Electronic Supplementary Information (ESI)

Process Exploration and Assessment for the Production of Methanol and Dimethyl Ether from Carbon Dioxide and Water

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Equilibrium conversion of syngas to methanol. Conversion of syngas as a function of H_2:CO_2:CO ratios was investigated in an *REquil* reactor in Aspen Plus V8.8 at 250 °C and 50 bar. The molar fraction of methanol in the reactor effluent, the molar methanol yield from CO_2 + CO, the extents of CO_2, CO and H_2 conversion and molar fraction of water in the product were evaluated (Fig. 1S).

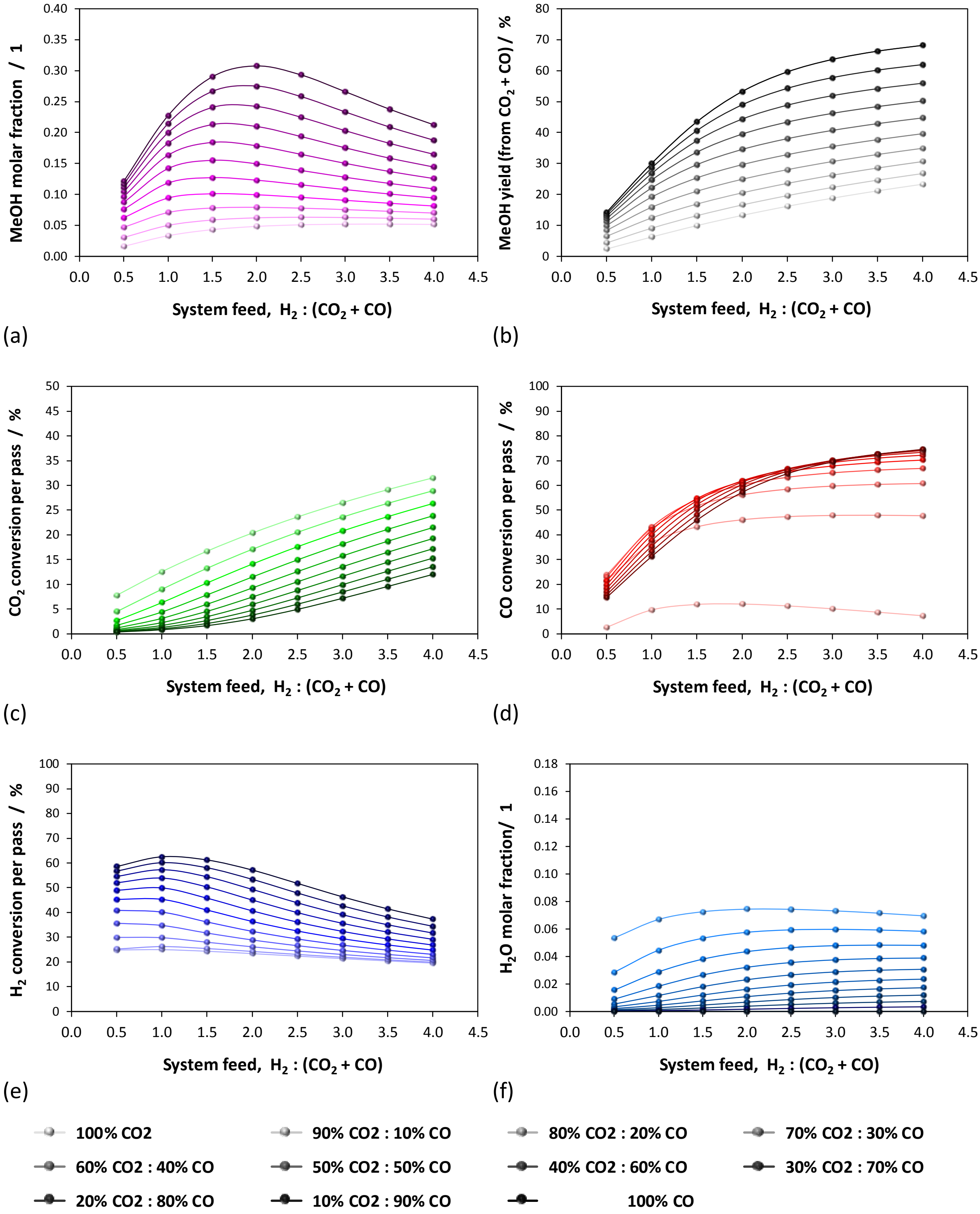

Fig. 1S. Results of equilibrium calculations for methanol synthesis from syngas at T = 250 °C and P = 50 bar at varying molar ratios of hydrogen to carbon, H_2:(CO_2+CO), in the system feed. The total molar carbon flux: (CO_2 + CO) was fixed, while the CO_2:CO molar ratio was varied between 1 and ≈0.

Equilibrium conversion of syngas to DME in the direct process. Conversion of syngas comprised of a range of H_2:CO_2:CO ratios was investigated in an *REquil* reactor in Aspen Plus V8.8 at 250℃ and 50 bar. The molar fraction of DME in the reactor effluent, the molar DME yield from CO_2 + CO, the extents of CO_2, CO and H_2 conversion and molar fraction of water in the product were evaluated.

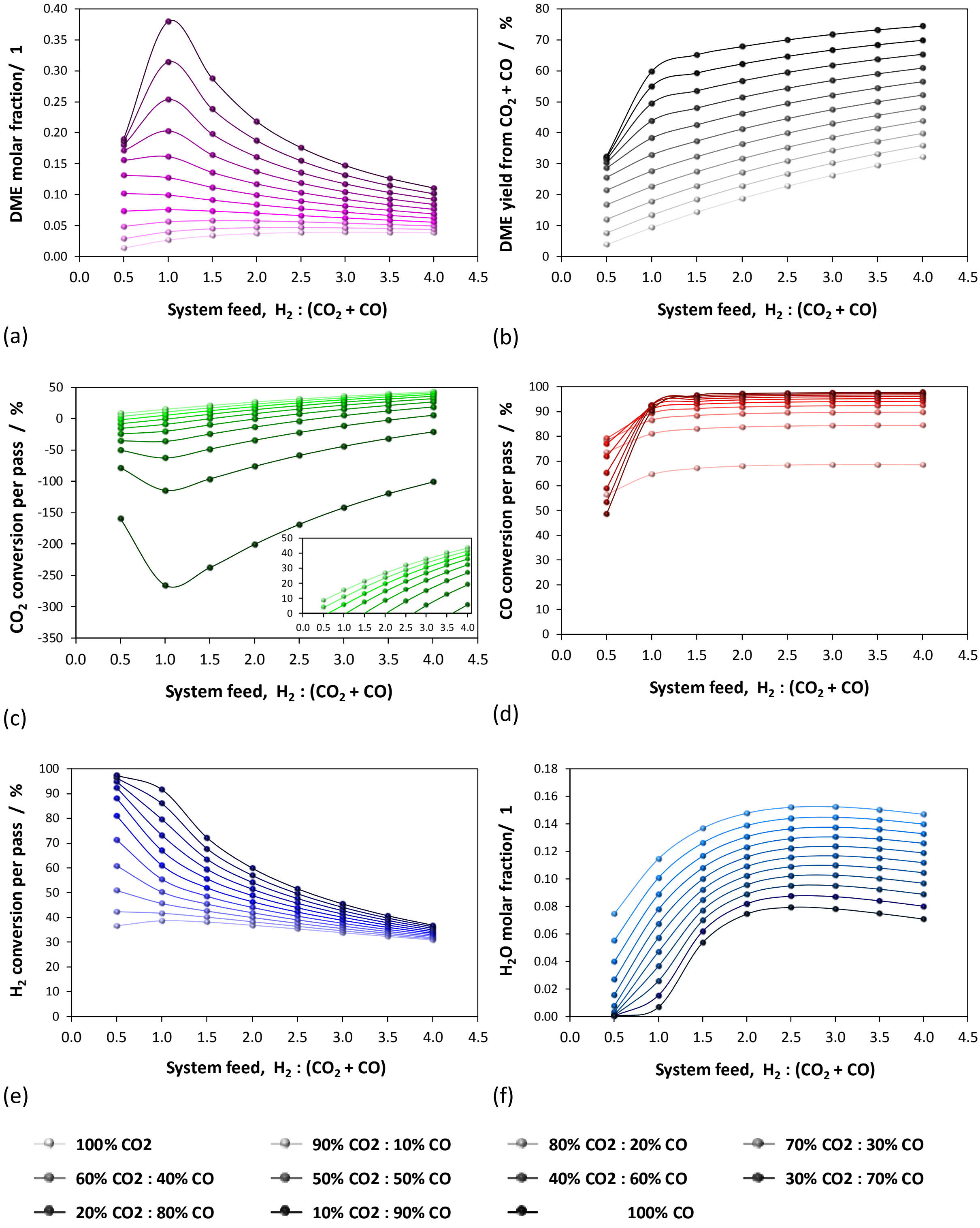

Fig. 2S. Results of equilibrium calculations for direct DME synthesis from syngas at *T* = 250℃ and *P* = 50 bar at varying molar ratios of hydrogen to carbon, H_2:(CO_2+CO), in the system feed. The total molar carbon flux: (CO_2 + CO) was fixed, while the CO_2:CO molar ratio was varied between 1 and ≈0. The inset in Fig. (c) shows a smaller section of the overall graph.

Equilibrium DME yield in the conventional two-step process in the absence of recycle loop (with CO, CO_2, H_2 and H_2O separation before second reactor). Conversion of syngas comprised of a range of H_2:CO_2:CO ratios was investigated in an *REquil* reactor in Aspen Plus V8.8 at 250 °C and 50 bar. The molar fraction of DME in the reactor effluent, the molar DME yield from CO_2 + CO and molar fraction of water in the product were evaluated. The extents of CO_2, CO and H_2 conversion are the same as those in the methanol system.

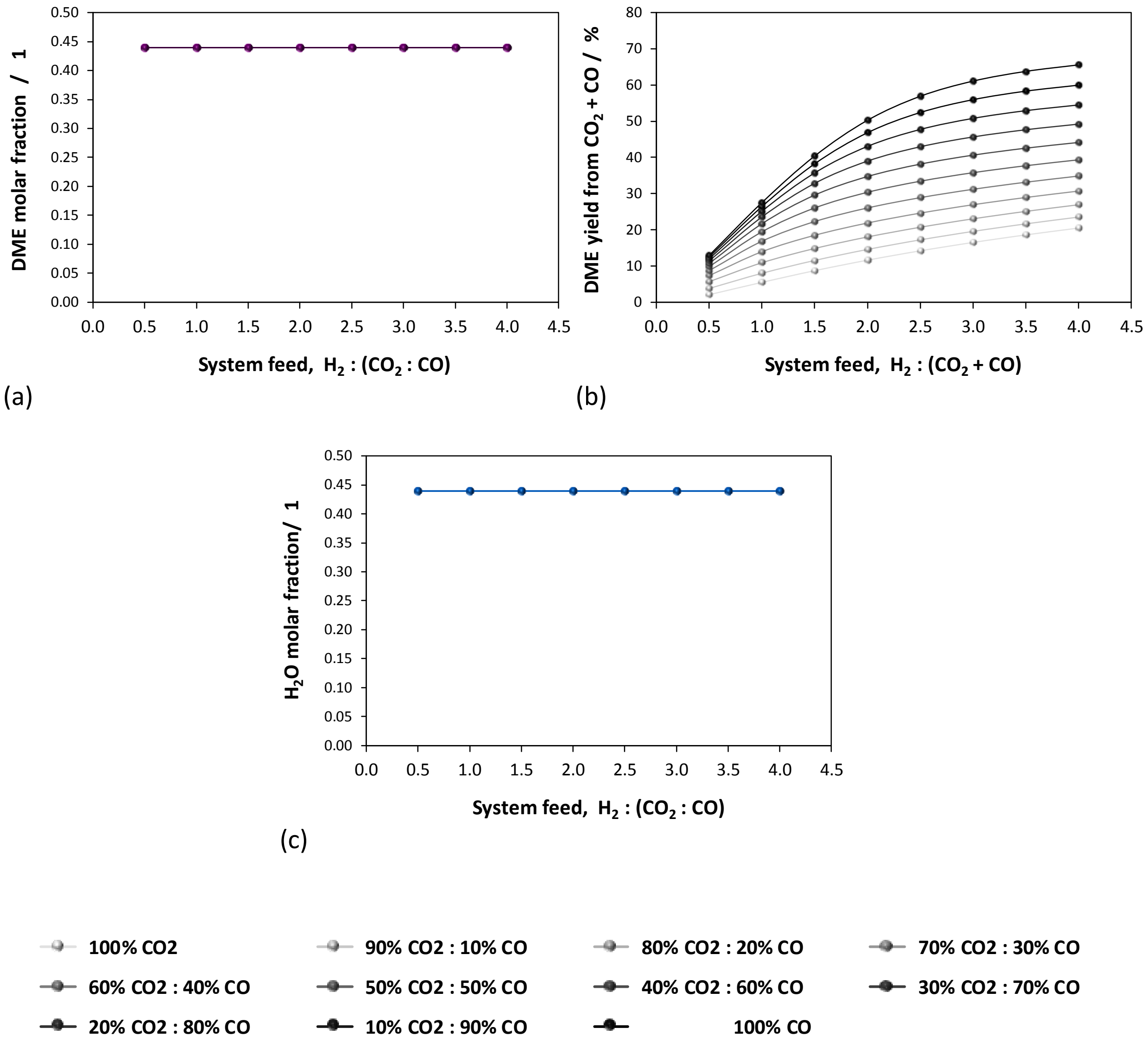

Fig. 3S. Results of equilibrium calculations for the conventional two-step DME synthesis from syngas at T = 250 °C and P = 50 bar at varying molar ratios of hydrogen to carbon, H_2:(CO_2+CO), in the system feed. The total molar carbon flux: (CO_2 + CO) is fixed, while the CO_2:CO molar ratio is varied between 1 and zero. The modification introduced was to separate the unreacted H_2, CO_2, CO from the product stream before diverting the remaining methanol and water into the second reactor for DME synthesis.

Equilibrium DME yield in the conventional two-step process in the absence of recycle loop (without separation and without shift allowed in second reactor). Conversion of syngas comprised of a range of H_2:CO_2:CO ratios was investigated in an *REquil* reactor in Aspen Plus V8.8 at 250℃ and 50 bar. The molar fraction of DME in the reactor effluent, the molar DME yield from CO_2 + CO and molar fraction of water in the product were evaluated. The extents of CO_2, CO and H_2 conversion are the same as those in the methanol system.

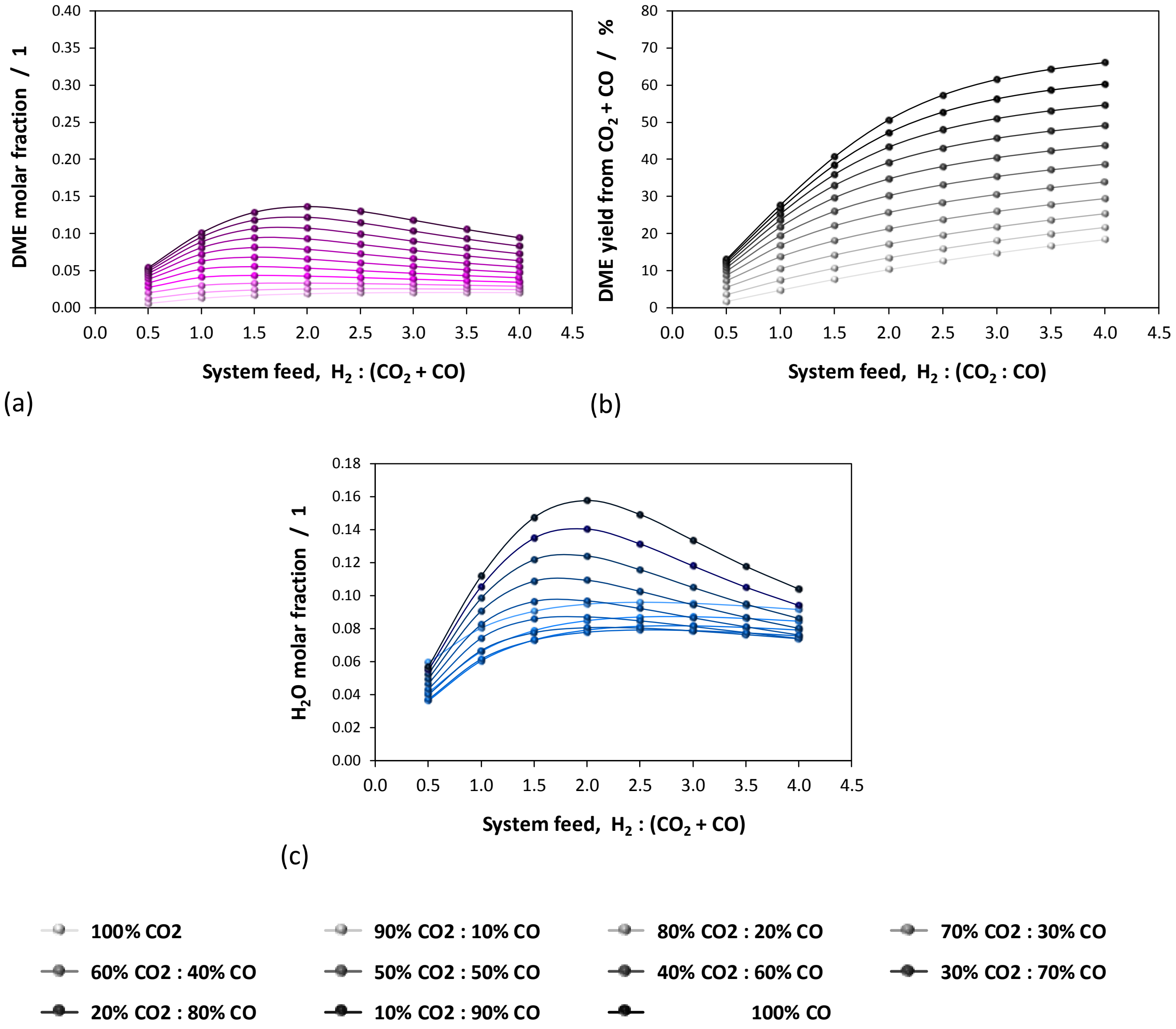

Fig. 4S. Results of equilibrium calculations for the conventional two-step DME synthesis from syngas at *T* = 250℃ and *P* = 50 bar at varying molar ratios of hydrogen to carbon, H_2:(CO_2+CO), in the system feed. The total molar carbon flux: (CO_2 + CO) is fixed, while the CO_2:CO molar ratio is varied between 1 and zero. The assumptions in the simulation were that the water gas shift (WGS) reaction does not occur simultaneously with methanol dehydration in the second step of the process.

Optimised system performance. The efficiencies of systems operating with maximum energy savings is presented in Fig. 5 for three feed compositions: 100 % CO_2, 100 % CO and 50 % CO_2 : 50 % CO. The net energy outputs of each system were normalised against the energies contained in the CO and H_2 gases in the system feeds.

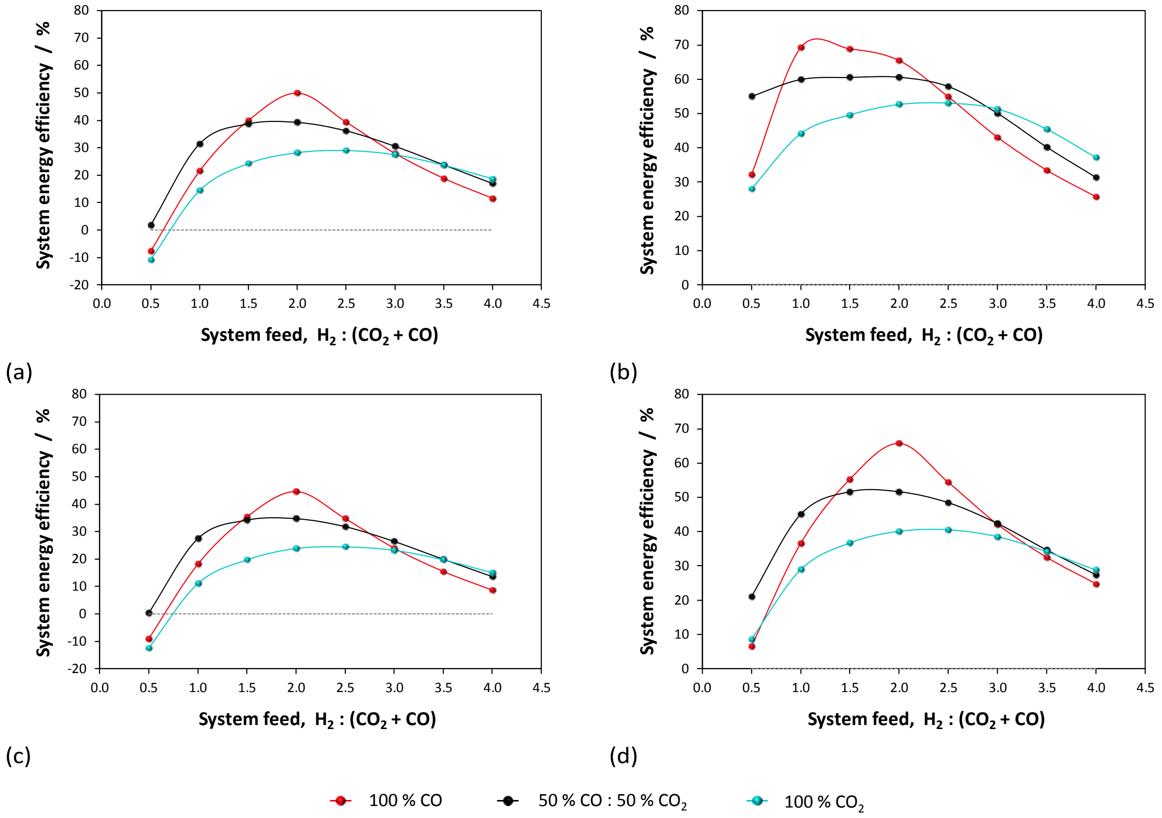

Fig. 5S: Net energies obtained with different ratios of CO:CO_2 in the system feed with the (a) methanol, (b) direct DME, (c) 2-step DME synthesis with an interposed syngas separation step and (d) 2-step DME synthesis with no separation step between the two reactors.

Flash separation efficiencies. The efficiencies of systems operating with maximum energy savings is presented in Fig. 5S for three feed compositions: 100 % CO_2, 100 % CO and 50 % CO_2 : 50 % CO. The net energy outputs of each system were normalised against the energies contained in the CO and H_2 gases in the system feeds.

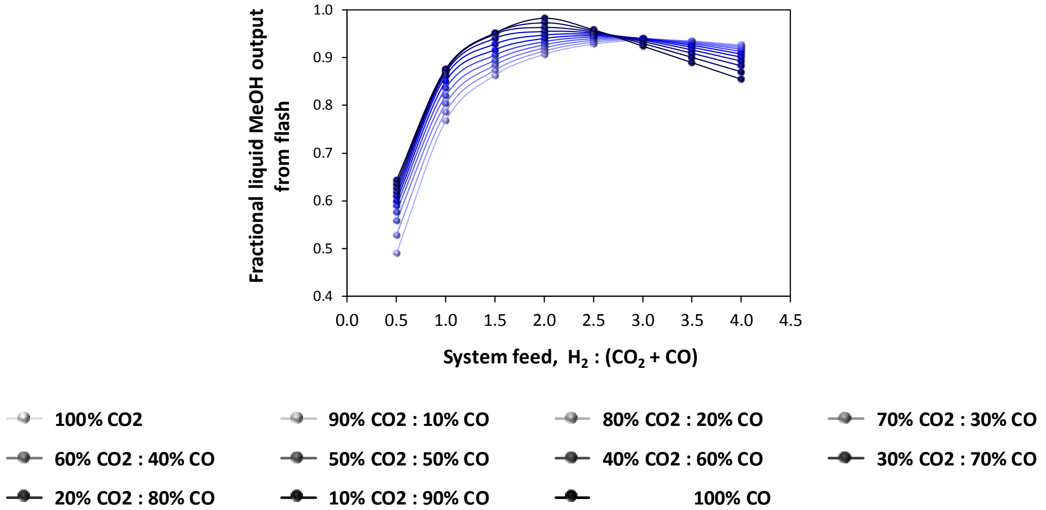

Fig. 6S: Fractional yield of methanol from the flash separator column operating at 35°C and 45 bar in the methanol synthesis system.

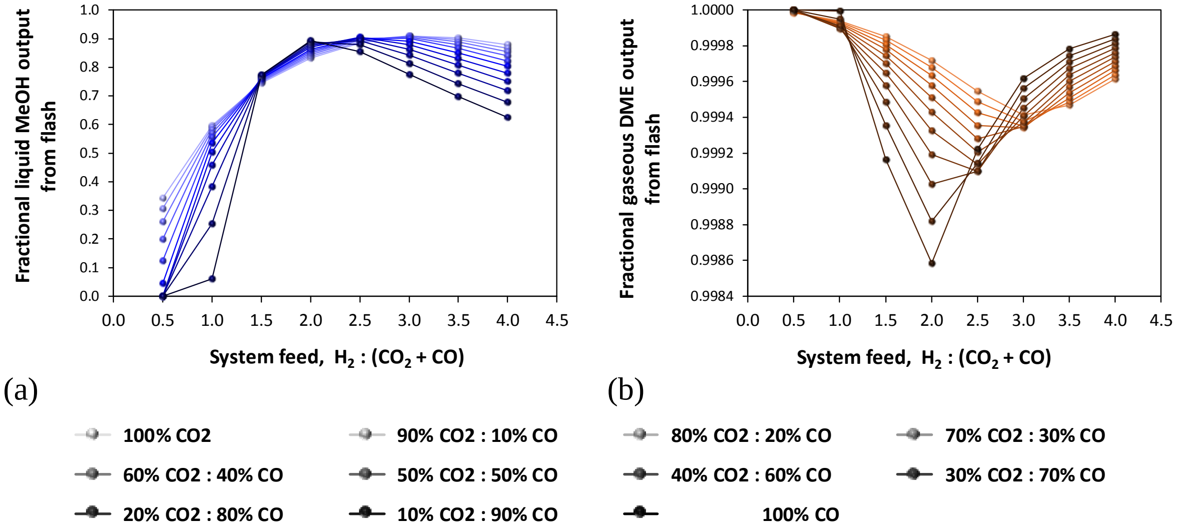

Fig. 7S: Fractional yields of (a) liquid methanol and (b) gaseous DME from the flash separator column operating at 35°C and 45 bar in the direct DME synthesis system.

Useful heat from methanol/DME synthesis. The heat output during methanol/DME synthesis by exothermic reactions (CO and CO_2 hydrogenation, WGS reaction and methanol dehydration) under isothermal conditions can be utilised up-stream. Fig. 8S shows the total heat output by the four systems under investigations during equilibrium syngas conversion at 250 ℃ and 50 bar, normalised by the energy contained in the gas feed to the systems.

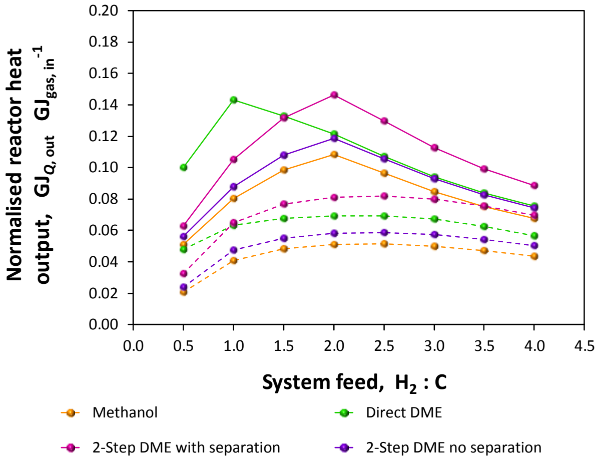

Fig. 8S: Heat liberated by the methanol/DME synthesis reactors in order for isothermal reaction conditions (250 ℃ and 50 bar) to be maintained. Solid and dashed lines represent results obtained with H_2-CO and H_2-CO_2 system feeds.

Useful heat from methanol/DME synthesis systems. The heat liberated by reactors supporting exothermic processes (Stages 1 / 2) and also by heat exchangers (Stage 1) have been compared with the energy demands of the corresponding syngas production processes (Stage 1) in Fig. 9S.

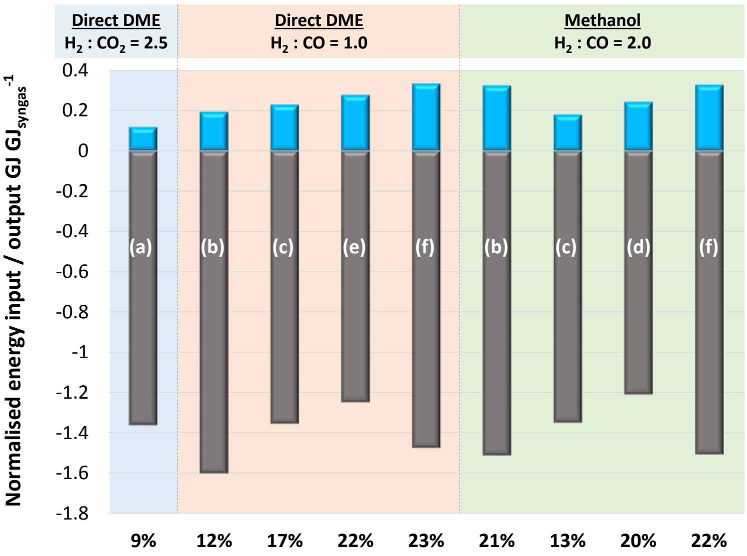

Fig. 9S: Combined energy consumption and energy release (as heat) occurring in Stages 1 and 2 of systems for the production of methanol and direct DME (energy savings from coupled heat exchangers in Stage 2 were excluded from this analysis). Negative values (grey) represent energy demands, normalised by the energy contained in the syngas output in Stage 1. Positive values (blue) represent the energies removed as heat from exothermic reactions and heat exchangers in Stages 1 and 2 or each system / syngas production scheme investigated.