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Effect of operating conditions and effectiveness factor on hydrogenation of CO₂ to hydrocarbons

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HIGHLIGHTS

- Effectiveness factor and Thiele modulus for all reactions are calculated.
- Sensitivity analysis is performed via the mathematical modeling of reactor.
- Variations of reaction rates and reactor temperature are analyzed.
- Effect of temperature, pressure and space velocity on products are studied.

GRAPHICAL ABSTRACT

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ABSTRACT

The development of an efficient reactor for hydrocarbons (C₂–C₄) production through hydrogenation of CO₂, requires a deep understanding of the operating conditions effects. Subsequently, a model is proposed to analyze the reaction rates and investigate the sensitivity of hydrocarbons yield and products distribution to the variations of temperature, pressure and space velocity (SV). Besides, Thiele modulus and effectiveness factor are calculated for all of the reactions considered in the model. Results reveal that simultaneous occurrence of both endothermic reverse water gas shift (RWGS) and exothermic Fischer-Tropsch (FT) reactions, may be the main reason of temperature and rate fluctuations at the fixed-bed reactor inlet. In addition, increasing temperature and pressure, and decreasing SV can shift the process to produce more light olefins. Finally, sensitivity analysis demonstrates that reactor behavior is independent of the changes in pressure and SV at high temperature, which is an indication of high temperature dependency of this process. These findings can be effectively employed to achieve a better insight about appropriate operating conditions of hydrocarbons production via hydrogenation of CO₂.

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Nomenclature

A_c	cross sectional area of reactor [m^2]
a_v	specific surface area of catalyst pellet [$m^2 m^{-3}$]
a_{sH,H_2O}	inhibition coefficient for H_2O in shift reaction [-]
a_{FTi,H_2O}	inhibition coefficient for H_2O in Fischer-Tropsch reaction [-]
a_{DH,H_2O}	inhibition coefficient for H_2O in direct hydrogenation reaction [-]
b_{sH,CO_2}	inhibition coefficient for CO_2 in shift reaction [-]
b_{FTi,CO_2}	inhibition coefficient for CO_2 in Fischer-Tropsch reaction [-]
b_{DH,CO_2}	inhibition coefficient for CO_2 in direct hydrogenation reaction [-]
B_1	constant parameter in Eq. (33) [K]
B_2	constant parameter in Eq. (33) [-]
C_{pg}	specific heat of the gas at constant pressure [$J mol^{-1} K^{-1}$]
c_t	total concentration [$mol m^{-3}$]
D_0	reactor outside diameter [m]
D_f	furnace diameter [m]
D_p	particle diameter [m]
E_i	apparent activation energy [$kJ mol^{-1}$]
f_s	correction factor [-]
f_t	total gas molar flow rate in reactor [$mol s^{-1}$]
h_0	gas-catalyst heat transfer coefficient [$Wm^{-2} K^{-1}$]
K_{eq}	equilibrium constant of CO_2 shift reaction [-]
K_g	thermal conductivity of gas [$Wm^{-1} K^{-1}$]
K_w	thermal conductivity of reactor wall [$Wm^{-1} K^{-1}$]
$k_{i,0}$	pre-exponential factor in Arrhenius law [$mol s^{-1} g^{-1} MPa^{-1}$]
k_i	reaction rate constant for reaction “i” [$mol s^{-1} g^{-1} MPa^{-1}$]
k_{gi}	mass transfer coefficient between gas and solid phase for component “i” [$m s^{-1}$]
L	reactor length [m]
Mw	molecular weight [mol/kg]
m_c	catalyst weight [kg]
P_0	initial Pressure [Pa]
P	reactor pressure [Pa]
P_i	pressure of component “i” [Pa]

R	universal gas constant [$J mol^{-1} K^{-1}$]
Re	Reynolds number [-]
r_i	reaction rate of component “i” [$mol mol^{-1} s^{-1}$]
S_{v0}	space velocity at standard temperature and pressure (STP) [$m s^{-1}$]
S_v	space velocity at inlet condition [$m s^{-1}$]
T_0	initial gas temperature [K]
T	bulk gas phase temperature [K]
$T_{B,i}$	boiling point of component “i” [K]
T_f	temperature of furnace [K]
T_s	temperature of solid phase [K]
UA_t	overall heat transfer coefficient between jacket and gas phase [$Wm^{-2} K^{-1}$]
u_g	linear velocity of gas phase [$m s^{-1}$]
y_i	mole fraction of component “i” in the gas phase [$mol mol^{-1}$]
y_{is}	mole fraction of component “i” in the solid phase [$mol mol^{-1}$]
S_i	Sutherland constant of pure component “i” [K]
S_{ij}	geometric mean of S_i and S_j [K]
z	axial dimension [m]

Greek letters

η	catalyst effectiveness factor [-]
μ_g	viscosity of gas phase [$kg m^{-1} s^{-1}$]
ΔH_{fj}	enthalpy of formation of component j [$J mol^{-1}$]
ΔH_{298}	enthalpy of reaction at 298 K [$J mol^{-1}$]
ρ_p	density of catalyst [$kg m^{-3}$]
ρ_B	density of catalytic bed [$kg m^{-3}$]
ε_b	bed porosity [-]
θ_{ij}	constant parameter in Eq. (11.A) [-]

Abbreviations

DH	Direct Hydrogenation
FT	Fischer-Tropsch
SV	Space Velocity
HC	Hydrocarbon
LHHW	Langmuir-Hinshelwood-Hougen-Watson
RWGS	Reverse Water Gas Shift
RDS	Rate Determining Step
WGS	Water Gas Shift

Introduction

Due to the declining fossil fuel resources and environmental challenges related to the increase of anthropogenic CO_2 emissions, great attention has been paid to investigate various methods of using CO_2 as an energy source [1–4]. The feasible paths for CO_2 recycle are catalytic hydrogenation to hydrocarbons [5], methane [6,7], methanol and ethanol [8–11], dimethyl ether [12,13] and formic acid [14–16] (Scheme 1). Although some progresses have been achieved in this area [17,18], establishing competent and efficient paths of CO_2 hydrogenation for the production of value-added and “greener” fuels and chemicals has remained a critical subject. In other words, due to the thermodynamic stability of the CO_2

Scheme 1 – Products from hydrogenation of CO_2 with special emphasis on the scope of this study.

molecule, which results in difficult activation and high demand for energy, CO₂ transformation is an energy demanding process [19,20]. Hydrogen is a high-energy material, which can be employed as an appropriate reagent for CO₂ transformation. Hydrogen can be obtained from various sources including fossil fuels (steam reforming, auto thermal reforming and catalytic partial oxidation) [21,22], water splitting (electrolysis, thermolysis and photo-reduction) and biomass gasification [23–26]. In a potential scenario of low cost hydrogen generation from nuclear energy through off-peak electrolysis, production of light olefins as the most demanded raw chemicals from CO₂ may become a very attractive technology. However, efficient operating conditions for CO₂ transformation are still needed to be developed [27,28].

The by-products formation especially CO and H₂O via the strongly competing RWGS, results in the formation of less desired products and thereby low selectivity [29]. Thus, the production of only hydrocarbons cannot be accomplished easily [21,30]. To catalyze the reaction between CO₂ and H₂, surface sites responsible in binding and activation of CO₂ as well as appropriate sites for H₂ dissociation are needed to co-exist and cooperate. Activation of CO₂ via heterogeneous catalysis is often occurred in the presence of basic or amphoteric reducible oxides such as alumina, titania, ceria or zirconia, while metals are regularly used for H₂ dissociation [18,31]. In the case of direct hydrogenation (DH) of CO₂ to hydrocarbons, most of the reported catalysts are Fe-based materials [32–35]. The main reason behind the stimulating behavior of Fe lies in the fact that it can successfully catalyze both the RWGS and FT reactions [36].

In the present study, hydrogenation of CO₂ begins with a two-step mechanism [37–40]. The first step includes conversion of CO₂ to CO according to the RWGS reaction Eq. (1). Afterwards, the produced CO from RWGS involves in the FT reactions for hydrocarbons production according to Eq. (2). As proposed by Fiato et al. [41] the DH of CO₂ to hydrocarbons could be possible in the presence of iron carbide catalysts (Eq. (3)). Moreover, this reaction is suggested to be improved through CO₂ dissociative adsorption on catalyst active sites followed by the hydrogenation of adsorbed carbon species.

A few studies have been devoted to investigate the influence of operating conditions in CO₂ hydrogenation process [17]. For instance, Riedel et al. [42] investigated the effects of temperature and residence time on the CO₂ hydrogenation using a plug flow model. It was reported that light olefins and paraffins were the main products in the 300–400 °C temperature range and 1 MPa pressure. Besides, CO₂ conversion and CO yield increased at lower residence

times of about 12 g s cm^{−3}. In addition, direct CO₂ hydrogenation had a negligible role in hydrocarbons formation compared to the two-step mechanism with CO as intermediate. Rohde et al. [43] modeled a fixed-bed plug flow reactor to study the influence of temperature and hydrogen amount on CO₂ hydrogenation to hydrocarbons. Results showed that, a 50 °C increment in temperature led to higher conversions and consequently more hydrocarbons production. Moreover, the main impact of temperature elevation was increase in the formation of short-chain hydrocarbons. Indeed, the key role of reaction temperature was ascribed to shift RWGS equilibrium instead of increasing the reaction rates at the studied temperature range. Willauer et al. [40] studied the CO₂ hydrogenation in a fixed-bed reactor both experimentally and theoretically. It was revealed that FT was the rate-limiting step for olefin production through the two-step process consisting RWGS and FT reactions. It was indicated that maximum hydrocarbons yield in fixed-bed reactor was 38.4% at 0.000093 L g^{−1}s^{−1}, which was 49% higher with respect to that achieved in CSTR reactor, while it decreased to 13.6% when SV increased to 0.0015 L g^{−1}s^{−1}. Moreover, it was proved that increasing the reaction temperature, pressure and feed ratio all gave higher CO₂ conversion with enhanced hydrocarbons yield. Higher yield of hydrocarbons was usually accompanied by a distribution shifted toward long-chain products except in the case of increasing temperature. Simultaneous increases in the yield of hydrocarbons and olefin/paraffin ratio were obtained only when the reaction temperature was increased [17]. However, the parametric studies of this two-step process (RWGS-FT) have been restricted compared to those of WGS and FT reactions and more comprehensive investigations are required.

Exploiting mathematical models is one of the most important techniques for the assessment, development and design of appropriate reactors [44]. Sensitivity analysis using modeling can provide helpful information about the dependencies of reactor outputs to input variables while offering the trend of alterations along the reactor length [45].

The present research focuses on sensitivity analysis of the recently developed mathematical model [46] to analyze the simultaneously occurring RWGS and FT reaction rates. In addition to estimate the effectiveness factors for each reaction, the influences of operating conditions on the hydrocarbons yield are investigated as well. Accordingly, the validated model in the previous study [46] is used to accomplish the

Table 1 – Reactor properties and operating conditions.

Parameter	Value	Unit
Reactor length	0.6	m
Reactor diameter	0.8 e −2	m
H ₂ /CO ₂ molar ratio	3	–
Feed gas temperature	300–350	°C
Reactor Pressure	1–20	MPa
SV	0.5–2	ml/g _{cat} .h

sensitivity analysis. This systematic approach helps distinguishing the most influential factors to achieve higher hydrocarbons yield.

Sensitivity analysis

Sensitivity analysis helps estimating how sensitive the model outputs are to changes in input variables. This can help us determining the key factors as well as their impacts on the process [45]. Accordingly, the reactor specifications and the range of operating conditions are depicted in Table 1. The governing equations of the previously developed model and the reactions presented in Table 2 are employed to accomplish sensitivity analysis. In this regard, the influence of change in one input variable on the outputs is observed while other variables are kept constant to analyze the effect of each parameters independently. This is called one-at-a-time technique and is used when we need to indicate the most important parameter while providing appropriate insight about the developed model.

Indeed, hydrocarbons yield and distribution, which are the model outputs, are the most significant factors in evaluating the performance of CO₂ hydrogenation to hydrocarbons production. At first, reaction time step is considered as the selected input variable to assess the sensitivity of reactor temperature, RWGS, FT and CO rates, which helps finding a better insight about the progress of reactions along the reactor. Afterwards, feed temperature, pressure, and SV were considered separately as input variables and sensitivity analysis accomplished to estimate their effects on hydrocarbons yield and distribution in the reactor outlet. Fig. 1 illustrates the schematic of volume element in the fixed-bed reactor used in modeling.

Fig. 1 – Volume element of the fixed-bed reactor.

The species and energy balances are represented as follows:

$$\frac{dy_1}{dz} = -\Delta t A_c (1 - \epsilon_b) \rho_B (\eta_1 r_1 + 3\eta_2 r_2 + 4\eta_3 r_3 + 5\eta_4 r_4 + 6\eta_5 r_5 + 7\eta_6 r_6 + 8\eta_7 r_7 + 9\eta_8 r_8 + \eta_9 r_9) \quad (4)$$

$$\frac{dy_2}{dz} = -\Delta t A_c \rho_B (\eta_1 r_1 + \eta_9 r_9) \quad (5)$$

$$\frac{dy_3}{dz} = \Delta t A_c (\eta_1 r_1 - \eta_2 r_2 - 2\eta_3 r_3 - 2\eta_4 r_4 - 3\eta_5 r_5 - 3\eta_6 r_6 - 4\eta_7 r_7 - 4\eta_8 r_8) \quad (6)$$

$$\frac{dy_4}{dz} = \Delta t A_c \rho_B (\eta_2 r_2) \quad (7)$$

$$\frac{dy_5}{dz} = \Delta t A_c \rho_B (\eta_3 r_3) \quad (8)$$

$$\frac{dy_6}{dz} = \Delta t A_c \rho_B (\eta_4 r_4) \quad (9)$$

$$\frac{dy_7}{dz} = \Delta t A_c \rho_B (\eta_5 r_5) \quad (10)$$

$$\frac{dy_8}{dz} = \Delta t A_c \rho_B (\eta_6 r_6) \quad (11)$$

$$\frac{dy_9}{dz} = \Delta t A_c \rho_B (\eta_7 r_7) \quad (12)$$

Table 2 – System of reactions.

$$\frac{dy_{10}}{dz} = \Delta t A_c \rho_B (\eta_8 r_8) \quad (13)$$

$$\frac{dy_{11}}{dz} = \Delta t A_c \rho_B (\eta_1 r_1 + \eta_2 r_2 + 2\eta_3 r_3 + 2\eta_4 r_4 + 3\eta_5 r_5 + 3\eta_6 r_6 + 4\eta_7 r_7 + 4\eta_8 r_8 + \eta_9 r_9) \quad (14)$$

Surface concentrations can be calculated using mass transfer coefficients.

$$y_{S1} = y_1 - \frac{\rho_B (rs_1 + 3rs_2 + 4rs_3 + 5rs_4 + 6rs_5 + 7rs_6 + 8rs_7 + 9rs_8 + rs_9)}{a_v k g_1 P / RT} \quad (15)$$

$$y_{S2} = y_2 - \frac{\rho_B (rs_1 + rs_9)}{a_v k g_2 P / RT} \quad (16)$$

$$y_{S3} = y_3 + \frac{\rho_B (rs_1 - rs_2 - 2rs_3 - 2rs_4 - 3rs_5 - 3rs_6 - 4rs_7 - 4rs_8)}{a_v k g_3 P / RT} \quad (17)$$

$$y_{S4} = y_4 + \frac{\rho_B (rs_2)}{a_v k g_4 P / RT} \quad (18)$$

$$y_{S5} = y_5 + \frac{\rho_B (rs_3)}{a_v k g_5 P / RT} \quad (19)$$

$$y_{S6} = y_6 + \frac{\rho_B (rs_4)}{a_v k g_6 P / RT} \quad (20)$$

$$y_{S7} = y_7 + \frac{\rho_B (rs_5)}{a_v k g_7 P / RT} \quad (21)$$

$$y_{S8} = y_8 + \frac{\rho_B (rs_6)}{a_v k g_8 P / RT} \quad (22)$$

$$y_{S9} = y_9 + \frac{\rho_B (rs_7)}{a_v k g_9 P / RT} \quad (23)$$

$$y_{S10} = y_{10} + \frac{\rho_B (rs_8)}{a_v k g_{10} P / RT} \quad (24)$$

$$y_{S11} = y_{11} + \frac{\rho_B (rs_1 + rs_2 + 2rs_3 + 2rs_4 + 3rs_5 + 3rs_6 + 4rs_7 + 4rs_8 + rs_9)}{a_v k g_{11} P / RT} \quad (25)$$

The energy balance can be written as follows:

$$Q = \eta_1 r_1 \Delta H_{f1} + \eta_2 r_2 \Delta H_{f2} + \eta_3 r_3 \Delta H_{f3} + \eta_4 r_4 \Delta H_{f4} + \eta_5 r_5 \Delta H_{f5} + \eta_6 r_6 \Delta H_{f6} + \eta_7 r_7 \Delta H_{f7} + \eta_8 r_8 \Delta H_{f8} + \eta_9 r_9 \Delta H_{f9} \quad (26)$$

$$\frac{dT}{dz} = \frac{\Delta t A_c}{f_t C p_g} (\rho_B Q + U A_t (T_j - T)) \quad (27)$$

Correlations to calculate physical properties and other parameters are represented in Appendix.

According to the study by Wolf et al. [47], effectiveness factor of RWGS reaction can vary with temperature, pressure,

particle size and H_2/CO_2 ratio. In addition, effectiveness factor of FT reaction, was reported to change in the range of 0.095–0.13 over iron catalysts [48], which can be remarkably reduced by temperature increase. Therefore, the procedure that was reported by Gottifredi et al. [49,50] has been used in the model analysis for the system of equations in Table 2.

The species balance within the catalyst can be represented by Eq. (28) [49].

$$r_A = \frac{D_A}{x^m} \frac{d}{dx} \left(x^m \frac{dC_A}{dx} \right) \quad (28)$$

where m is the geometrical factor that can be 0, 1 or 2 for slab, cylindrical and spherical catalyst particles. Accordingly, for gas component A in the presence of a spherical particle Eq. (29) is valid.

$$r_A = \frac{D_A}{RT} \frac{1}{x^2} \frac{d}{dx} \left(x^2 \frac{dP_A}{dx} \right) \quad (29)$$

x is the coordinate through catalyst. A is CO_2 in the first and the last reactions while it is assumed to be CO in the rest of the reactions. Mathematical manipulations of differential equations result in the following equation [51,52]:

$$\frac{dP_A}{dx} = \sqrt{2} \left(\int r_A dP_A \right)^{1/2} \quad (30)$$

By substituting r_A with the reaction rates in Table 3 and relating the partial pressures of each species to P_A via stoichiometric coefficients of reactions, effectiveness factor can be calculated using Eq. (31) [53]:

$$\eta_A = \frac{m+1}{\phi^2} \left(\frac{dC_A}{dx} \right)_{x=R} \quad (31)$$

$$\phi^2 = \frac{r_{As} R^2}{D_A C_{As}} \quad (32)$$

where ϕ is Thiele modulus, R is the characteristic length of the porous catalyst and r_{As} is the reaction rate at catalyst surface.

The governing equations have been solved via MATLAB software using the algorithm proposed in our previous paper [46], and the effectiveness factors and Thiele modulus are calculated. Fig. 2 demonstrates the effectiveness factor versus Thiele modulus for 8 reactions. Reaction 9 was considered to be of negligible importance since CO_2 can't be transferred directly into hydrocarbons due to high stability.

The changes of effectiveness factor with reactor length are depicted in Fig. 3. It can be observed that η is considerably higher for reaction 1 (Fig. 3 (a)) compared to other reactions (Fig. 3 (b)). The values of approximately 0.23, 0.014, 0.013, 0.022, 0.023, 0.031, 0.020, 0.032 are calculated at the reactor outlet for reactions 1 to 8, respectively.

Results and discussion

Based on the kinetic parameters obtained via optimization through the proposed model in our previous study [46], the analysis of reaction rates as well as sensitivity analysis are carried out to give a more detailed understanding of the whole

Table 3 – Reaction rates [46].

Reactions	Rate equations
CO ₂ shift	$r_1 = k_{sH} \frac{P_{CO_2} P_{H_2} - P_{CO} P_{H_2O} / K_{eq}}{P_{CO} + a_{sH,H_2O} P_{H_2O} + b_{sH,CO_2} P_{CO_2}}$
FT (CH ₄)	$r_2 = k_{FTCH_4} \frac{P_{CO} P_{H_2}}{P_{CO} + a_{FTCH_4,H_2O} P_{H_2O} + b_{FTCH_4,CO_2} P_{CO_2}}$
FT (C ₂ H ₄)	$r_3 = k_{FTC_2H_4} \frac{P_{CO} P_{H_2}}{P_{CO} + a_{FTC_2H_4,H_2O} P_{H_2O} + b_{FTC_2H_4,CO_2} P_{CO_2}}$
FT (C ₂ H ₆)	$r_4 = k_{FTC_2H_6} \frac{P_{CO} P_{H_2}}{P_{CO} + a_{FTC_2H_6,H_2O} P_{H_2O} + b_{FTC_2H_6,CO_2} P_{CO_2}}$
FT (C ₃ H ₆)	$r_5 = k_{FTC_3H_6} \frac{P_{CO} P_{H_2}}{P_{CO} + a_{FTC_3H_6,H_2O} P_{H_2O} + b_{FTC_3H_6,CO_2} P_{CO_2}}$
FT (C ₃ H ₈)	$r_6 = k_{FTC_3H_8} \frac{P_{CO} P_{H_2}}{P_{CO} + a_{FTC_3H_8,H_2O} P_{H_2O} + b_{FTC_3H_8,CO_2} P_{CO_2}}$
FT (C ₄ H ₈)	$r_7 = k_{FTC_4H_8} \frac{P_{CO} P_{H_2}}{P_{CO} + a_{FTC_4H_8,H_2O} P_{H_2O} + b_{FTC_4H_8,CO_2} P_{CO_2}}$
FT (C ₄ H ₁₀)	$r_8 = k_{FTC_4H_{10}} \frac{P_{CO} P_{H_2}}{P_{CO} + a_{FTC_4H_{10},H_2O} P_{H_2O} + b_{FTC_4H_{10},CO_2} P_{CO_2}}$
DH	$r_9 = k_{DH} \frac{P_{CO_2} P_{H_2}}{P_{CO} + a_{DH,H_2O} P_{H_2O} + b_{DH,CO_2} P_{CO_2}}$

process. The model considered seven different reaction rates for seven different hydrocarbons as the products of CO₂ hydrogenation that made the model capable for the estimation of hydrocarbons distribution in details.

Analysis of reaction rates

Due to the coexistence of endothermic RWGS and exothermic FT reactions, CO formation and consumption occur simultaneously, and a thermal conflict exists since CO formation in RWGS reaction requires high temperatures while CO hydrogenation to hydrocarbons in FT reactions takes place at lower temperatures. Besides, the magnitude of the reaction rates and the time of their occurrence are of paramount importance in determining the reactor performance. Therefore, a detailed analysis is required to provide a comprehensive insight about the dependency of the rates to the reaction time and temperature. We are indeed using a steady-state model, the time described in the paper is the residence time. In fact, this analysis was accomplished to

find the required residence time to complete this process at specific inlet operating conditions.

The magnitude of the RWGS and FT reaction rates can be compared to determine the limiting step of the whole process. Estimations show that initially ($t \approx 0$), the maximum initial RWGS rate is $2.1 \times 10^5 \text{ s}^{-1}$ over K–Fe/Al₂O₃ at 300 °C and 1 MPa which is in agreement with that reported by Willauer et al. [40] ($3.5 \times 10^5 \text{ s}^{-1}$) for RWGS reaction in the presence of K–Mn–Fe/Al₂O₃ at 300 °C and 1.8 MPa. Moreover, the evaluated FT reaction rate is 0.017 s^{-1} which is almost in accordance with 0.032 s^{-1} that reported by Willauer et al. [40] for FT reaction. However, the maximum FT reaction rate occurs after 70 s, which is considerably different from 2 s in the mentioned study and can be attributed to different reactor volumes and catalysts. Therefore, RWGS reaction is accomplished with 7 orders of magnitude faster than the maximum FT rate, which indicates that FT reaction controls the overall rate of the process as the rate determining step (RDS). According to this difference, the normalized reaction rates (rates divided by the maximum (initial) rate of RWGS reaction) are employed for further analysis.

Since RWGS reaction is endothermic and no heat source is available (wall temperature is kept constant using furnace), reactor temperature (Fig. 4) initially decreases to provide the required heat for this reaction. Subsequently, the rate of RWGS reaction (Fig. 5) decreases continuously while the rate of FT reaction (Fig. 6) increases sharply due to the provided CO from RWGS reaction. Indeed, the CO consumption in FT reactions helps shifting the equilibrium to the right side [46]. Meanwhile, production rate of CO via RWGS reaction is higher than its consumption rate through FT reactions, resulting in a steep slope in the net CO rate as can be observed in Fig. 7.

As the residence time increases, exothermic FT reaction proceeds that leads to an increase in reactor temperature and a minimum in Fig. 4 occurs as a result. Therefore, RWGS reaction can proceed again via the provided heat of FT reaction and the rate of RWGS increases, which leads to the occurrence of a minimum in Fig. 5.

Consequently, more CO is produced and the progress of FT reaction continues with a slower slope as a result of increased

Fig. 2 – Effectiveness factor versus Thiele modulus.

Fig. 3 – Effectiveness factor versus reactor length.

Fig. 4 – Reactor temperature versus residence time at different wall temperatures and 1 MPa.

Fig. 6 – Normalized FT rate versus residence time at different temperatures and 1 MPa.

Fig. 5 – Normalized RWGS rate versus residence time at different temperatures and 1 MPa.

Fig. 7 – Normalized CO rate versus residence time at different temperatures and 1 MPa.

temperature which is a drawback for exothermic FT reaction. Meanwhile, higher CO production rate than its consumption rate leads to a slow slope in the net rate of CO amount.

After several seconds, the progress of RWGS reaction reaches to its maximum value and the maximum amount of CO is produced; Afterwards, the rate of RWGS reaction starts

decreasing as can be observed in Fig. 5. This is the time when maximum equilibrium constant (Eq. (33)) occurs which are illustrated for different temperatures in Fig. 8 (a) to (c). Therefore, due to equilibrium limitations of this reversible reaction, it does not proceed further and rate of RWGS reaction reaches to zero. This point was defined by Herranz et al. [54] as “approach to equilibrium”, which is depicted in Fig. 8 (d). In addition, the rate of production and consumption of CO is equal at equilibrium, which results in the net CO rate of zero. Inevitably, FT reaction rate diminishes (Fig. 6) as a result of CO absence leading to less released heat and consequently temperature decrease (Fig. 4). Equilibrium constant and “approach to equilibrium” are defined according to Eq. (33) and (34).

$$\log(K_{eq}) = \left(\frac{B_1}{T} - B_2 \right) \quad (33)$$

$$\text{“approach to equilibrium”} = \frac{P_{CO}P_{H_2O}}{P_{CO_2}P_{H_2}} \times \frac{1}{K_{eq}} \quad (34)$$

where B_1 and B_2 are constants calculated based on the ABC algorithm and exhibit the values of 1700 and 1.5, respectively. However, T is the reaction temperature, which is a time dependent parameter.

This phenomenon is more sensible at higher temperatures compared to 300 °C as can be observed in Figs. 4–7. Accordingly, all of the normalized reaction rates (RWGS, FT and CO) are depicted in Fig. 9 for better comparison of the progress of the process based on the above explanations.

Effect of operating conditions

The substantial influences of operating conditions on the production of different hydrocarbons through hydrogenation of CO₂ [55–59] have motivated us to accomplish this research. Therefore, the impact of temperature, pressure and SV are investigated as follows:

Fig. 9 – Comparison of the normalized reaction rates at 350 °C.

Fig. 8 – Equilibrium constants at (a) 300 °C (b) 325 °C and (c) 350 °C and (d) approach to equilibrium at 1 MPa.

Effect of temperature

It was indicated that the effect of operating conditions on hydrocarbons production efficiency is of great importance [17]. According to the temperature dependencies of the reaction rates, products distributions change with temperature. The trajectories of hydrocarbons yield in terms of $100 \times (\text{mol/mol feed})$ along the reactor length are presented in Fig. 10 (a) to 10 (g) as temperature changes from 300 to 350 °C. It can be observed that the trend of each component yield with temperature alterations, differ from each other which can be ascribed to the nature of the reactions which in turn are influenced by the determined kinetic parameters [46]. Generally, Fig. 10 (a) to 10 (g) illustrate that hydrocarbon production increases sharply for all components at the reactor entrance, which is referred to CO production via RWGS reaction and then slightly increases in the rest of the reactor and finally remains constant due to gradually finishing CO and equilibrium limitations of RWGS reaction. Although this trend is almost the same for all components at a distinct temperature, the influence of temperature is different for each one, which is shown with different arrows.

In order to provide more detailed comparison of hydrocarbons distribution with temperature changes, final hydrocarbons yield at the reactor outlet ($L = 0.6 \text{ m}$) and the amount of their changes with respect to the values at 300 °C are depicted in Fig. 11 (a) and 11 (b), respectively.

Relative changes in hydrocarbon yield with respect to

$$\text{temperature} = \frac{(y_T - y_{300\text{ }^\circ\text{C}})}{y_{300\text{ }^\circ\text{C}}} \times 100 \quad (35)$$

According to Fig. 11 (a), yields of C_2H_4 , C_2H_6 and C_3H_6 increase with temperature rise while those of CH_4 , C_3H_8 , C_4H_{10} and C_4H_8 decrease. It can be observed in Fig. 11 (b) that these changes are more obvious for the increment in C_2H_4 and C_3H_6 and decline in C_3H_8 , C_4H_{10} and C_4H_8 yields. It can be inferred that temperature rise has a positive effect for the production of light olefins (i.e. C_2H_4 and C_3H_6) while imposes inverse effect on the yields of heavier molecules in the range of 300–350 °C which also can be observed in Fig. 10. The experimental investigations of Riedel et al. [42] also showed that products included 90% of primary olefins when temperature increased, and at higher temperatures (about 400 °C) formation of long-chain and heavier hydrocarbons was not the dominant trend.

Besides, CH_4 is the only light hydrocarbon molecule that undergoes reduction of yield with temperature increase. The same trend for CH_4 formation was also addressed by Owen et al. [60] between 230 and 330 °C. They observed high CH_4 selectivity at low temperatures, while at high temperatures product distribution shifted to C_2+ hydrocarbons.

This fact is more pronounced in Fig. 12 that depicts the olefins and paraffins yield as a function of their carbon number. However, the economic issues and the catalyst

Fig. 10 – Hydrocarbons yield along the reactor length at different temperatures after 24 h at 1 MPa.

Fig. 11 – (a) Effect of temperature on hydrocarbons yield at the reactor outlet and (b) The amount of changes in hydrocarbons yield at different temperatures with respect to $T = 300\text{ }^{\circ}\text{C}$ at 1 MPa.

deactivation related to the temperature increase should also be considered in order to find the optimum temperature.

It can be observed that in contrast to light hydrocarbons with 2 carbons, yield of hydrocarbons with 4 carbons experiences considerable decrease as temperature elevates to 350 °C. However, saturated and unsaturated hydrocarbons with 3 carbons behave differently with temperature increase and the olefin (C₃H₆) yield increases sharply contrary to that of its corresponding paraffin (C₃H₈).

Indeed, the breakage of carbon-carbon chain (cracking effect) seems to be serious at high temperatures, leading to higher CH₄ concentration in the product. It should be mentioned that the above explanations are valid for the

proposed model while disregarding catalyst deactivation since our range of study is less than 360 °C. However, at elevated temperatures the dependence of hydrocarbons yield on temperature is not so obvious in the compromise between higher driving force in activity and larger tendency of deactivation due to inert carbon deposition. In other words, the enhancement of temperature leads to higher CO₂ sorption while facilitating the elimination of hydrogen in terminals of carbon-carbon compounds. This can highly increase the growth of carbon chains on the surface and consequently distorts the reaction pathway to Boudouard reaction (Eq. (36)). Therefore, hydrogen concentration should be adjusted appropriately to avoid this phenomenon.

Fig. 12 – Effect of temperature on the yield of (a) olefins and (b) paraffins at 1 MPa.

Effect of pressure

Since RWGS reaction is reversible, the pressure elevation should have no effect on CO_2 conversion unless the CO produced via the RWGS reaction is subsequently consumed by the FT reaction. Regarding to the dependencies of the reaction rates to the partial pressures of components, products distribution have various trends. The yields of hydrocarbons at the reactor outlet ($L = 0.6 \text{ m}$) are presented in Fig 13 (a) and 13 (b) as pressure changes from 0.5 to 20 MPa. Fig. 13 (a) demonstrates that hydrocarbons are produced according to the order: $\text{C}_3\text{H}_6 > \text{C}_2\text{H}_4 > \text{CH}_4 > \text{C}_4\text{H}_8 > \text{C}_2\text{H}_6 >$

$\text{C}_3\text{H}_8 >$ and C_4H_{10} at all pressures and pressure rise cannot alter this order. It can be observed that, at higher pressures, especially 20 MPa, lighter olefins (C_3H_6 and C_2H_4) undergo higher increase in their yields.

Besides, the yields of almost all components (except C_4H_{10}) increase with pressure elevation to 5 MPa, while at 10 MPa remarkable reductions happen in the yields of C_4H_8 and C_4H_{10} which are heavier hydrocarbons. This trend can be observed in Fig. 13 (b) which shows the relative changes of yields at 2, 5, 10 and 20 MPa with respect to those at 0.5 Pa.

Relative change in hydrocarbons yield with respect to

$$\text{pressure} = \frac{(y_P - y_{0.5\text{MPa}})}{y_{0.5\text{MPa}}} \times 100 \quad (37)$$

Fig. 13 – (a) Effect of pressure on hydrocarbons yield at the reactor outlet and (b) the amount of changes in hydrocarbons yield at different pressures with respect to $P = 0.5$ MPa at 300 °C.

Accordingly, pressure increase has a considerable positive effect on the yields of C₃H₆ and C₂H₄, which are light olefins. In contrast, pressure increase has opposing impact on yields of heavier hydrocarbons. Since hydrocarbons yield depends on both pressure and temperature, Fig. 14 is presented to demonstrate the interaction of these two important parameters on the total hydrocarbons yield.

Fig. 14 depicts the influence of pressure at different temperatures on the total hydrocarbons yield. It shows that hydrocarbons yield is more pressure dependent at lower temperatures while at higher temperatures, pressure rise has no considerable improving effect. As can be observed in Table 3, reaction rates are dependent on both partial pressures and

reaction constants k_i , which can be defined by Arrhenius law as presented in Eq. (38).

$$k_i = k_{i,0} \exp\left(-\frac{E_i}{RT}\right) \quad (38)$$

Therefore, as temperature increases k_i increases exponentially while partial pressures undergoes a linear trend with pressure rise. Clearly, the low dependency of hydrocarbons yield to partial pressure at high temperatures can be ascribed to this phenomenon. As indicated by Owen et al. [60] pressure independency may be attributed to the saturation type of Langmuir-Hinshelwood (LH) rate expressions.

Fig. 14 – Effect of pressure at different temperatures on the total hydrocarbons yield at 1 MPa.

Fig. 15 – Effect of SV on hydrocarbons yield at different temperatures after 24 h at 1 MPa.

Fig. 16 – Effect of SV on hydrocarbons yield at different pressures after 24 h at 300 °C.

Effect of space velocity

The effect of SV on CO and hydrocarbons yield at different temperatures are illustrated in Fig. 15. It can be observed that at low temperatures, especially 300 °C, the decrease of hydrocarbons yield with increment in SV is more remarkable compared to that of higher temperatures.

As explained in "Effect of pressure" section, pressure plays an important role in hydrocarbons yield. Therefore, the influence of SV at different pressures are examined and results are illustrated in Fig. 16.

It can be observed in Fig. 16 that, in a distinct SV, pressure increase leads to enhanced hydrocarbons yield and this increase is more considerable at higher space velocities. It can be also inferred that, at a constant pressure, hydrocarbons yield reduced and this reduction occurs clearly at higher space velocities. Besides, it can be deduced that, pressure dependency is less at higher space velocities since the hydrocarbons yield doesn't change noticeably compared to that at low pressure ($P = 2$ MPa).

As a whole, it can be inferred that increasing temperature and pressure and decreasing SV have positive effects on hydrocarbons yield only to some extent and further improvement cannot be achieved by altering the operating conditions. This is an indication of "approach to equilibrium" as depicted in Fig. 7. For this reason, the overall yield becomes less sensitive to temperature at higher values [60]. Besides, the partial pressures of the reacting components decrease and finally the production of water as a by-product can hamper the reactions through kinetic inhibition limits [42].

Conclusions

Following our previous modeling and optimization investigations, sensitivity analysis was accomplished to provide a comprehensive insight about the operating conditions of the process. Moreover, Thiele modulus and effectiveness factors

for all the reactions were estimated along with concentration predictions. Consequently, reaction rates and reactor temperature were analyzed at different time steps. It was concluded, that the RWGS reaction occurred rapidly to produce CO, which was consumed gradually in FT reactions to achieve hydrocarbons. Reaction rate analysis revealed that, co-occurrence of both endothermic RWGS along with exothermic FT reactions resulted in temperature conflictions. This phenomenon was possibly the main reason of the temperature and rate variations and instabilities at the initial time steps of the reaction.

It was proved that inlet temperature played the key role in determining equilibrium shift and subsequently reaction rates. Results revealed that, light olefins (i.e. C_3H_6 and C_2H_4) were the most important products of this process while hydrocarbons exhibiting 4 carbons were produced less. It was confirmed that CO and hydrocarbons yield were highly temperature dependent whereas the influence of other parameters such as pressure and SV were less noticeable. In other words, at high temperatures, hydrocarbons yield became less sensitive to the variations of pressure and SV; therefore, the process was almost solely temperature dependent. However, at mild temperature (i.e. around 300 °C), pressure rise and SV reduction had positive effects on hydrocarbons yield. Moreover, it was indicated that

pressure had improving effect only to some extent, and further increase in pressure beyond 10 MPa had no remarkable positive influence on hydrocarbons yield. As a whole, it was concluded that this process was considerably temperature dependent while pressure and SV had enhancing impacts on hydrocarbons yield only at low temperatures. These analyses can be exploited to obtain a comprehensive overview about effective parameters about hydrocarbons production through CO_2 hydrogenation. However, further studies about reactor configurations to assess the effect of water along with hydrogen permeation are also required to find the best conditions of this process, which are ongoing.

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Appendix

Table A.1 Auxiliary equations of the proposed model.

$$UA_t = \left(\frac{\ln \frac{D_f}{D_o}}{2\pi K_w L} + \frac{1}{h_o \pi D_o L} \right)^{-1} \quad (1.A)$$

$$h_o = \frac{K_g}{D_p} \left(2.58 Re^{1/3} Pr^{1/3} + 0.094 Re^{0.8} Pr^{0.4} \right) \quad (2.A)$$

$$Re = \frac{\rho_g u_g D_p}{\mu_g} \quad (3.A)$$

$$Pr = \frac{C_{pg} \mu_g}{K_g} \quad (4.A)$$

$$u_g = \frac{m_c S_v}{A_c \epsilon_b} \quad (5.A)$$

$$\epsilon_b = 0.38 + 0.073 \left(1 - \frac{\left(\frac{D_o}{D_p} - 2 \right)^2}{\left(\frac{D_o}{D_p} \right)^2} \right) \quad (6.A)$$

Physical properties

$$\rho_g = \frac{MwP}{RT} \quad (7.A)$$

$$\rho_B = (1 - \epsilon_B) \rho_p \quad (8.A)$$

$$C_{pg,i} = \sum_{i=1}^{N_s} y_i C_{pg,i} \quad (9.A)$$

$$K_g = \sum_{i=1}^N \frac{y_i K_{g,i}}{\sum_{j=1}^N y_j \theta_{ij}} \quad (10.A)$$

$$\theta_{ij} = \frac{1}{4} \times \left[1 + \left[\left(\frac{\mu_i}{\mu_j} \right) \left(\frac{Mw_j}{Mw_i} \right)^{\frac{3}{4}} \left(\frac{T + S_i}{T + S_j} \right) \right]^{\frac{1}{2}} \right]^2 \times \frac{(T + S_{ij})}{(T + S_i)} \quad (11.A)$$

$$f_s = \begin{cases} 1 & \text{nonpolar} \\ 0.733 & \text{polar} \end{cases} \quad S_i = \begin{cases} 79 & \text{for } H_2 \text{ only} \\ 1.5 \times T_{B,i} & \text{for other components} \end{cases} \quad (12.A)$$

$$\mu_g = \sum_{i=1}^N \frac{y_i \mu_{g,i}}{\sum_{j=1}^N y_j \sqrt{Mw_j / Mw_i}} \quad (13.A)$$

$$S_v = S_{v0} \times \frac{T_0}{273.15} \times \frac{101325}{P_0} \quad (5.A)$$

$$C_{pg,i} = (A1_i + A2_i \times T + A3_i \times T^2 + A4_i \times T^{-2}) \times R \quad (9.A)$$

$$K_{g,i} = \frac{B1_i T^{B2_i}}{1 + \frac{B3_i}{T} + \frac{B4_i}{T^2}} \quad (10.A)$$

$$S_{ij} = f_s \sqrt{S_i S_j} \quad (11.A)$$

$$\mu_{g,i} = \frac{C1_i T^{C2_i}}{1 + C3_i + \frac{C4_i}{T^2}} \quad (13.A)$$

Table A.2 Constants for gas species corresponding to Eq. (9.A) [61].

Component	A1	A2 $\times 10^{-3}$	A3	A4 $\times 10^{-5}$
H ₂	3.249	0.422	0	0.083
CO ₂	5.457	1.045	0	−1.157
CO	3.376	0.557	0	−0.031
CH ₄	1.702	9.081	−2.164	0
C ₂ H ₄	1.424	14.394	−4.392	0
C ₂ H ₆	1.131	19.225	−5.561	0
C ₃ H ₆	1.637	22.706	−6.915	0
C ₃ H ₈	1.213	28.875	−8.824	0
C ₄ H ₈	1.967	31.630	−9.873	0
C ₄ H ₁₀	1.935	36.915	−11.402	0
H ₂ O	3.470	1.450	0	0.21

Table A.3 Constants for gas species corresponding to Eq. (10.A) [62].

Component	B1	B2	B3	B4	T _B (K)
H ₂	0.002653	0.7452	12	0	20.4
CO ₂	3.69	−0.3838	964	1860000	194.7
CO	0.00059882	0.6863	57.13	501.92	81.7
CH ₄	8.3983e-6	1.4268	−49.654	0	111.7
C ₂ H ₄	8.6806e-6	1.4559	299.72	−29403	169.4
C ₂ H ₆	0.000073869	1.1689	500.73	0	184.5
C ₃ H ₆	0.0000449	1.2018	421	0	225.4
C ₃ H ₈	−1.12	0.10972	−9834.6	−7535800	231.1
C ₄ H ₈	0.000096809	1.1153	781.82	0	266.9
C ₄ H ₁₀	0.051094	0.45253	5455.5	1979800	272.7
H ₂ O	6.2041e-6	1.3973	1.3973	0	373.2

Table A.4 Constants for gas species corresponding to Eq. (13.A) [61].

Component	C1	C2	C3	C4
H ₂	1.79e-7	0.685	−0.59	140
CO	1.1127e-6	0.5338	94.7	0
CO ₂	2.148e-6	0.46	290	0
CH ₄	5.2546e-7	0.59006	105.67	0
C ₂ H ₄	2.0789e-6	0.4163	352.7	0
C ₂ H ₆	2.5906e-7	0.67988	98.902	0
C ₃ H ₆	7.73919e-7	0.5423	263.73	0
C ₃ H ₈	4.9054e-8	0.90125	0	0
C ₄ H ₈	6.9744e-7	0.5462	305.25	0
C ₄ H ₁₀	3.4387e-8	0.94604	0	0
H ₂ O	1.7096e-8	1.1146	0	0

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