0000	0.0000	0.0000
Mass Frac CO2	0.7902	0.8198	0.8198	0.6788	0.6788	0.7902	0.7902	0.0637	0.0000	0.0000	1.0000
Mass Frac H2	0.1242	0.1067	0.1067	0.0873	0.0873	0.1242	0.1242	0.0001	0.0001	0.0001	0.0000
Mass Frac H2O	0.0000	0.0000	0.0000	0.0578	0.0578	0.0000	0.0000	0.3338	0.3693	0.3693	0.0001
Mass Frac CH3OH	0.0141	0.0121	0.0121	0.1148	0.1148	0.0141	0.0141	0.6023	0.6306	0.6306	0.0000
Mole Frac CO	0.0309	0.0296	0.0296	0.0324	0.0324	0.0309	0.0309	0.0001	0.0000	0.0000	0.0000
Mole Frac CO2	0.2175	0.2514	0.2514	0.2278	0.2278	0.2175	0.2175	0.0373	0.0000	0.0000	0.9999
Mole Frac H2	0.7462	0.7139	0.7139	0.6395	0.6395	0.7462	0.7462	0.0008	0.0009	0.0009	0.0000
Mole Frac H2O	0.0000	0.0000	0.0000	0.0474	0.0474	0.0000	0.0000	0.4775	0.5097	0.5097	0.0001
Mole Frac CH3OH	0.0053	0.0051	0.0051	0.0529	0.0529	0.0053	0.0053	0.4844	0.4894	0.4894	0.0000

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	F-H2	H2-HP	H2-STRIP	HEAVIES	LIGHTS	LIQ	MEOH	PURGE	RX-IN	RX-OUT	VAP
Temperature C	35.0	170.0	47.0	104.9	39.0	30.0	39.0	30.0	225.0	250.0	30.0
Pressure bar	1.1	45	45	1.1	1.013	45	1.013	45	50	50	45
Vapor Frac	1	1	1	0	1	0	0	1	1	1	1
Mole Flow kmol/hr	1190.00	1190.00	1213.51	407.56	1.04	3.48	390.43	0.01	9041.05	8259.03	1210.03
Mass Flow kg/hr	2658.87	2658.87	3985.80	7346.68	12.52	89.96	12508.71	0.10	122002.69	122002.69	3895.84
Volume Flow cum/hr	27734.24	992.69	735.89	8.05	26.70	0.11	16.12	0.00	7644.01	7304.78	695.46
Enthalpy Gcal/hr	-0.86	0.28	-3.13	-27.45	-0.02	-0.22	-22.11	0.00	-208.89	-212.71	-3.10
Mass Flow kg/hr											
CO	0.00	0.00	2.11	0.00	0.00	0.00	0.00	0.01	7492.57	7492.57	2.11
CO2	0.00	0.00	1344.95	0.00	0.00	0.71	0.00	0.08	100018.93	82810.73	1344.24
H2	2366.14	2366.14	2365.99	0.00	1.40	0.01	0.05	0.01	13011.73	10647.05	2365.99
H2O	292.73	292.73	28.08	7336.52	0.00	27.66	1.20	0.00	4.80	7048.93	0.41
CH3OH	0.00	0.00	244.67	10.16	11.12	61.58	12507.46	0.00	1474.66	14003.40	183.09
Mass Frac CO	0.0000	0.0000	0.0005	0.0000	0.0000	0.0000	0.0000	0.0715	0.0614	0.0614	0.0005
Mass Frac CO2	0.0000	0.0000	0.3374	0.0000	0.0000	0.0079	0.0000	0.7902	0.8198	0.6788	0.3450
Mass Frac H2	0.8899	0.8899	0.5936	0.0000	0.1119	0.0001	0.0000	0.1242	0.1067	0.0873	0.6073
Mass Frac H2O	0.1101	0.1101	0.0070	0.9986	0.0000	0.3075	0.0001	0.0000	0.0000	0.0578	0.0001
Mass Frac CH3OH	0.0000	0.0000	0.0614	0.0014	0.8880	0.6846	0.9999	0.0141	0.0121	0.1148	0.0470
Mole Frac CO	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0309	0.0296	0.0324	0.0001
Mole Frac CO2	0.0000	0.0000	0.0252	0.0000	0.0000	0.0046	0.0000	0.2175	0.2514	0.2278	0.0252
Mole Frac H2	0.9863	0.9863	0.9672	0.0000	0.6671	0.0009	0.0001	0.7462	0.7139	0.6395	0.9700
Mole Frac H2O	0.0137	0.0137	0.0013	0.9992	0.0000	0.4416	0.0002	0.0000	0.0000	0.0474	0.0000
Mole Frac CH3OH	0.0000	0.0000	0.0063	0.0008	0.3329	0.5528	0.9998	0.0053	0.0051	0.0529	0.0047

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2 **Table 7.** Key performance indicators and consumption figures for the proposed process for
3 methanol synthesis by CO₂ hydrogenation

Parameter	Value	Unit
MeOH production rate	100.07	kton/year
Purge to feed ratio	0	mol/mol
Recycle to feed ratio	5.47	mol/mol
H ₂ : CO ₂ ratio (feed / reactor inlet)	3.0 / 2.84	mol/mol
H ₂ conversion in reactor (per pass)	18.17	%
CO ₂ conversion (per pass)	17.20	%
MeOH yield (overall process)	99.83	%
Power of H ₂ feed compressor (COMP1)	5962.96	kW
Power of recycle compressor (COMP2)	911.96	kW
Heat generated in the reactor	-4448.72	kW
Heat duty of reboiler (distillation column)	7618.42	kW
Electricity usage (per ton methanol)	550	kWh/ton MeOH
Steam usage (per ton methanol) – no heat integration	1.16	ton steam / ton MeOH
Steam usage (per ton methanol) – heat integrated*	0.48	ton steam / ton MeOH
Electricity cost (at 0.08 €/kWh)	49.37	Euro/ton MeOH
Steam cost (at 25 €/ton steam) – no heat integration	29.03	Euro/ton MeOH
Steam cost (at 25 €/ton steam) – heat integrated*	12.08	Euro/ton MeOH
Pure CO ₂ use (per unit of methanol product)	1.3758	kg/kg
Pure H ₂ use (per unit of methanol product)	0.1892	kg/kg
Wet H ₂ use (per unit of methanol product)	0.2126	kg/kg

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5 * NOTE: The heat integrated option means that part of the steam required in the reboiler of the
6 distillation column is produced by using the heat generated in the reactor.

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2 **Table 8.** Comparison of key performance indicators for two cases (without and with stripper)
3 – as described in the patent of Kiss et al. (2013)

Key performance indicators	Case A-	Case A+	Case B-	Case B+
CO ₂ conversion per pass (%)	20.90	21.51	21.50	21.55
CO ₂ conversion overall (%)	95.18	99.78	95.18	99.78
Electricity usage (kW.h/ton MeOH)	607	588	597	581
Steam usage (ton steam/ton MeOH) – no HI	1.92	1.52	1.77	1.52
CO ₂ use per unit of methanol product (kg/kg)	1.494	1.376	1.443	1.376
H ₂ usage per unit of methanol product (kg/kg)	0.197	0.189	0.190	0.189

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5 * NOTE: Case A: Wet hydrogen feed. Case B: Dry hydrogen feed. Both cases are considered
6 without (–) or with (+) stripper. Operating conditions: P=50 bar, T=225 °C, H₂:CO_x=6:1.

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1 **Figure captions**

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3 **Figure 1.** Effect of temperature on the equilibrium constants of the main chemical reactions

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5 **Figure 2.** Effect of temperature on the MeOH and CO yield, at fixed pressure and various
6 reactants ratios (simulated results)

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8 **Figure 3.** Effect of temperature on the MeOH and CO yield, at fixed reactants ratio and
9 various pressures (simulated results)

10

11 **Figure 4.** Effect of pressure on the MeOH and CO yield, at fixed temperature and various
12 reactants ratios (simulated results)

13

14 **Figure 5.** Effect of the catalyst loading on the MeOH and CO yield (simulated results), at
15 various reactants ratios and fixed pressure and temperature (p=50 bar, T=200 and T=250 °C)

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17 **Figure 7.** Generic processing scheme for methanol synthesis from syngas or by CO₂
18 hydrogenation

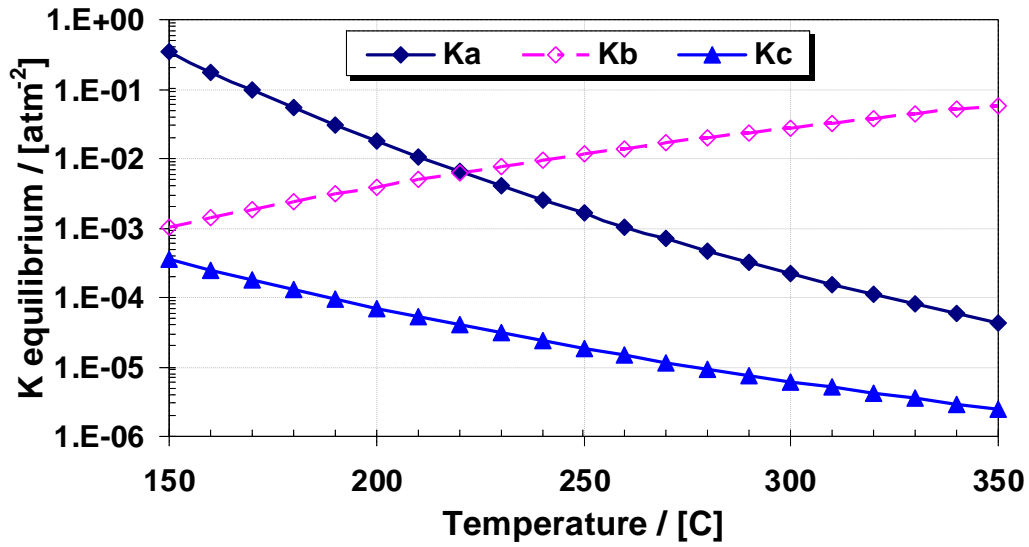
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20 **Figure 8.** Aspen Plus flowsheet of an efficient process for methanol synthesis by CO₂
21 hydrogenation

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Figure 1. Effect of temperature on the equilibrium constants of the main chemical reactions

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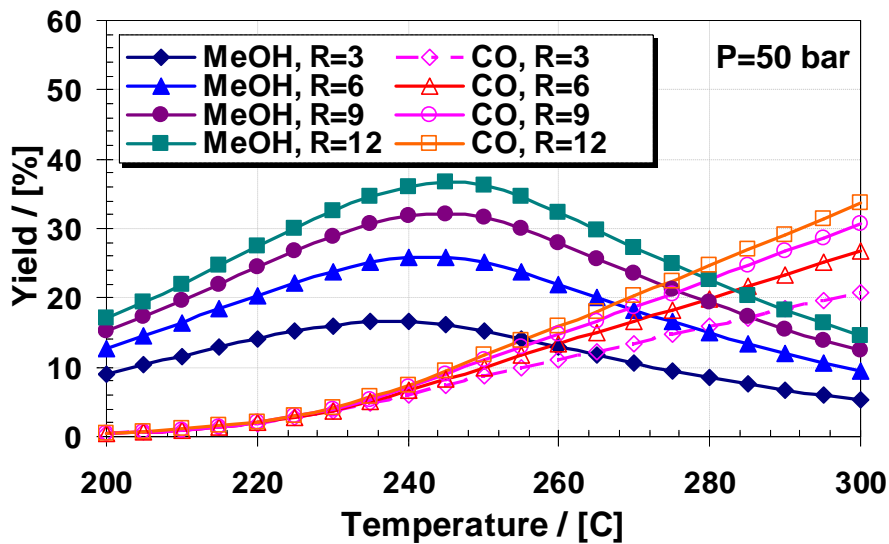
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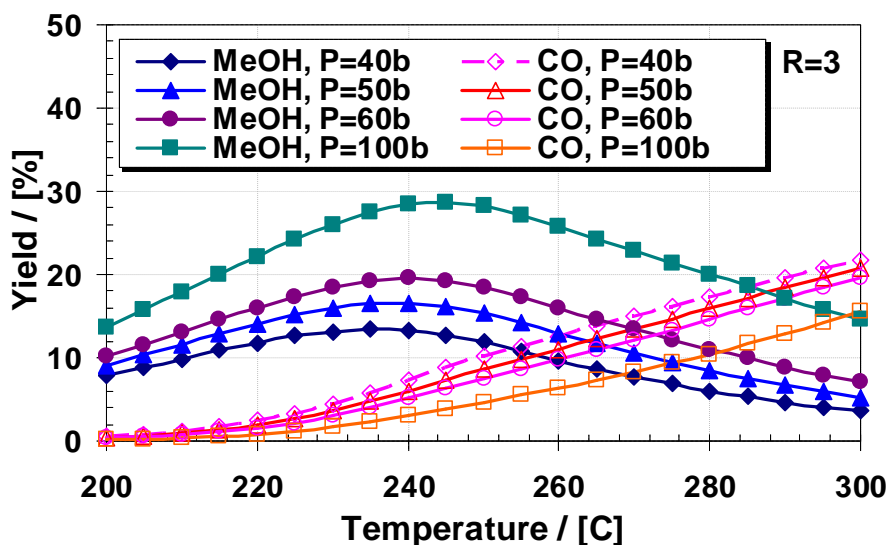
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Figure 2. Effect of temperature on the MeOH and CO yield, at fixed pressure and various reactants ratios (simulated results)

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Figure 3. Effect of temperature on the MeOH and CO yield, at fixed reactants ratio and various pressures (simulated results)

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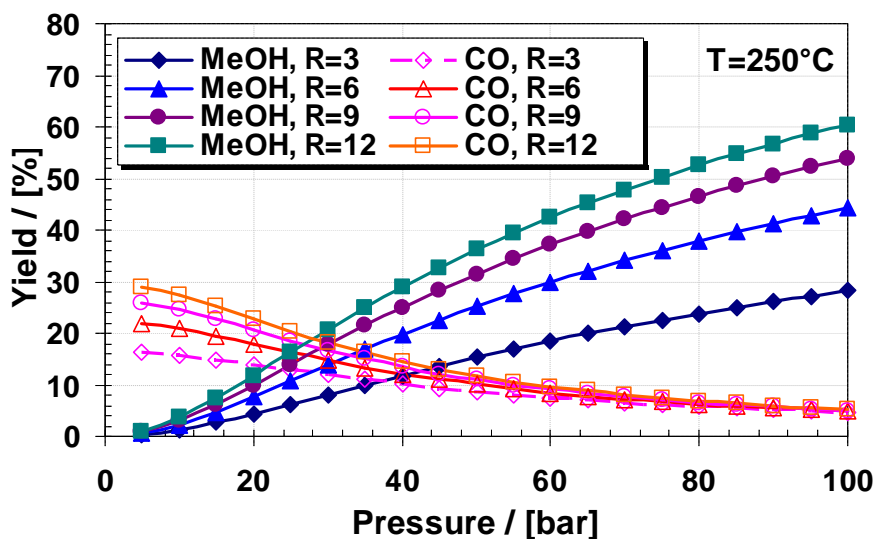
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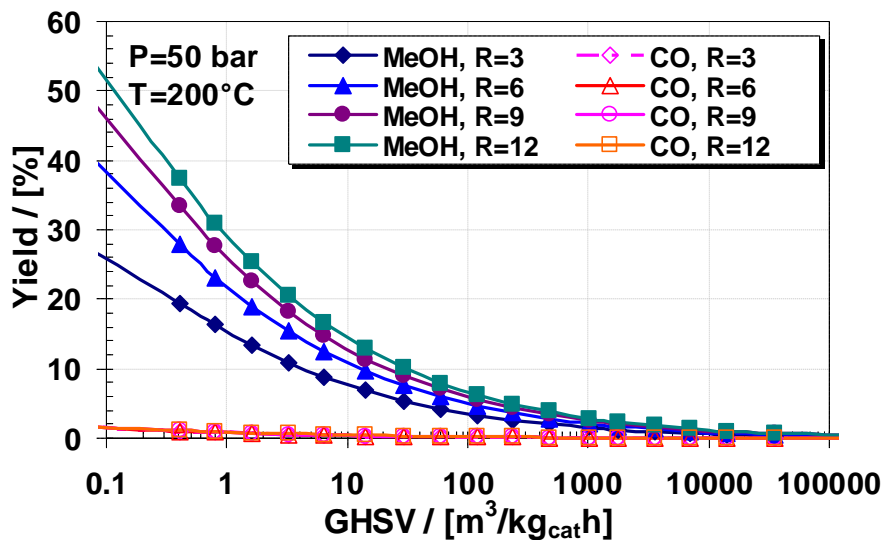


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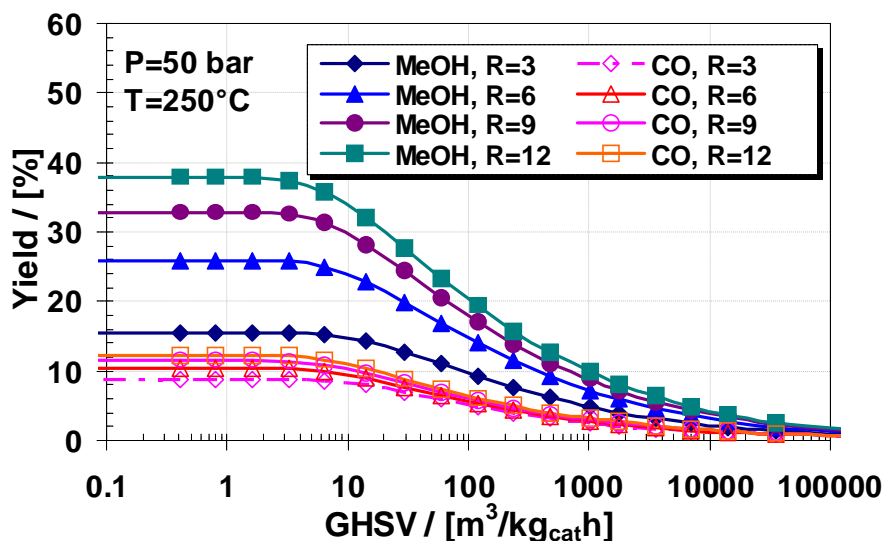
Figure 4. Effect of pressure on the MeOH and CO yield, at fixed temperature and various reactants ratios (simulated results)

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3 **Figure 5.** Effect of the catalyst loading on the MeOH and CO yield (simulated results), at
 4 various reactants ratios and fixed pressure and temperature (p=50 bar, T=200 and T=250 °C)

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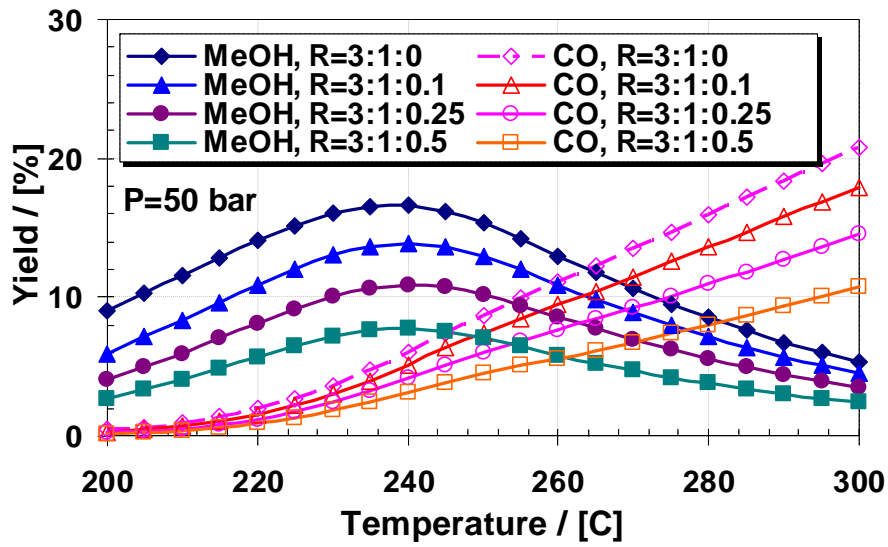


Figure 6. Effect of water presence (R=H₂:CO₂:H₂O) on the MeOH and CO yield, at fixed pressure and along a temperature range (simulated results)

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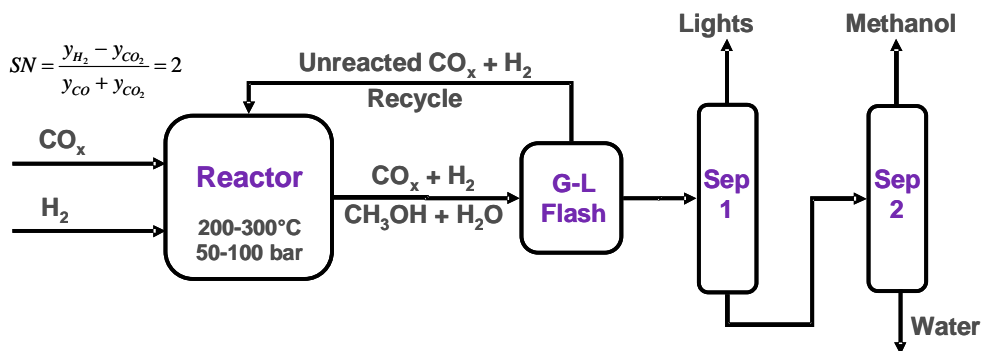


Figure 7. Generic processing scheme for methanol synthesis from syngas or by CO₂ hydrogenation

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