398f Dynamic Modeling of a Methanol Reformer/Pemfc for Analysis and Design

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Limited petroleum supplies and the increasing price of oil are helping to push the design of alternative fuel vehicles both here in the U.S. and abroad. One promising technology appears to be hydrogen-powered proton exchange membrane fuel cells (PEMFCs) to power vehicles with electrical energy. However, major design hurdles still exist in terms of both onboard hydrogen storage and national distribution infrastructure. Therefore, some consider the most viable option of hydrogen storage in near- to mid-term to be liquid fuels such as methanol or ethanol, which can be reformed onboard to produce hydrogen. While the use of liquid fuels allows for continued use of the current distribution network and should be safer than onboard high-pressure H2 storage, it signi cantly complicates the overall design of the system [6].

A major concern with onboard reforming is that the gas fed to the fuel cell stack is no longer pure H2, but rather a mixture of H2, CO2, H2O, N2, and other impurities such as CO and NH3. Given the reduced concentration of H2, the fuel cell stack anode would need to operate at a higher pressure to achieve the same partial pressure of H2. Additionally, the presence of CO and NH3 in the anode feed reduces the ef ciency of the PEMFC, and CO in particular can permanently deactivate the catalyst in the fuel cell. Thus, it is critical to operate the reforming reactor or reactor/separation unit in a regime where fewer than 50 ppm CO is present in the anode feed.

Another important issue is the additional energy required to operate the reformer and its impact on the overall ef ciency of the power system. Standard steam reforming is unlikely, considering the energy needed to maintain the high temperatures required to achieve satisfactory activity in the catalyst. Partial-oxidation and autothermal reforming reactors operate at substantially lower temperatures and are exothermic or nearly energy-neutral. However, the lower temperature and heat demand is achieved at the expense of a lower production of H2 per mole of methanol. This necessitates a larger than stoichiometric storage of methanol to obtain the same driving range as a given quantity of pure hydrogen gas. Heat and water integration will be crucial to the ef ciency of such a system. The reformate stream is at a signi cantly higher temperature than what can be tolerated by a standard PEMFC. A design that considers the cooling of the reformate and the preheating of the reformer and PEMFC stack feeds jointly has the potential for considerable energy savings. Finally, the amount of exogenous water necessary to run the system can be greatly reduced if the water produced in the PEMFC stack is collected and recycled to the methanol reformer.

Both the reformer and the PEMFC stack have dynamic transients associated with load changes. Considering the inherently dynamic operation of a passenger vehicle, the transient behaviors of all components must be carefully studied. Traditional steady-state design methodologies are not suf cient. In order to meet these challenges, systemlevel models of a packed-bed methanol reformer and a PEMFC stack have been implemented. The methanol reformer has been treated as a PFR. The method of lines approach has been used where the spatial derivatives are discretized using nite differences, thereby reducing the model to a coupled set of ordinary differential equations. The reaction kinetics are taken predominantly from Mizsey et al. [4] with an overall modeling approach similar to that presented in Section 14.2 of Nauman [5] or more speci cally, Dams et al. [1]. Results presented in that work were used to validate the current model. Implementation was done in native code ñ C and Fortran ñ for the sake of computational performance. However, an interface to Matlab and Simulink has been constructed for ease of analysis and integration with other model components.

The system-level fuel cell model is derived from the work of Pathapati et al. [7]. While the original fuel cell model assumes a pure hydrogen feed to the anode, this model expands to include a multicomponent

anode mass balance so that the simulated stack can be powered by reformate. This model assumes that the anode and cathode volumes are well-mixed, which is not truly the case, but should provide a reasonable approximation to the thermal, electrical, and material transients observed from a stack unit without the computational burden of full computation uid dynamics calculations inside the ow channels. Again, the current model has been implemented as a C-MEX le within the Matlab / Simulink environment.

The system obtained by coupling the material and energy streams of the reformer and PEMFC stack becomes an integral component in the design of the fuel cell vehicle system-at-large. If the principle design speci cation of a fuel cell vehicle were simply nominal power rating, then steady-state tools would be suf cient to size the plant. However, performance during transient situations such as startup, acceleration, and braking are critical to the safety, reliability, and convenience of fuel cell vehicles. Therefore, the dynamic behavior of the system must be considered during design. The U.S. government provides a standardized Federal Urban Driving Schedule (FUDS) and Federal Highway Driving Schedule (FHDS), which detail representative time-resolved velocity pro les for vehicles driving in a city or highway, respectively. By making some rudimentary assumptions about the weight of the vehicle and the power losses in the tires, differential, gearbox, and electric motor, time-resolved electrical power pro les can be estimated for city and highway driving. After simulating a particular reformer/fuel cell stack con guration, its performance can be compared against the desired power pro les to determine whether the design is suf cient.

However, ability to meet the desired power pro le is not the sole design constraint. For vehicular applications, both size and weight, as well as energy ef ciency and nancial cost are all important. A truly optimal design must consider all of these factors. Consequently, a number of design variables appear such as length and diameter of the reformer, fuel cell membrane area, desired reformer operating temperature, reformer feed pressure, and stack feed pressure. Similarly, Mitsos and Barton [3] have explored many of the design parameters and constraints for microscale fuel cell power systems. While a number of the objectives and constraints differ, the overall approach to an optimal design is similar. Once all of the design metrics are mathematically combined into a single objective function, nonlinear optimization techniques can be used to adjust the design parameters until the optimal design has been found.

Most deterministic nonlinear optimization routines require the evaluation of the gradient of the objective function at a given point. For complicated, nonalgebraic objective functions such as the dynamic simulation described above, it is impossible to obtain an analytical gradient; it must be approximated by nite differences. For an objective function of N variables (equivalently, design parameters), N + 1 function evaluation simulations must be performed for a single gradient calculation. Given the complicated objective function described previously which requires the solution to a stiff set of ODEs or DAEs, the vast majority of the computational effort needed in optimization will be utilized in the repeated evaluation of the objective function. To help alleviate this problem, the authors have developed a parallel implementation of a quasi-Newton BFGS linesearch algorithm for the solution of bound-constrained NLPs. Schnabel [8] has discussed the potential applications of parallelism in nonlinear optimization. For this application, the C-language version of the Message Passing Interface (MPI) was used to allow for the simultaneous evaluation of the objective function at the points needed for gradient calculations on multiple processors. High and LaRoche [2] speci cally address the possibilities of parallel nonlinear optimization for chemical process design purposes. For truly objective-function dominated optimizations, nearly N-fold speedup can be obtained assuming the number of available processors exceeds the dimensionality of the optimization problem.

[1] R. A. J. Dams, P. R. Hayter, and S. C. Moore. Continued Development of a Mathematical Model for a Methanol Reformer. Technical Report ETSU F/02/00152/REP, Wellman CJB Ltd., 2001.

[2] K. A. High and R. D. LaRoche. Parallel Nonlinear Optimization Techniques For Chemical Process Design Problems. Comput. Chem. Eng., 19(6/7):807ñ825, 1995.

[3] A. Mitsos and P. Barton. Optimal Design and Operation of Fuel Cell Systems for Micro Power Generation. In Proceedings of Foundations of Computer Aided Process Design 2004, pages 377ñ380. CACHE/AIChE, 2004.

[4] P. Mizsey, E. Newson, T. b. Truong, and P. Hottinger. The Kinetics of Methanol Decomposition: A Part of Autothermal Partial Oxidation to Produce Hydrogen for Fuel Cells. Appl. Cat. A: General, 213:233ñ237, 2001.

[5] E. B. Nauman. Chemical Reactor Design, Optimization, and Scaleup. McGraw-Hill, New York, 2001.

[6] U.S Dept. of Energy and U.S. Environmental Protection Agency. Fuel Cell Vehicles. Technical report, www.fueleconomy.gov/feg/fcv_fuels.shtml, May 2005.

[7] P. R. Pathapati, X. Xue, and J. Tang. A New Dynamic Model for Predicting Transient Phenomena in a PEM Fuel Cell System. Renewable Energy, 30:1ñ22, 2005.

[8] R. B. Schnabel. A View Of The Limitations, Opportunities, and Challenges In Parallel Nonlinear Optimization. Parallel Computing, 21:875ñ905, 1995.