

Markov Chain Monte Carlo Optimization of Visible Light-Driven Hydrogen Production

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Abstract—This paper uses Markov Chain Monte Carlo techniques to draw out insight in optimizing the visible light-driven hydrogen production process of Tolod et. al. by specifying which reactions to promote in order to increase the rate of hydrogen gas production from a water-based solution. The objective is to minimize the time it takes to form a new hydrogen gas molecule through controlling the initial concentration of the reactants. An agent-based program has been created to model and simulate the reactor setup. Gibbs sampling has been used to determine a unique and stationary distribution suggesting that reactions producing carbon dioxide and hydronium, when increased, will yield faster hydrogen production for the reactor under study.

Index Terms—Optimization, Markov Process, Monte Carlo methods, Hydrogen

I. INTRODUCTION

Sustainable and clean energy technologies are considered relatively new, but highly important fields of research. One of the most promising of these sustainable technologies is the utilization of hydrogen energy. It is believed that the human quality of life will be better served by the envisioned hydrogen economy rather than the current one based on fossil fuels. Experimentation in this field necessitates building reactors and using costly measuring equipment. Each experimental run also takes days to complete. Modeling and simulation can provide insight in optimizing future experiments and increasing the hydrogen yield for a particular reactor setup.

This paper uses Markov Chain Monte Carlo techniques to draw out insight in optimizing the hydrogen production process in [1] by specifying which reactions to promote in order to increase the rate of hydrogen gas production from a water-based solution. The objective is to minimize the time it takes to form a new hydrogen gas molecule through controlling the initial concentration of the reactants.

II. THE MODEL

The traditional method of analysis is based on a deterministic formulation of chemical kinetics that leads to a coupled set of ordinary differential equations. The species concentrations are represented by continuous, single-valued functions of time. The time evolution of the concentrations of chemical species is calculated by solving a set of coupled

differential equations, with each equation describing the time rate of change of the concentration of a chemical species. The equations are based on the stoichiometry of the reaction and the reaction rate constant under an assumption of mass action kinetics [2]. The inference problem is estimating the reaction rate parameters. Several estimation techniques ranging from parameter tuning to model-based Bayesian methods are mentioned in [3].

An agent-based program, shown in Figure 1 on page 3, has been created to model and simulate the reactor setup. The program incorporates the different chemical reactions known to occur in the reactor as listed below [4].

- 1) $2H^+ + 2e^- \rightarrow H_2$
- 2) $CH_3OH + H_2O + 6h^+ \rightarrow CO_2 + 6H^+$
- 3) $2OH^\bullet + 2h^+ \rightarrow O_2 + 2H^+$
- 4) $H_2O \rightarrow H^+ + OH^-$
- 5) $H_2O + h^+ \rightarrow H^+ + OH^\bullet$
- 6) $OH^- + h^+ \rightarrow OH^\bullet$
- 7) $SrTiO_3 + hv \rightarrow e^- + h^+ + SrTiO_3$
- 8) $e^- + h^+ \rightarrow \emptyset$
- 9) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
- 10) $H^+ + OH^- \rightarrow H_2O$

There are two extremes in modeling chemical reaction mechanisms. One is to have a one-step global mechanism that resembles a “black-box” approach. The other extreme is a very detailed mechanism from elementary reactions [5]. This work strives for a balance of mechanism detail in order to capture the behavior relevant to the goal of increasing hydrogen yield through varying input concentrations, while at the same time limiting complexity and computational cost.

Chemical reaction kinetic quantities such as the frequency of collision, the orientation factor and the activation energy are incorporated within the model under isothermal laboratory condition assumptions. The relative physical dimensions of the reactor as well as the relative concentrations of the different reactant species are also incorporated in the model. Options such as light intensity, initial concentrations of reactants and catalyst are controlled through sliders. Non-spatial dependent reaction factors such as the orientation factor and the activation energy for each of the reactions are

set as probabilities conditioned on the event that the required species collide in the simulated reactor. The concentrations of the different species are monitored as well as shown through animation.

Plots of species concentration against time were generated based on experimental and simulated runs and were used as input for the optimization process. Analysis of the plots easily produce an input matrix, where each row is comprised of the concentration of each of the species and the number of time steps it took for such a combination of concentrations to produce hydrogen.

III. OPTIMIZATION METHOD

A Bayesian approach was used for optimization. A primer to this approach is found in [6]. Markov Chain Monte Carlo techniques using Gibbs sampling were employed to provide an approximate inference on the units of time necessary for a particular set of reactant concentrations to form hydrogen. Let us have a set of random variables $\mathbf{B} = [\mathbf{B}_1, \mathbf{B}_2, \dots, \mathbf{B}_n]'$ with values $\beta = Val(\mathbf{B}_i) \in \mathbb{R}$, representing the impact of reactant i to the formation time of hydrogen gas. Let us define an evidence matrix \mathbf{e} , containing the values of concentrations for a particular chemical species at a particular time. We then seek some unique and stationary distribution $P(\beta | \mathbf{e})$ that would give the probability that a particular set of reactant impact coefficients predicts the relative amount of time it takes to produce hydrogen gas for a given set of reactant concentrations given evidence concentration data \mathbf{e} . Each evidence concentration datum consists of reactant concentrations with a corresponding number of time steps to hydrogen formation. The data is taken from simulations using the agent-based program in Figure 1 on the next page. These concentration data are matched with the impact coefficient random variables in a linear regression manner as shown in (1), where the mean function $\mu_{time}(\mathbf{B})$ estimates the time to hydrogen formation and β_0 represents the error term accounting for timesteps not directly explainable by any of reactant concentrations. Reactant concentration is in $moles/volume$ and β is in $time \cdot volume/moles$.

$$\mu_{time}(\mathbf{B}) = \mathbb{E} \left[\beta_0 + \sum \beta_i \cdot y_i \right] \quad (1)$$

where,

- $\mu_{time}(\mathbf{B})$ is the expectation of the time for hydrogen formation
- β_i are regression coefficients
- y_i is the concentration of reactant i

The possible values of vector \mathbf{B} constitute a state in the state space. States constrained by a particular datum D_l , with respect to (1), have local interactions between themselves defined by Φ_l . Each set of concentration data D_l with its corresponding time to hydrogen formation value constitute a factor Φ of distribution P_Φ , where P_Φ is equivalent to the solution distribution $P(\beta | \mathbf{e})$. $\Phi = \{\Phi_1(D_1), \Phi_2(D_2), \dots, \Phi_N(D_N)\}$ factorizes over the Markov Network of allowable states in the manner of (2).

$$P_\Phi(\mathbf{B}) = P(\beta | \mathbf{e}) = \frac{1}{z} \prod_l \Phi_l(D_l) \quad (2)$$

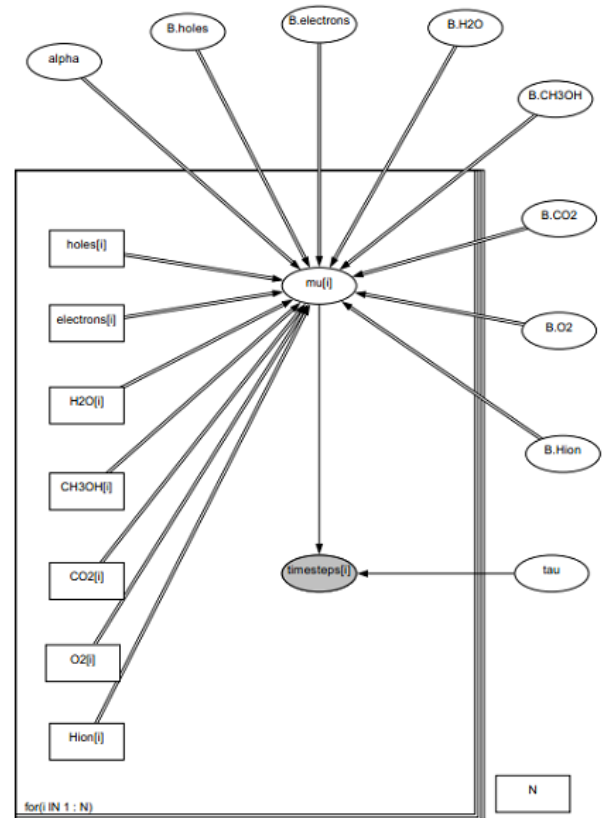


Figure 2. Graphical representation of the complex statistical model

where,

- $P_\Phi(\mathbf{B})$ is the probability that a given set of concentration regression coefficients to produce a hydrogen molecule in the next time step.
- Z here is the partition function that normalizes the local factors to define a probability distribution
- D_l is a set of concentration data that has a corresponding number of time steps to hydrogen production
- $\Phi_l(D_l)$ is a factor over the Markov Network for a particular concentration data set D_l

A graphical representation of the complex statistical model for the impact distributions of the different chemical species is presented in Fig. 2 on page 2. Analysis is done to determine unique and invariant distributions of the impact coefficients β_i , represented in the graphical model as alpha and B coefficients. The reactant coefficients are in vectors of index $[i]$ out of N data points gathered from the simulations of the agent-based model. The sum of the products of the impact factor with the corresponding reactant concentration becomes the mean for the distribution of timesteps or the expected amount of time for a given set of reactant concentrations to produce hydrogen.

We seek the convergence to a unique stationary distribution that is reachable from any starting state, starting from an initial state and transitioning randomly, initially according to a non-informative Bayesian prior to a distribution closer to the posterior with every timestep. A transition probability τ specifies the probability $\tau(\beta \rightarrow \beta')$ of going to state β' from state β . Where the distribution over the states at

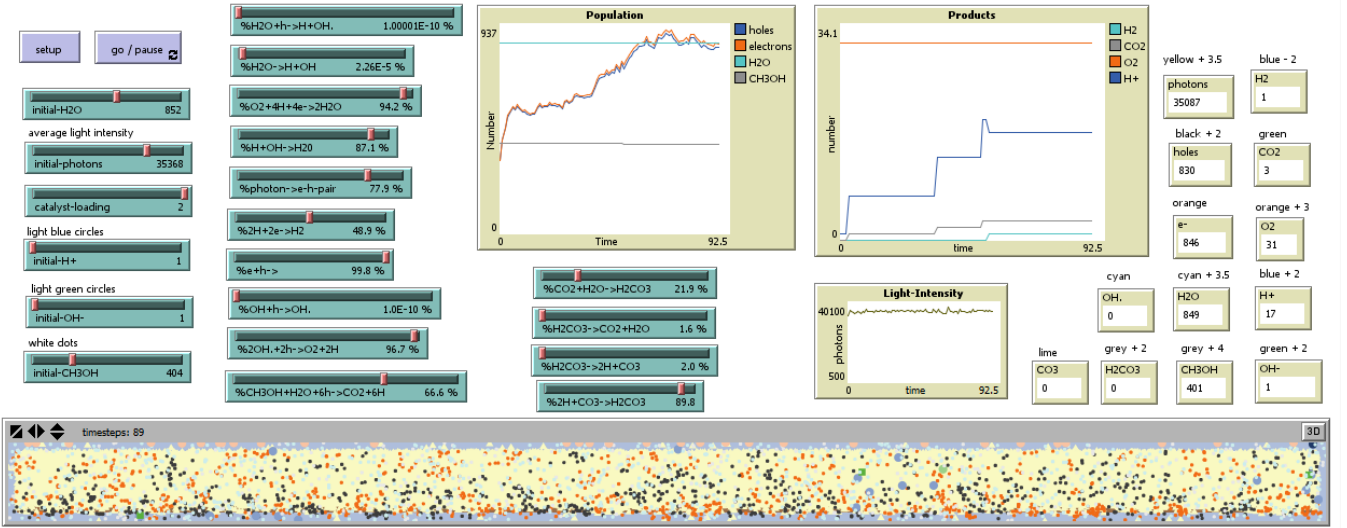


Figure 1. Interface of the agent-based simulator for visible light-driven hydrogen production

the next timestep $t + 1$ can be defined using the chain dynamics $P^{(1)}(\mathbf{B}^{(1)}), P^{(2)}(\mathbf{B}^{(2)}), \dots, P^{(t)}(\mathbf{B}^{(t)})$, of the distributions of the preceding timesteps. The probability that the impact coefficients are of a particular value β' is the sum over all possible states β that the chain could have been at time t of the probability in state β times the probability that the chain transitions from state β to state β' as show in (3).

$$P^{(t+1)}(\mathbf{B}^{(t+1)} = \beta') = \sum_{\beta \in \text{Val}(\mathbf{B})} P^{(t)}(\mathbf{B}) \tau(\beta \rightarrow \beta') \quad (3)$$

where,

- $P^{(t)}(\mathbf{B})$ is the probability for a given set of regression coefficients to transition to another set of regression coefficients β'
- $\tau(\beta \rightarrow \beta')$ specifies the from and to states that the transition probability is describing

The transition model τ is decomposed into a set of transition models τ_i , assigning a kernel to each random variable representing the impact of the chemical concentrations. Once the distributions of the impact coefficients converge as in (4), the chemical species with high absolute values of coefficients are the ones likely to impact the amount of time necessary for hydrogen production.

$$P^{(t+1)} \approx P^{(t)} \quad (4)$$

IV. RESULTS AND ANALYSIS

The results listed in Table I show that promoting the reactions producing carbon dioxide (CO_2) and hydrogen ion (H^+) has the highest impact to the probability of producing hydrogen in the next timestep. The reaction that produces the most carbon dioxide molecules and hydrogen ions is $CH_3OH + H_2O + 6h^+ \rightarrow CO_2 + 6H^+$. This suggests that a 1:1 methanol-water ratio may improve hydrogen production rates.

The results were collected after 100,000 iterations with the first 10,000 iterations set aside for burn-in time and mixing

time. However, the convergence for this case is not guaranteed since the set of impact coefficient values ψ is not finite. Standard checks for divergence such as plotting the running quantiles, kernel densities, variable traces and the Brooks-Gelman-Rubin diagrams were performed.

The means of the resulting impact coefficient distributions together with 95% confidence intervals are plotted against the iterations in Figure 3 on the next page. The deviation from 0 of the graphs for carbon dioxide and hydrogen ions are apparent. The graphs are also constant, suggesting convergence to a stationary distribution. Two Markov chains with different initial values were run, a red and a blue. The blue chain overlapping the red suggests that the probability of convergence to a unique distribution. Each impact coefficient was modeled as a kernel dimension for the MCMC algorithm to take a random walk. The vague priors used were centered Gaussian distributions with a large variance. The law of large numbers suggest that repeated sampling would produce a normal distribution with a mean that is likely to be a good estimate of the true value being sought. The plots of the resulting distributions in Figure 4 on the following page exhibit near Gaussian form. A converged system will pick values from a stationary distribution and produce a random trace of values with a fixed mean and variance. Two chains were used to provide greater confidence in the results. The absence of increasing or decreasing trends suggest convergence. The trace plots for each variable is shown in Figure 5. The Gelman-Rubin statistic, which is equal to 1 when denoting convergence, is computed for each of the variables. Figure 6 on page 5 shows the computed Gelman-Rubin statistic as the red graph. Brooks-Gelman criterion adds that for convergence, the blue and green graphs should be equal and constant [7]. The diagrams suggest system convergence.

Markov Chain Monte Carlo (MCMC) simulation suggested that the concentration of methanol be made equal to the concentration of water. The suggestion was tested using the Agent-based model and resulted in 806 units of hydrogen predicted over the original 629 units of hydrogen predicted.

Table I
RESULTS

node	mean	sd	MC error	2.5%	median	97.5%	start	sample
B.CH3OH	6.871	25.83	0.08232	-44.03	6.949	57.52	10001	100000
B.CO2	-18.62	16.7	0.05299	-51.4	-18.61	14.21	10001	100000
B.H2O	-2.93	12.31	0.03928	-27.08	-2.944	21.3	10001	100000
B.Hion	-8.076	18.68	0.05945	-44.51	-8.123	28.47	10001	100000
B.O2	-0.745	31.46	0.09969	-62.48	-0.6846	60.89	10001	100000
B.electrons	-2.006	18.2	0.05828	-37.54	-1.978	33.56	10001	100000
B.holes	3.078	18.22	0.05817	-32.54	3.053	38.68	10001	100000
alpha	0.1619	31.61	0.1021	-61.81	0.313	61.82	10001	100000
tau	1.907E-5	4.592E-6	1.592E-8	1.116E-5	1.87E-5	2.898E-5	10001	100000

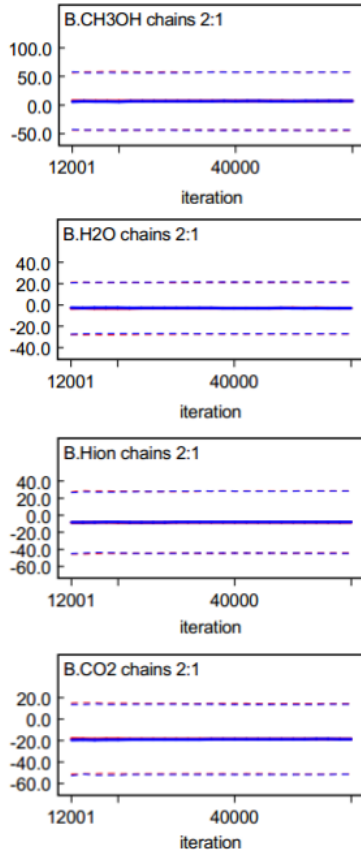


Figure 3. Running quantiles of impact coefficient means vs. iterations

This is a 28% improvement in the expected hydrogen production as shown in Table II. The scenario where the methanol concentration is lowered was also simulated. It resulted in a lowering in expected hydrogen production and supports the inference obtained from the MCMC optimization.

V. CONCLUSION

The visible light-driven hydrogen production process is highly likely to improve hydrogen formation time through promoting reactions producing carbon dioxide and hydrogenium. The results provide us a technique by which optimization can be done for hydrogen production experiments with existing agent-based models. The insight is determined through Gibbs sampling and convergence is verified through kernel density plotting, time-series tracing, and Brooks-

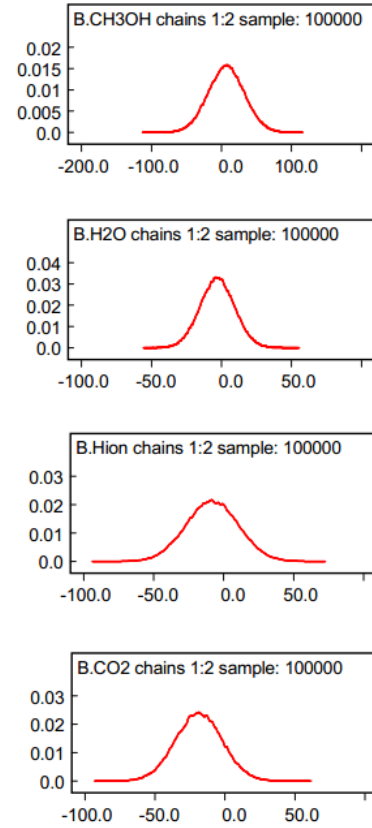


Figure 4. Kernel densities of the impact coefficients

Gelman-Rubin diagrams. The results may aid in pushing hydrogen energy research towards economical viability.

Further experiments will be done to validate the predicted 28% improvement in hydrogen production experimentally. The program and experiments will also be adjusted to remove the need for an isothermal assumption.

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Table II
SIMULATION RESULTS

	original ratio	lowered [MeOH]	equal concentrations
concentration ratio	[MeOH]=1/2[H ₂ O]	[MeOH]=1/3[H ₂ O]	[MeOH]=[H ₂ O]
timesteps	105	104	104
Hydrogen units	629	617	806

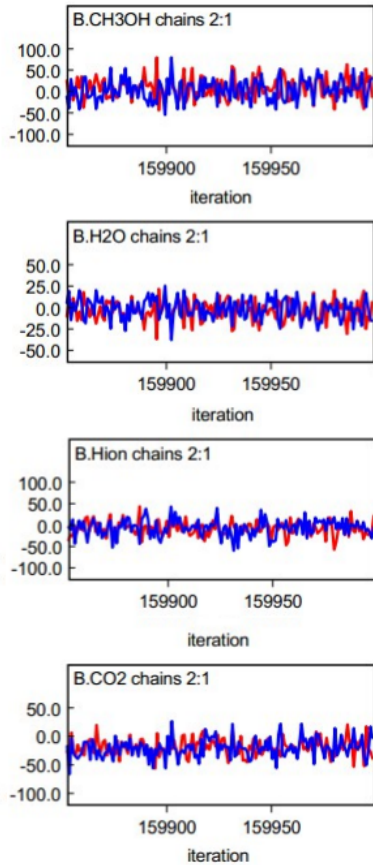


Figure 5. Plots of variables values for every iteration

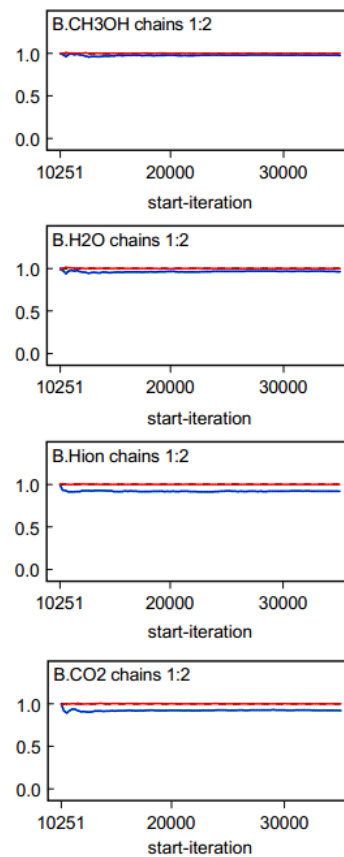


Figure 6. Brooks-Gelman-Rubin Diagrams

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