Dynamic simulation and analysis of a packed bed reactor for methanol steam reforming to hydrogen for shipboard fuel cells

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Highlights

- A novel 2D unsteady model predicts potential internal hotspots and production of unwanted species in time.
- Adverse temperature gradients may create a positive feedback loop which further degrade the catalyst.
- Careful control over process variables can help to extend the catalyst lifetime and maintain high hydrogen yield.

1. Introduction

The maritime sector shows growing interest in fuel cell power due to the necessity for emission reductions. The hydrogen required to power polymer electrolyte membrane fuel cells (PEMFCs) is challenging to efficiently store and transport. Possible solutions include hydrogen carriers and on-board hydrogen production. One such carrier is methanol which can be converted to hydrogen in a catalytic packed bed reactor by steam reforming. The reformer must reliably match the required hydrogen supply, which fluctuates with variable PEMFC power output. Additionally, PEMFC also requires low amounts of contaminants in the hydrogen stream. The most challenging contaminant to manage is carbon monoxide (CO) because must be kept below 10ppm. Consequently, its production in the reformer must be as low as possible. Primary applications of methanol reformer are within the petrochemical industry for steady hydrogen production, so dynamic operations are not extensively researched. Furthermore, a reformer has a slower transient response than a PEMFC, making it the limiting factor in ship transient power supply. Reformer hydrogen production increases also cannot be too steep in order to avoid internal hot spots potentially damaging the catalyst via sintering. Spikes in CO production may also occur in ramp ups, harming the downstream PEMFC. To quantify the operating limits, the present work demonstrates computationally efficient simulations of dynamic operation of a methanol steam reformer. We identify case-specific limits of reformer dynamic operation, and consequently the response of the power production system.

2. Methods

A new 2D unsteady model of catalytic packed bed reactor for methanol steam reforming is developed as an extension of the kinetic model of Peppley et.al. [1] and 2D steady state reformer model of Zhu et.al [2]. The new model is purposed for simulating transient events, which allows temporal analyses of reformer operation. We simulated a small experimental reactor, designed for full conversion at methanol flow rate of 102 g/h at 260 °C. The present model is used to simulate several hydrogen production increase cases. These simulations provide insight into unsteady internal fields, which are used to identify harmful local conditions and the length of their appearance. Specifically, we analyze how dynamic operation induces hot spots and variations in reformate composition. We attempt to correlate the input process variables with adverse effects in the reactor. Finally, we use correlations to characterize the reformer dynamic operation limits.

3. Results and discussion

The simulated unsteady temperature and species concentration fields indicate that locations of elevated local temperature and increased CO productions coincide. The coincidence occurs because CO production increases with temperature via the reverse water gas shift (RWGS) reaction, often in regions

where all methanol has already been converted. This occurs predominantly near the reactor outlet, and in near wall regions in extreme ramp up scenarios. Furthermore, as recurring hot spots cause loss of activity in the catalyst, the effect is amplified with time since less heat is consumed by the endothermic reactions. The temperature hence appears as the single most influential variable. Reactant flow rate, reactant temperature, and reactor wall temperature can be used to control temperature gradients in axial and radial directions. The simulations also show that thermal equilibrium is reached around 15 or more minutes after a transient event, mainly due to the thermal mass of the catalyst. These results imply that the optimal hydrogen yield and transient response should consider the reformer and catalyst pellet sizes.

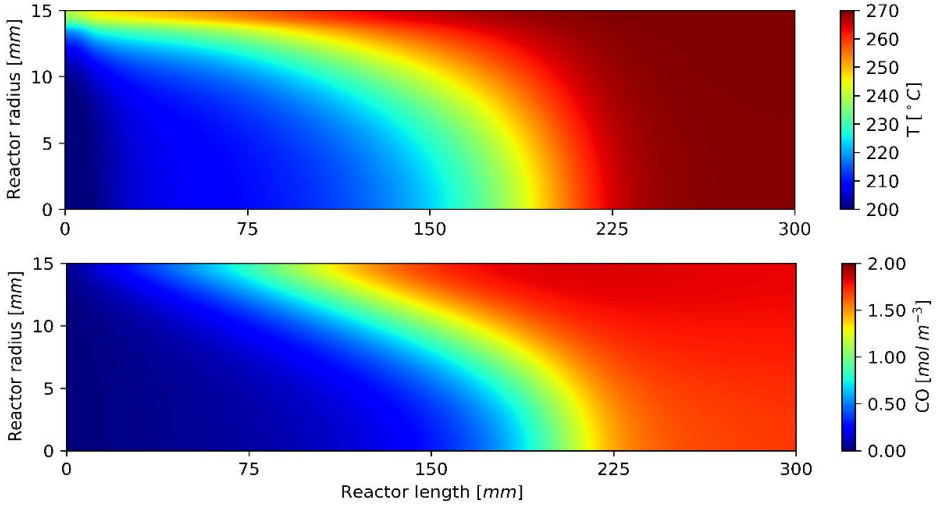

Figure 1Internal reactor temperature and CO concentration fields

4.Conclusions

The 2D dynamic methanol reformer model is shown to be essential in investigations of internal reformer fields in transient conditions. The temperature field was shown to be most important in controlling the products and catalyst lifetime. The thermal mass of the catalyst often causes large gradients in the transient temperature field, which should be countered with adequate control over process variables. The operation dynamics must simultaneously remain as fast as possible since methanol reformers in that respect are slower than PEMFC. A good, non-destructive reformer control strategy is vital to preserve a reliable hydrogen supply over long operating hours. Alternatively, the model can be used to dimension the reactor and catalyst pellet size distribution. The developed model is shown to be valuable for large transport applications such as maritime that pair methanol reformers with PEMFC.

5. References

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6. Acknowledgements

Funded by the Netherlands Enterprise Agency (Rijksdienst voor Ondernemend Nederland) as part of MENENS project under the grant number MOB21012.

Keywords
"methanol","packed bed reactor", "dynamic simulation", "PEMFC", "maritime"