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METHANOL ECONOMY AND NET ZERO EMISSIONS: Critical Analysis of Catalytic Processes, Reactors and Technologies

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Table S1: Kinetic models were developed by various researchers.

Table S1

Rate equations	Operating conditions	authors	Ref.
$r_{CH_3OH} = k\,(\frac{p_{CO}^{0.5}P_{H_2}}{p_{CH_3OH}^{0.66}} - \frac{P_{CH_3OH}^{0.66}}{p_{CO}^{0.5}p_{H_2}K_2^*})$	493-533 K; 40-55 atm	Leonov et al., 1973	77
$r_{CH_3OH} = const\,\frac{K_{redox}^3\left(p_{CO_2}/p_{CO}\right)^3\left(p_{CO}p_{H_2}^2 - \frac{r_{CH_3OH}}{K_2^*}\right)}{\left[1 + K_{redox}p_{CO_2}/p_{CO}\right]^3\left(F + K_{CO_2}p_{CO_2}\right)^n} + k^{'}(p_{CO_2} - \left(1/K_1^*\right)\,(p_{CH_3OH}p_{H_2O}/p_{H_2}^3))$	498-523 K, 75 atm	Klier et al. 1982	65
$r_{CH_3OH} = \frac{\left(f_{CO}f_{H_2}^2 - \frac{r_{CH_3OH}}{K_2^*}\right)}{(A + Bf_{CO} + Cf_{H_2} + Gf_{CO_2})^3}$	488-518 K, 30-95 atm	Villa et al. 1985	71
$r_{RWGS} = \frac{f_{CO}f_{H_2}^2 - f_{CH_3OH}/K_2^*}{M^2}$			
$r_{CO\rightarrow CH_3OH} = f_1(f_{CO}f_{H_2}^{2.5})^{0.35}\left[1 - \left(\frac{f_{CH_3OH}}{K_{eq}}f_{CO}f_{H_2}^2\right)^{0.8}\right]$	488-574 K 40-95 atm	Takagawa and Ohsugi, 1987	64
$r_{CO\rightarrow CH_3OH} = \frac{k_1K_{CO}\left(f_{CO}f_{H_2}^{3/2} - f_{CH_3OH}/f_{H_2}^{1/2}K_1^{eq}\right)}{\left(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2}\right)\left(f_{H_2}^{1/2} + \left(K_{H_2O}/K_{H_2}^{1/2}\right)\right)f_{H_2O}}$	483-518K 15-50 atm	Graaf et al., 1988	63
$r_{RWGS} = \frac{k_1K_{CO_2}\left(f_{CO_2}f_{H_2} - f_{H_2O}f_{CO}/K_2^{eq}\right)}{\left(1 + K_{CO}f_{CO} + K_{CO_2}f_{CO_2}\right)\left(f_{H_2}^{1/2} + \left(K_{H_2O}/K_{H_2}^{1/2}\right)\right)f_{H_2O}}$			

$$r_{CO_2\to CH_3OH}=\frac{k_3K_{CO_2}\left(f_{k_1K_{CO_2}}f_{H_2}^{3/2}-{}^{f_{CH_3OH}f_{H_2O}}\!\big/ f_{H_2}^{3/2}K_3^{eq}\right)}{\left(1+K_{CO}f_{CO}+K_{CO_2}f_{CO_2}\right)\left(f_{H_2}^{1/2}+\left({}^{K_{H_2O}}\!\big/ K_{H_2}^{1/2}\right)\right)f_{H_2O}}$$

$$r_{CO\to CH_3OH}=\frac{A_1A_2A_3^{1/2}\left[f_{CO_2}f_{H_2}-{}^{f_{CH_3OH}f_{H_2O}}\!\big/(f_{H_1}^{2}K_{eq.CO_2}\right]}{\left(1+A_2f_{CO_2}\right)\left[1+A_3^{0.3}f_{H_2}^{1/2}+{}^{A_4f_{H_2O}}\!\big/\left(A_3f_{H_2}\right)^{0.5}\right]}$$

Dybkjaer, 1985 [79]

$$r_{RWGS}=\frac{A_5A_2A_3^{1/2}\left[f_{CO_2}f_{H_2}^{1/2}-{}^{f_{CO}f_{H_2O}}\!\big/(f_{H_2}^{1/2}K_{eq.WGS})\right]}{\left(1+A_2f_{CO_2}\right)\left[1+A_3^{0.5}f_{H_2}^{1/2}+{}^{A_4f_{H_2O}}\!\big/\left(A_3f_{H_2}\right)^{0.5}\right]}$$

$$r_{CO/CO_2\to CH_3OH}=\frac{\left[p_{CO_2}p_{H_2}^{2}-p_{CH_3OH}/K_{eq}\right]}{\left[ap_{CO}p_{H_2}^{1/2}+bp_{H_2}+cp_{CO_2}\right]}+\frac{\left[p_{CO_2}pf_{H_2}-p_{CH_3OH}p_{H_2O}/(\cdots\right.}{\left[a'p_{CO_2}p_{H_2}^{1/2}+b'p_{CO_2}+c'\cdots\right.}$$

McNeil et al., 1989 [61]

$$r_{CO_2\to CH_3OH}=\frac{k_1K_{H_2}^{2}K_{CO_2}\left[p_{CO_2}p_{H_2}^{2}-p_{CH_3OH}p_{H_2O}/(p_{H_2}K_{eq}^{r_{CO_2\to CH_3OH}})\cdots\right.}{\left[1+K_{H_2}p_{H_2}+K_{CO_2}p_{CO_2}+K_{CH_3OH}p_{CH_3OH}+K_{H_2O}p_{H_2O}+K\cdots\right.}$$

Skrzypek et al., 1991 [69]

$$r_{RWGS}=\frac{k_2K_{H_2}K_{CO_2}\left[p_{CO_2}p_{H_2}-p_{CO}p_{H_2O}/(K_{eq}^{r_{RWGS}}\right]}{\left[1+K_{H_2}p_{H_2}+K_{CO_2}p_{CO_2}+K_{CH_3OH}p_{CH_3OH}+K_{H_2O}p_{H_2O}+K_{CO}p_{CO}\cdots\right.}$$

$$r_{CO_2\to CH_3OH}=\frac{k'_{5a}K'_2K_3K_4K_{H_2}p_{CO_2}p_{H_2}\left[1-\left(1/K^*\right)\left({}^{p_{CH_3OH}p_{H_2O}}\!\big/ p_{CO_2}p_{H_2}^{3}\right)\cdots\right.}{\left(1+\left({}^{K_{H_2O}}\!\big/ K_8K_9K_{H_2}\right)\left({}^{p_{H_2O}}\!\big/ p_{H_2}\right)+\sqrt{K_{H_2}p_{H_2}}+K_{H_2O}p_{H_2O}\cdots\right.}$$

Vanden Bussche and Froment, 1996 [70]

$$r_{RWGS}=\frac{k'_1p_{CO_2}\left[1-K_3^{*}\left({}^{p_{CO}p_{H_2O}}\!\big/ p_{CO_2}p_{H_2}\right)\right]}{\left(1+\left({}^{K_{H_2O}}\!\big/ K_8K_9K_{H_2}\right)\left({}^{p_{H_2O}}\!\big/ p_{H_2}\right)+\sqrt{K_{H_2}p_{H_2}}+K_{H_2O}p_{H_2O}\right)}$$

$$r_{+}=k_{-11}K_5^{-3/2}K_8^{-1}K_9K_{10}K_{11}\left(\frac{p_{H_2}}{p_0}\right)^{3/2}\left(\frac{p_{CO_2}}{p_O}\right)\Theta^2$$

$$r_{-}=k_{-11}K_5^{-3/2}K_8^{-1}K_9K_{10}K_{11}\frac{1}{K_G}\left(\frac{p_{H_2O}p_{CH_3OH}}{p_{H_2}^{3/2}p_0^{1/2}}\right)\Theta^2$$

$$r_{CO_2\to CH_3OH}=r_{+}-r_{-}$$

Askgaard et al., 1995

$r_{CO\rightarrow CH_3OH}=\frac{k_{CO\rightarrow CH_3OH}K_{CO}K_{H_2}^{2}K_{CH,CO}\left[p_{CO}p_{H_2}^{2}-{p_{CH_3OH}}/{(K_{Pr_{CO\rightarrow CH_3OH}})}\right]}{(1+K_{CO}p_{CO})\left(1+K_{H_2}^{0.5}p_{H_2}^{0.5}+K_{H_2O}p_{H_2O}\right)}$ $r_{CO_2\rightarrow CH_3OH}=\frac{k_{CO_2\rightarrow CH_3OH}K_{H_2}K_{CO_2}K_{CH,CO_2}\left[p_{CO_2}p_{H_2}^{3}-{p_{CH_3OH}p_{H_2O}}/{(K_{Pr_{CO_2}}}\right.}{\left(1+K_{CO_2}p_{CO_2}\right)\left(1+K_{H_2}^{0.5}p_{H_2}^{0.5}+K_{H_2O}p_{H_2O}\right)p_{H_2}^{2}}$ $r_{RWGS}=\frac{k_{RWGS}K_{CO_2}K_{H_2}^{0.5}\left[p_{CO_2}p_{H_2}-{p_{CO}p_{H_2O}}/{(K_{Pr_{RWGS}})}\right]}{\left(1+K_{CO_2}p_{CO_2}\right)\left(1+K_{H_2}^{0.5}p_{H_2}^{0.5}+K_{H_2O}p_{H_2O}\right)p_{H_2}^{0.5}}$	523-553 K 40 bar	Lim et al., 2009	82
$r_{CO_2}=\frac{k_1K_2f_{CO_2}f_{H_2}^{1.5}EQ_1}{\left(1+K_1f_{CO}+K_2f_{CO_2}\right)\left(f_{H_2}^{0.5}+K_3f_{H_2O}\right)}$ $r_{rWGS}=\frac{k_2K_2f_{CO_2}f_{H_2}EQ_2}{\left(1+K_1f_{CO}+K_2f_{CO_2}\right)\left(f_{H_2}^{0.5}+K_3f_{H_2O}\right)}$ $EQ_1=1-\frac{f_{MEOH}f_{H_2O}}{f_{CO_2}f_{H_2}^{3}K_{EQ_1}}$ $EQ_2=1-\frac{f_{CO}f_{H_2O}}{f_{CO_2}f_{H_2}K_{EQ_2}}$		Henkel 2011	62
$r_{CO\rightarrow CH_3OH}=\frac{k'_{r_{CO\rightarrow CH_3OH}}K_{CO}\left[f_{CO}f_{H_2}^{0.5}-{f_{CH_3OH}}/{(f_{H_2}^{0.5}K_{eqCO\rightarrow CH_3OH})}\right]}{(1+K_{CO}f_{CO})\left(1+K_{H_2}^{0.5}f_{H_2}^{0.5}+K_{H_2O}f_{H_2O}\right)}$ $r_{CO_2\rightarrow CH_3OH}=\frac{k'_{r_{CO_2\rightarrow CH_3OH}}K_{CO_2}\left[f_{CO_2}f_{H_2}^{1.5}-{f_{H_2O}f_{CH_3OH}}/{(f_{H_2}^{1.5}K_{eqCO_2\rightarrow CH_3O}}\right.}{\left(1+K_{CO_2}f_{CO_2}\right)\left(1+K_{H_2}^{0.5}f_{H_2}^{0.5}+K_{H_2O}f_{H_2O}\right)}$ $r_{RWGS}=\frac{k'_{r_{RWGS}}K_{CO_2}\left[f_{CO_2}f_{H_2}-{f_{CO}f_{H_2O}}/{K_{Pr_{RWGS}}}\right]}{\left(1+K_{CO_2}f_{CO_2}\right)\left(1+K_{H_2}^{0.5}f_{H_2}^{0.5}+K_{H_2O}f_{H_2O}\right)}$		Park et al., 2014	85

$r_{CO} = k_1 b_{CO} \left\{ \frac{P_{CO} P_{H_2}^{3/2} - \frac{P_{CH_3OH}}{K_1 P_{H_2}^{0.5}}}{\left(1 + b_{CO} P_{CO} + b_{CO_2} P_{CO_2}\right)\left[P_{H_2}^{1/2} + \frac{b_{H_2O}}{b_{H_2}^{1/2}} P_{H_2O}\right]} \right\}$ $r_{CO_2} = k_2 b_{CO_2} \left\{ \frac{P_{CO_2} P_{H_2} - \frac{P_{CO} P_{H_2O}}{K_2}}{\left(1 + b_{CO} P_{CO} + b_{CO_2} P_{CO_2}\right)\left[P_{H_2}^{1/2} + \frac{b_{H_2O}}{b_{H_2}^{1/2}} P_{H_2O}\right]} \right\}$ $r_{RWGS} = k_3 b_{CO_2} \left\{ \frac{P_{CO_2} P_{H_2}^{3/2} - \frac{P_{CH_3OH} P_{H_2O}}{K_3 P_{H_2}^{3/2}}}{\left(1 + b_{CO} P_{CO} + b_{CO_2} P_{CO_2}\right)\left[P_{H_2}^{1/2} + \frac{b_{H_2O}}{b_{H_2}^{1/2}} P_{H_2O}\right]} \right\}$	473-503K 50-80 atm	Portha et al, 2017	83
$r_{CO} = k_1 p_{CO} p_{H_2}^2 \left(1 - \frac{1}{K_{P1}} \frac{p_{CH_3OH}}{p_{CO} p_{H_2}^2}\right) \theta^{\odot} \theta^{\otimes 4}$ $r_{CO_2} = k_2 p_{CO_2} p_{H_2}^2 \left(1 - \frac{1}{K_{P2}} \frac{p_{CH_3OH} p_{H_2O}}{p_{CO_2} p_{H_2}^3}\right) \theta^{\odot 2} \theta^{\otimes 4}$ $r_{RWGS} = k_3 p_{CO_2} \left(1 - \frac{1}{K_{P3}} \frac{p_{CO} p_{H_2O}}{p_{CO_2} p_{H_2O}}\right) \theta^{\odot} \theta^{*}$ $\theta^{\odot} = 1 + K_{CO} p_{CO} + K_{CH_3OH}^{\odot} p_{CH_3OH} + K_{CO_2}^{\odot} CO_2$ $\theta^{\otimes} = \sqrt{K_{H_2}} \sqrt{p_{H_2}}$ $\theta^{*} = 1 + \frac{K_O K_{H_2O}}{K_{H_2}} \frac{p_{H_2O}}{p_{H_2}} + K_{CO_2} p_{CO_2} + K_{CH_3OH}^{*} p_{CH_3OH} + K_{H_2O} p_{H_2O}$	503.15-522.15 K 30-60 bar	Seidel et al., 2018	60
$r_{CO_2} = k_1 K_2 \left\{ \frac{f_{CO_2} f_{H_2}^{1.5} - \frac{f_{CH_3OH} f_{H_2O}}{K_{eq1} f_{H_2}^{3/2}}}{\left(1 + K_1 f_{CO} + K_2 f_{CO_2}\right)\left[f_{H_2}^{1/2} + K_3 f_{H_2O}\right]} \right\}$	423-623 K 50-80 atm GHSV 10000^{-1}	Nestler et al. 2020	88

$r_{rWGS} = k_2 K_2 \left\{ \frac{f_{C0_2} f_{H_2} - \frac{f_{CO} f_{H_2O}}{K_{eq2}}}{\left(1 + K_1 f_{CO} + K_2 f_{C0_2}\right)\left[f_{H_2}^{1/2} + K_3 f_{H_2O}\right]} \right\}$			
$r_{CO} = k_3 K_1 \left\{ \frac{f_{C0_2} f_{H_2}^{1.5} - \frac{f_{CH_3OH} f_{H_2O}}{K_{eq1} f_{H_2}^{3/2}}}{\left(1 + K_1 f_{CO} + K_2 f_{C0_2}\right)\left[f_{H_2}^{1/2} + K_3 f_{H_2O}\right]} \right\}$			
$r_{C0_2} = k_{C0_2} f_{C0_2} f_{H_2}^2 \left(1 - \frac{1}{K_{p_{C0_2}}^{o}(T)} \frac{f_{CH_3OH} f_{H_2O}}{f_{H_2}^3 f_{C0_2}}\right) \Theta^{*2}$	450-600 K 20-100 atm	Slotboom et al., 2020	76
$r_{RWGS} = k_{RWGS} f_{C0_2} f_{H_2}^{0.5} \left(1 - \frac{1}{K_{RWGS}^{o}(T)} \frac{f_{CO} f_{H_2O}}{f_{C0_2} f_{H_2}}\right) \Theta^{*}$			
$\Theta^{*} = \left(f_{H_2}^{0.5} k_{H_2} + f_{H_2O} k_{H_2O/9} + f_{H_2O}\right)$			