Supplementary information

Derivation of the equation for calculation of components' concentrations in the outlet stream.

Considering two main reaction – carbon dioxide hydrogenation to methanol and RWGS – outlet flowrate of each component can be determined in the following way:

$$F_{outi} = F_{ini} - \vartheta_{MeOHi} \cdot x_{MeOH} \cdot F_{ini} - \vartheta_{RWGSi} \cdot x_{RWGS} \cdot F_{ini} \tag{1}$$

where:
F_{ini} – i-component inlet flowrate, Nml/min;
F_{outi} – i-component outlet flowrate, Nml/min
ϑ_{MeOHi} and ϑ_{RWGSi} – stoichiometric coefficient of i-component for carbon dioxide hydrogenation and RWGS reactions respectively;
x_{MeOH} and x_{RWGS} – reaction extent values for carbon dioxide hydrogenation and RWGS reactions respectively.

The overall outlet flowrate will be thus determined as:

$$F_{out\Sigma} = \sum_{i \in I}\left(F_{ini} - \vartheta_{MeOHi} \cdot x_{MeOH} \cdot F_{ini} - \vartheta_{RWGSi} \cdot x_{RWGS} \cdot F_{ini}\right) \tag{2}$$

where:
$F_{out\Sigma}$ - overall outlet flowrate, Nml/min.

This way:

$$y_i = \frac{F_{outi}}{F_{out\Sigma}} = \frac{F_{ini} \cdot \left(1 + \vartheta_{MeOHi} \cdot x_{MeOH} + \vartheta_{RWGSi} \cdot x_{RWGS}\right)}{\sum_{i \in I} F_{ini} \cdot \left(1 + \vartheta_{MeOHi} \cdot x_{MeOH} + \vartheta_{RWGSi} \cdot x_{RWGS}\right)} \tag{3}$$

A.2 Expressions for the kinetic constants used for the reactor modeling

Kinetic constants are determined based on the following equations:

$$k_1 = 2.69 \cdot 10^7 \cdot e^{\left(\frac{-109\,900}{R \cdot T}\right)} \tag{4}$$

$$k_2 = 7.31 \cdot 10^8 \cdot e^{\left(\frac{-123\,400}{R \cdot T}\right)} \tag{5}$$

$$k_3 = 4.36 \cdot 10^2 \cdot e^{\left(\frac{-65\,200}{R \cdot T}\right)} \tag{6}$$

$$K_{CO} = 7.99 \cdot 10^{-7} \cdot e^{\left(\frac{58\,100}{R \cdot T}\right)} \tag{7}$$

$$K_{CO_2} = 1.02 \cdot 10^{-7} \cdot e^{\left(\frac{67\,400}{R \cdot T}\right)} \tag{7}$$

$$\frac{K_{H_2O}}{\sqrt{k_{H_2}}} = 4.13 \cdot 10^{-11} \cdot e^{\left(\frac{104\,500}{R \cdot T}\right)} \tag{8}$$

where:
R – universal gas constant, J/mol/K;

T – reactor temperature, K.

Equilibrium constants are determined based on the following equations:

$$\ln K_1^0(T) = \frac{a1 + a2 \cdot T + a3 \cdot T^2 + a4 \cdot T^3 + a5 \cdot T^4 + a6 \cdot T^5 + a7 \cdot T \cdot \ln(T)}{R \cdot T} \qquad (9)$$

where:
$a1 = 74414$;
$a2 = 189.26$;
$a3 = 3.2443 \cdot 10^{-2}$;
$a4 = 7.0432 \cdot 10^{-6}$;
$a5 = -5.6053 \cdot 10^{-9}$;
$a6 = 1.0344 \cdot 10^{-12}$;
$a7 = -64.364$;

$$\ln K_2^0(T) = \frac{b1 + b2 \cdot T + b3 \cdot T^2 + b4 \cdot T^3 + b5 \cdot T^4 + b6 \cdot T^5 + b7 \cdot T \cdot \ln(T)}{R \cdot T} \qquad (10)$$

where:
$b1 = -39412.1$;
$b2 = -54.1516$;
$b3 = -5.5642 \cdot 10^{-2}$;
$b4 = 2.576 \cdot 10^{-5}$;
$b5 = 7.6594 \cdot 10^{-9}$;
$b6 = 1.0161 \cdot 10^{-12}$;
$b7 = 18.429$;

$$K_3^0 = K_1^0 \cdot K_2^0 \qquad (11)$$

Table 1. Comparative analysis of the experimental data for the pressure varied experiments

Outlet mole fraction, mol.% (95% confidence interval) \ Pressure, bar	20	30	40	50	60
CO_2 outlet molar fraction experimental value	20.069 (± 0.079)	19.760 (± 0.103)	19.417 (± 0.069)	19.173 (± 0.165)	19.038 (± 0.231)
CO_2 outlet molar fraction kinetic model value	20.882	20.371	19.963	19.616	19.309
H_2 outlet molar fraction experiment value	63.625 (± 0.066)	62.644 (± 0.145)	61.606 (± 0.088)	60.921 (± 0.267)	59.497 (± 0.373)
H_2 outlet molar fraction kinetic model value	64.567	63.163	61.952	60.879	59.910
N_2 outlet molar fraction experimental value	9.405 (± 0.103)	9.526 (± 0.132)	9.571 (± 0.093)	9.648 (± 0.226)	9.794 (± 0.223)
N_2 outlet molar fraction kinetic model value	9.386	9.535	9.667	9.790	9.899
CO outlet molar fraction experimental value	2.550 (± 0.094)	2.410 (± 0.071)	2.241 (± 0.101)	1.977 (± 0.092)	1.891 (± 0.128)
CO outlet molar fraction kinetic model value	0.961	1.025	1.031	1.015	0.991
Methanol outlet molar fraction experimental value*	1.739 (± 0.069)	2.357 (± 0.117)	2.974 (± 0.067)	3.380 (± 0.318)	4.542 (± 0.364)
Methanol outlet molar fraction kinetic model value	1.622	2.440	3.177	3.842	4.449

*Note: * - experimental values of methanol outlet concentration determined from the reaction extent approach based data processing algorithm*

95% confidence interval values for experimentally determined concentrations are provided in parenthesis

Table 2. Comparative analysis of the experimental data for the temperature varied experiments

Temperature, °C / Outlet mole fraction, mol.%	210	220	230	240	250	260
CO_2 outlet molar fraction experimental value	20.083 (± 0.105)	19.710 (± 0.094)	19.417 (± 0.069)	19.254 (± 0.144)	19.071 (± 0.700)	19.129 (± 0.116)
CO_2 outlet molar fraction kinetic model value	21.337	20.692	19.963	19.343	18.898	18.552
H_2 outlet molar fraction experiment value	63.333 (± 0.052)	62.582 (± 0.089)	61.606 (± 0.088)	61.119 (± 0.094)	60.736 (± 0.118)	61.572 (± 0.150)
H_2 outlet molar fraction kinetic model value	64.653	63.264	61.952	61.330	61.445	61.736
N_2 outlet molar fraction experimental value	9.143 (± 0.163)	9.598 (± 0.128)	9.571 (± 0.093)	9.447 (± 0.131)	9.629 (± 0.152)	9.833 (± 0.186)
N_2 outlet molar fraction kinetic model value	9.447	9.571	9.669	9.669	9.575	9.469
CO outlet molar fraction experimental value	0.982 (± 0.056)	1.388 (± 0.072)	2.241 (± 0.101)	2.283 (± 0.097)	2.404 (± 0.097)	1.982 (± 0.102)
CO outlet molar fraction kinetic model value	0.321	0.594	1.031	1.651	2.376	3.041
Methanol outlet molar fraction experimental value*	1.931 (± 0.116)	2.389 (± 0.086)	2.974 (± 0.067)	3.220 (± 0.111)	3.447 (± 0.082)	2.830 (± 0.129)
Methanol outlet molar fraction kinetic model value	1.961	2.643	3.177	3.179	2.665	2.081

*Note: * - experimental values of methanol outlet concentration determined from the reaction extent approach based data processing algorithm*

95% confidence interval values for experimentally determined concentrations are provided in parenthesis