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Supplementary information for

Methane-to-Methanol via chemical looping – economic potential and guidance for future research

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Economic analysis

The prices used below are mainly based on historical prices reported on public websites.

1.1 Natural gas costs

At a price of \$3.5/GJ or \$175/t and 90 C% methanol yield, the methane cost will amount to $\frac{Methane\ price\ M_{methane}}{Methanol\ yield\ M_{methanol}} = \frac{175 \cdot 16}{0,9 \cdot 32} = \$97/t$ of methanol.

The 10% loss could provide 0.1•50•16/32 = 2.5 GJ/t methanol of process energy. A higher loss might have to be taken into account to meet the energy requirement of the process. This is not expected to have a severe impact on the overall economics, considering the low methane feed cost. As air is assumed as oxygen source, it is considered as free of charge.

1.2 Active material costs and working capital

Based on typical process parameters from the literature, the process cycle is assumed to take about 1h, which would allow 8000 cycles over one year of operation. With a productivity of 1 g/kg of zeolite per cycle, the life productivity amounts to 8 kg methanol/kg

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of active material, well below the typical industrial threshold of ~1000 kg/kg [S1, S3]. With amaterial cost of \$30/kg, that is based on private information, the material consumption cost reaches therefore \$940/t methanol and a material working capital (loss of interests) of \$140/t methanol (with 15% charge).

1.3 Capital expenses

The capital expenses (CAPEX) will be based on the capex-duty correlation (Figure S1, eq. 1) that has been validated for numerous refining and petrochemical processes [S1] and which is updated [S2]. The data and correlation are reported in the Fig. S1. It is important to recognize that the accuracy of the correlation is about -50% to +100%. Hence, the focus will be on identifying the main transfer duty contributions.

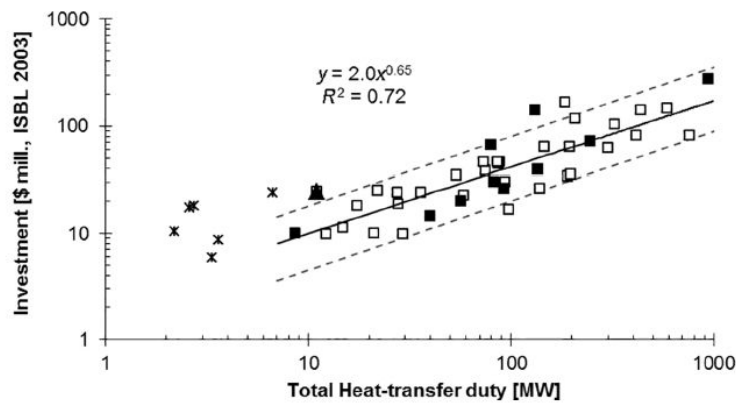$$\text{CAPEX (M\$, ISBL 2003)} = 2 \cdot (\text{duty MW})^{0.65} \qquad \qquad \text{(eq. 1)}$$

Fig. S1. The influence of energy transfer on the investment of process sections. [S2]

An important energy transfer duty is needed for withdrawing the overall heat of reaction of 3.95 kJ/g methanol. This duty will contribute to the CAPEX, irrespective of where and how it is removed. We will assume here 100% selectivity to methanol, which means that there is no need to withdraw heat for undesired side reactions. The reactor cost is here related to its duty and neither its size not its complexity, e.g. to allow cycling. Both matter, however. With a yield of 0.001 g/g, a bed density of 0.5 t/m^3 and the cycle time of 1h, the reactor production rate amounts to 0.5 kg/m^3/h, which is about a factor 200 lower than industrial practice of >0.1 t/m^3/h. [S1] The reactor may therefore lead to an unusually high cost. Mitigation of this is to increase the overall production rate e.g. through reducing the cycle time and/or increasing the zeolite productivity.

Beyond the reaction duty, each step requires specific and additional energy exchange duty. The 1st step in the process involves feeding air through feed-effluent a heat exchanger heat/cool from 50 to 200°C and back. This step can be performed at atmospheric pressure to avoid pressurizing large volume of air. Assuming that we need to feed ten times the

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stoichiometric oxygen requirement (10 atom of O per methanol) to oxidize the copper-exchanged zeolite, we need to feed 22 g air/g methanol. With a C_p of 1 J/g/K, this an integrated feed-effluent heat exchanger of 3.3 kJ/g methanol (Table 1). Such air flow corresponds to 22•0.001= 0.022 g air/g zeolite or, based on a bed density of 0.5 g/ml,

$$\frac{Air\ flow}{Bed\ density} \frac{M_{air}}{1\ mol\ gas\ volume} = \frac{0.022}{0.5} \frac{28}{24} = 0,038\ l$$ air per ml vessel, which is much more than is needed to flush the vessel.

The 2nd step involves pressurizing the vessel to 20 bar with methane to achieve a high material productivity. The pressurizing requires 20/0.5/24•16 = 27 g methane/kg zeolite or 27 g methane/g methanol. This is much more than the stoichiometric requirement of the reaction, 0.5 g methane/g methanol. We will then assume to run several reactors in swing mode to pressurize vessel #2 to 10 bar by adiabatic expansion of vessel #1 that finished its 2nd step at 20 bar of methane and then boosting the pressure to 20 bars by adiabatic compression of the remaining methane. We will neglect the makeup methane and eventual heating/cooling of methane during this transfer. This implies that half of the 27 g methane/g methanol is fed without duty and that the other half needs compression from 10 to 20 bars. The isentropic compressor duty is calculated to be 180 J/g compressed methane, i.e. 27/2•180=2.45 kJ/g methanol. It should be noticed that this crude analysis does not consider any purge step to avoid contacting CH_4 and air and, consequently, the eventuality to form an explosive mixture. It also neglects the need for heating CH_4 to reaction temperature, assuming the adiabatic pressurization would take care of it.

The 3rd step implies feeding wet gas to produce methanol. Assuming a ten molar equivalent of water for the reaction, which is typically used in the laboratory tests, we need to preheat and evaporate 5.6 g water/g methanol and perform a similar duty for cooling and condensing the water/methanol effluent. The feed-effluent needed for this task will have a duty of 5.6•2.2= 12 kJ/g methanol, neglecting here the latent heat needed to bridge the temperature gap between 50 and 200°C for simplicity. The 10 molar equivalent of water corresponds to 3.75 nL/L vessel, which is sufficient to fill the reactor. Hence, we can use 'pure' steam without gas dilution and without the need to heat and cool it.

The 4th step involves recovery of methanol from the wet gas by means of distillation. Using the concept of distillation resistance [S2] (Figures S2, S2), the distilling methanol (65°C) from water (100°C) has a product distillation resistance $\Omega_{Methanol}$ of 1/35=0.03 1/°C, which corresponds to a duty of 1.1•0.03 = 0.031 kJ/g Methanol.

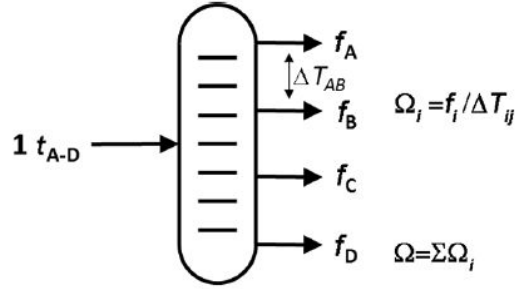$$\Omega \ [°C^{-1}] = 100 \times \sum (f_i \ [w/w]/\Delta T_i \ [°C]) \qquad (3)$$

Fig. S2. Illustration of the destillation resistance for separating 1 ton of feed mix. [S2]
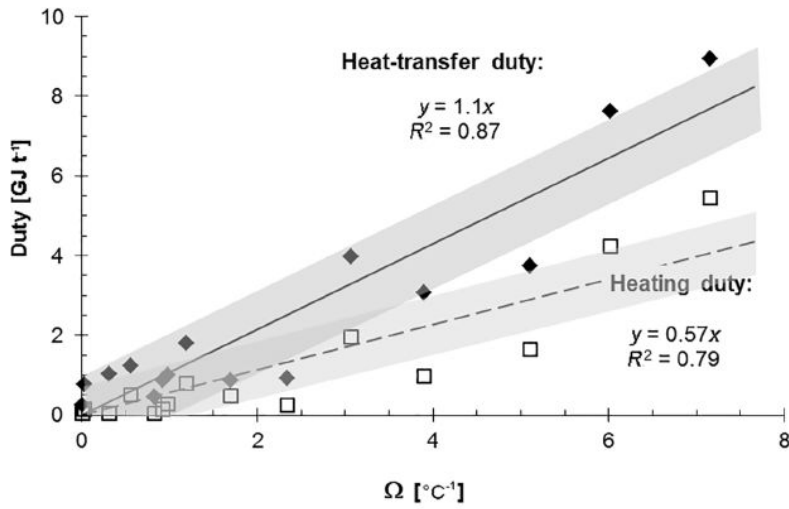

Fig. S3. Influence of the distillation resistance Ω on the heat-transfer and heating duty of distillation sections. [S2]

Accordingly, the overall duty of 3.9+3.3+2.4+12.4+0.03 = 22 kJ/g methanol. For a scale of 100 kt/a, the overall transfer duty corresponds to 77 MW and the ISBL to $34M, based on the capex-duty correlation presented above. This corresponds to $84/t methanol at 25% capital charge. An NTA+contingency of 100% would not be excessive for the crudeness of this evaluation, which would bring the inside battery limits to $168/t. A factor of three can then be used to consider OSBL, fixed cost, owner cost and project cost, which results in a CAPEX-related conversion cost of $504/t methanol. Considering the accuracy of -50% / +100% for the capex-duty correlation, the total capex-related cost should be estimated between $250 and $1000/t.

This very preliminary analysis is not based on detailed flow sheeting of the process. Instead, it only considered a limited number of energy transfer duties (Table S1) that are critical for the various steps of the process, namely the overall heat of reaction, the heating of air to reaction temperature (step 1), the pressurization and simultaneous heating of methane to

20 bars (step 2) and the vaporization of water (step 3) and the distillation of methanol from excess water (step 4). The analysis only considers the size of the duties required without yet specifying how they will be executed, e.g. being either fixed beds with switching feed or circulating/rotating bed with fixed feed commonly that are proposed for chemical looping [43]. It therefore assumes average industrial practice and likely underestimates the management of swing operation. The overall duty was estimated at 22 GJ/t methanol (Table 1), which corresponds to an ISBL cost of ~$34M (based on eq. 5) and an overall investment cost of ~$200/M for a capacity of 100 kt/a.

Table 1. Energy transfer duties.

Process step	Energy transfer	Duty, GJ/t methanol
Zeolite oxidation	Air heating/cooling	3.3
Methane reaction	Methane compression	2.5
Hydrolysis	Water evaporation	12.4
Methanol extraction	Methanol distillation	0.03
Overall process	Reaction heat	3.9

Before closing the discussion, however, it is valuable to come back to the comparison of temperature-swing and isothermal operation. The traditional T-swing operation requires switching between room temperature and 200°C. The low productivity of 1 g/kg methanol that has been used in our analysis will result in swinging 1000 t of material per t of methanol produced, which corresponds to a duty of ~150 GJ/t, based on a heat capacity Cp of 1 J/(g·K) for the zeolite and a temperature swing of 150°C. This swing duty is much larger than the total duty of 22 GJ/t estimated for the isothermal process. For reference, the FCC process operates with T-swing between riser and regenerator. However, it operates at about 1000x higher production rate (1-2 kg/kg/h) and allows thereby efficient heating or cooling of the solid by means of hot or cold feed stream.

Synthesis, characterization and testing of active material

All samples were prepared according to a conventional ion exchange protocol with water solution of copper nitrate. Commercial zeolite MOR (CBV10A, Zeolyst) was used as the starting material. For the ion exchange with copper, 5 g of each zeolite in the ammonium

form were stirred into a 500 ml of a 0.05M water solution of copper nitrate (99%, Sigma Aldrich) at 323K overnight. The ion exchange was repeated twice. The resulting sample was filtered, washed with deionized water, dried at 393K for 1 h and calcined at 773K for 4 h in a flow of dry synthetic air.

Cu K edge X-ray absorption spectroscopy (XAS) measurements were performed at the SNBL (BM31) beamlines at the European Synchrotron Radiation Facilities in Grenoble, France. Around 5 mg of copper zeolite was sandwiched between quartz wool layers and placed in a 1 mm diameter, thin-walled (0.01 mm) quartz capillary reactor. This was attached to a custom-made cell for controlled heating. Gas flows were monitored by mass flow controllers. Gases of grade 6.0 were used. The X-ray beam, the sample, and the X-ray detectors were in conventional transmission geometry mode. Cu K edge X-ray adsorption near-edge spectra (XANES), in the range of 8900 to 9200 eV were collected every 40 s. The spectrum of a copper foil was collected for calibration of the internal energy. The samples were activated in a flow of oxygen at 673K for 1 h and purged subsequently with helium at 673K for 1 h.

Methane oxidation reactions were conducted in a continuous, tubular flow reactor (stainless steel tube, O.D. 12 mm). The reactor tube was mounted on the inside of a single-zone furnace. Temperature was controlled by a thermocouple mounted into the oven. CuMOR particles (0.5 g), pelletized and sieved to a size of 0.25-0.5 mm, were packed between quartz wool plugs and placed in the middle of the furnace heating zone. For oxygen pre-treatment, CuMOR after synthesis was heated in a flow of oxygen (50 ml/min, Messer 4.8) for 1 h and then in helium (50 ml/min, Messer 6.0) at 673K and 1 bar at a heating rate of 5 K/min. The activated sample was cooled to 473K in a flow of helium, and thereafter a flow of methane (50 ml/min, Messer 4.8) was introduced and the total pressure increased to 7 bar. After 30 min of reaction, the methane pressure was released and the reactor was flushed with a flow of helium (40 ml/min, 1 bar) for 20 min. The methane conversion products were removed by interaction of the reacted material at 473K in a wet stream of helium (2.6-18 vol% H_2O, 40 ml/min, 1bar) prepared by bubbling through the saturator.

References

[S1]   J.-P. Lange, CatTech, 2001, 5(2), 82-95.

[S2]   J.-P. Lange, ChemSusChem 2017, 10, 245 – 252.

[S3]   J.-P. Lange; Catal. Sci. Technol., 2016, 6, 4759 – 4767.