# Exploiting Electricity Market Dynamics using Flexible Electrolysis Units for Retrofitting Methanol Synthesis Supplementary Information

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This supplementary information contains 11 pages and 2 sections. The first section gives details on chemical process simulation, optimization model, TEA model and density functional theory calculation; the second section gives details on techno-economic data and energy markets. All scripts and data needed to reproduce the results are available at: https://github.com/zavalab/JuliaBox/tree/master/MeOH

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## 1 Methods

#### 1.1 Chemical Process Simulation

We simulate steam reforming, methanol synthesis, and rWGS units using the process simulator Aspen Plus V10. The mass and energy balances obtained from simulation results are used for process optimization. Aspen RGibbs reactor model is used to predict the yield of steam reformer and rWGS reactor. Since the high-temperature reaction condition results in fast reaction kinetic rates, the reaction equilibrium can be precisely predicted using RGibbs model [4]. Moreover, a rigorous microkinetic model is used to predict the yield of methanol synthesis reactions. We use the Peng-Robinson property method [14], which is recommended for hydrocarbon processing applications. The material and energy balance obtained from Aspen simulations are inputs for optimization and techno-economic analysis models.

#### 1.2 Optimization and TEA Model



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Figure S1: Schematic of electrification system coupled with methanol synthesis process.

In Figure S1, solid lines are streams with constant flows. Dashed lines are streams with varying flows. In (1.1b),  $f^{sr}$  and  $f^e$  are the amounts of syngas produced by the steam reformer and the reverse water gas shift (rWGS) reactor. In this model, we partially replace the syngas produced by steam reforming using electrolysis and rWGS. To meet the syngas demand of MeOH systhesis unit  $f^d$ , we combine the syngas produced by rWGS ( $f^e$ ) and steam reformer ( $f^{sr}$ ). Since chemical reactors, including steam reformer, rWGS reactor, and MeOH reactor are not flexible as the electrolyzer, their feed and product streams are constant. We use  $f_i^h, f_i^{h,s}, f_i^{h,r}, f_i^{h,c}$  to denote the amount of hydrogen generated, stored, released, and directly consumed at time interval *i*, respectively. The hydrogen produced from electrolysis at each time interval is either directly consumed as stored. Therefore, in (1.1c), the sum of hydrogen directly consumed  $f_i^{h,c}$  and stored  $f_i^{h,s}$  equals to the hydrogen generated

 $f_i^h$  by electrolyzer at each time interval. In (1.1d), the hydrogen directly consumed  $f_i^{h,c}$  and released  $f_i^{h,r}$  from tank are merged, which provides a constant hydrogen supply for the rWGS reactor ( $f^{h,d}$ ). Equation (1.1e) shows the balance of the hydrogen storage tank.  $s_i$  represents the amount of hydrogen stored at time interval *i*. By adding the gas stored  $f_i^{h,s}$  and deducting the gas released  $f_i^{h,r}$  at the previous time interval *i*, the gas in the tank at current time interval i + 1 can be derived as  $s_{i+1}$ . In (1.1f-1.1g), the amount of water consumed  $f_i^w$  and the amount of oxygen generated  $f_i^o$  are correlated to the amount of hydrogen generated  $f_i^h$ .  $\gamma^o$  and  $\gamma^w$  are the correlation factors. In (1.1h), the amount of  $CO_2$  demanded by rWGS  $f^c$  is proportional to the amount of hydrogen demanded by rWGS  $f^{h,d}$ , and  $\gamma^c$  is the coefficient. Equations (1.1i-1.1j) are the capacity limit constraints of storage tank ( $\xi^t$ ) and electrolyzer ( $\xi^h$ ). In 1.1j,  $\gamma^h$  denotes the minimum part-load factor of the PEM electrolyzer, which is set as 3% in this work [16]. This constraints sets the lowest operating point of PEM electrolyzer, after which the device must turn off. The PEM electrolyzer is capable of ramping up and down within a second when operating between minimum part-load and full capacity. The objective is to minimize the system's total annual cost (TAC), which includes the operational cost of steam reforming, rWGS, electrification unit and the annualized capital investment of rWGS and electrolysis. To be specific, in (1.1a),  $\alpha^{sr}$  and  $\alpha^{r}$  are the operational cost factors of steam reformer and rWGS unit. To account the electricity cost of the electrification unit, we have  $\alpha_i^h$  as the electricity cost factor.  $\alpha_i^c$ ,  $\alpha_i^w$ ,  $\alpha_i^o$  are the cost factors of  $CO_2$ , deionized water and oxygen.  $\beta^h$ ,  $\beta^t$ ,  $\beta^r$  are the investment cost coefficients of electrification unit, gas tank and rWGS unit.

$$\min_{(f^{sr}, f^c, f^r, f^h, f^o, f^w, \xi_h, \xi_t)} \alpha^{sr} f^{sr} + \alpha^c f^c + \alpha^r f^r + \sum_{i \in \mathcal{I}} \alpha_i^h f_i^h - \sum_{i \in \mathcal{I}} \alpha_i^o f_i^o + \sum_{i \in \mathcal{I}} \alpha_i^w f_i^w + \beta^h \xi^h + \beta^t \xi^t + \beta^r f^{h,d}$$

$$(1.1a)$$

$$s.t. \quad f^d = f^{sr} + f^e \tag{1.1b}$$

$$f_i^h = f_i^{h,s} + f_i^{h,c}, i \in \mathcal{I}$$

$$(1.1c)$$

$$f^{h,d} = f_i^{h,c} + f_i^{h,r}, i \in \mathcal{I}$$

$$(1.1d)$$

$$s_{i+1} = s_i + f_i^{h,s} - f_i^{h,r}, i \in \mathcal{I}$$
 (1.1e)

$$f_i^h = \gamma^o f_i^o, i \in \mathcal{I} \tag{1.1f}$$

$$f_i^h = \gamma^w f_i^w, i \in \mathcal{I} \tag{1.1g}$$

$$f^{n,a} = \gamma^c f^c \tag{1.1h}$$

$$0 \le s_i \le \xi^c, i \in \mathcal{I} \tag{1.11}$$

$$\gamma^{h}\xi^{h} \leq f_{i}^{h} \leq \xi^{h}, i \in \mathcal{I}$$

$$(1.1j)$$

Equations (1.2a-1.2h) show the optimization model for the flexible hydrogen production system. We set a constant hydrogen demand  $f^{h,d}$  as 10 tonne/hr of hydrogen. The goal is to minimize the TAC of the proposed system, including electricity cost, deionized water cost, oxygen revenue, annualized capital cost of electrification unit and gas tank. The model formulation is identical to that of



Figure S2: Schematic diagram of hydrogen production via flexible electrification

the hydrogen production section of the above MeOH synthesis system.

$$\min_{(f^h, f^o, f^w, \xi_h, \xi_t)} \sum_{i \in \mathcal{I}} \alpha_i^h f_i^h - \sum_{i \in \mathcal{I}} \alpha_i^o f_i^o + \sum_{i \in \mathcal{I}} \alpha_i^w f_i^w + \beta^h \xi^h + \beta^t \xi^t$$
(1.2a)

s.t. 
$$f_i^h = f_i^{h,s} + f_i^{h,c}, i \in \mathcal{I}$$
 (1.2b)

$$f^{h,d} = f_i^{h,c} + f_i^{h,r}, i \in \mathcal{I}$$
(1.2c)

$$s_{i+1} = s_i + f_i^{h,s} - f_i^{h,r}, i \in \mathcal{I}$$
 (1.2d)

$$f_i^h = \gamma^o f_i^o, i \in \mathcal{I} \tag{1.2e}$$

$$f_i^h = \gamma^w f_i^w, i \in \mathcal{I} \tag{1.2f}$$

$$0 \le s_i \le \xi^t, i \in \mathcal{I} \tag{1.2g}$$

$$\gamma^h \xi^h \le f_i^h \le \xi^h, i \in \mathcal{I} \tag{1.2h}$$

These optimization models are linear programming (LP) models. We implement these models under in the algebraic modeling package JuMP [5] and solve them using Gurobi 9.1.0 [10]. The codes are executed on a computing server that contains a 32 cores Xeon(R) CPU E5-2698 v3 @ 2.30GHz. All the problems are solved within 1 hour.

Total annual cost (TAC) is the sum of annualized capital investment (CAPEX) and annual operational cost (OPEX):

$$TAC = Af \cdot CAPEX + OPEX \tag{1.3}$$

Annualized factor (Af), also known as the capital recovery factor, depends on the interest rate (i) and the plant lifetime (n). In this work, with a 10% of interest rate and a 20 years plant lifetime, the Af is calculated to be 0.117.

$$Af = \frac{i(1+i)^n}{(1+i)^n - 1} \tag{1.4}$$

Levelized cost of hydrogen (LCOH) is defined as the sum of costs over lifetime, divided by sum of hydrogen produced over lifetime. In the numerator,  $I_i$ ,  $M_i$  and  $E_i$  denote the investment cost, operation/maintenance cost, and electricity cost in year *i*, respectively. In the denominator,  $H_i$  is the hydrogen produced in year *i*. Symbol *r* denotes the discount rate and *n* is the expected lifetime of the system. In this work, we assume 10% discount rate and 20 years lifetime of the facility. We use the

results obtained from the above optimization models as inputs for computing LCOH. These inputs include capital cost, operational cost and hydrogen production of the system.

$$LCOH = \frac{\sum_{i=1}^{n} \frac{I_i + M_i + E_i}{(1+r)^i}}{\sum_{i=1}^{n} \frac{H_i}{(1+r)^i}}$$
(1.5)

The payback period  $\lambda$  is defined as initial project investment *I* divided by the annual cash flow  $\xi$ . The initial investment includes equipment purchase cost  $I_p$ , installation cost, contingency cost, site preparation cost, permitting and engineering design cost. As shown in (1.7), the installation, contingency, site preparation, engineering design cost are correlated to the equipment purchase cost. We take installation cost factor  $\alpha_i = 0.12$ , contingency cost factor  $\alpha_c = 0.2$ , site preparation cost factor  $\alpha_s = 0.02$ , permitting cost factor  $\alpha_p = 0.15$  and engineering design cost factor  $\alpha_d = 0.08$  [15].

$$\lambda = \frac{I}{\phi} \tag{1.6}$$

$$I = (\alpha_c + \alpha_s + \alpha_p + \alpha_d)\alpha_i I_p \tag{1.7}$$

Sourcing hydrogen via electrification lowers the hydrogen production of steam reforming. We consider the cost reduction of steam reforming as a revenue stream  $\phi_r$ . In (1.8), we define  $\bar{f}^{sr}$  and  $f^{sr}$  as the amounts of hydrogen produced by steam reforming before and after the retrofitting, respectively.  $\alpha^{sr}$  is the operational cost factor of steam reforming unit. Therefore, cost reduction of steam reforming is defined as  $\alpha^{sr}(\bar{f}^{sr} - f^{sr})$ . Meanwhile, the oxygen generated by electrolyzer also contributes to the system's revenue.

$$\phi_r = \alpha^{sr}(\bar{f}^{sr} - f^{sr}) + \sum_{i \in \mathcal{I}} \alpha_i^o f_i^o$$
(1.8)

The annual cash flow  $\phi$  is defined as the above revenue minus the operational cost of the electrolysis and rWGS units. The operational cost of the electrification and rWGS units includes fixed operational cost  $\phi_f$  and variable operational cost  $\phi_v$ .

$$\phi = \phi_r - \phi_f - \phi_v \tag{1.9}$$

The variable operational cost of the system includes  $CO_2$  and deionized water purchasing cost, electricity cost, and operational cost of rWGS. The fixed variable cost includes maintenance expenses, salary, property tax, insurance. The maintenance expenses, property tax and insurance are proportional to the initial investment. We take the maintenance cost factor  $\alpha^m = 0.03$  and the property tax and insurance cost factor  $\alpha^{p,i} = 0.02$  [15]. We assume a total staff number as 15 and the total labor cost  $\phi_l$  as 2 million USD/yr [15].

$$\phi_v = \alpha^c f^c + \alpha^r f^r + \sum_{i \in \mathcal{I}} \alpha_i^h f_i^h + \sum_{i \in \mathcal{I}} \alpha_i^w f_i^w$$
(1.10)

$$\phi_f = (\alpha^m + \alpha^{p,i})I + \phi_l \tag{1.11}$$

#### 1.3 Microkinetic Model

A first-principles informed microkinetic model was generated using energetics from density functional theory calculations for methanol synthesis over Cu(111) from the work by Grabow and Mavrikakis [9]. These parameters were adjusted to capture reaction kinetics experimental data over typcial supported Cu catalysts [9]. We make use of the fully optimized parameter set identified from this study to reproduce their experimentally-fitted microkinetic model. In total, this reaction scheme includes a series of 22 surface intermediates, 8 gas phase species, and 49 elementary reaction steps. These reactions steps include the hydrogenation of CO and CO2 to methanol as well as the reverse water-gas shift reaction. The resulting microkinetic model was used to predict the outlet stream composition leaving the methanol reactor based on the inlet feed composition and reactor conditions (Figure S1).

# 2 Techno-Economic Data

Table 51. 1 of ymer electroly te membrane (1 Elvi) electrolyzer parameters				
Item	Note	Reference		
Efficiency	80%	[12]		
Theoretical energy usage (100% efficiency)	39.4 kWh/kg of Hydrogen	[12]		
Stack energy usage	49.2 kWh/kg of Hydrogen	[12]		
Balance of plant (BOP) energy usage	5.4 kWh/kg of Hydrogen	[11]		
Stack investment cost	90 USD/kW	[13]		
BOP investment cost	258 USD/kW	[13]		
Lifespan of stack	50000 hours	[17]		

Table S1: Polymer electrolyte membrane (PEM) electrolyzer parameters

Table S2: rWGS system cost paramete	ers
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Items	CAPEX	OPEX	Reference
rWGS reactor	0.07 million USD	-	[4, 3]
rWGS catalyst	-	0.038 million USD	[4]
SMR catalyst	-	0.045 million USD	[18]
Pre-heater	0.67 million USD	-	[4, 3]
Furnace (Heater)	1.3 million USD	347 USD/hr	[4, 3]
Cooler	0.5 million USD	56 USD/hr	[3]
Flash tank	0.14 million USD	-	[3]
Compressor C1	6.7 million USD	117 USD/hr	[7,3]
Compressor C2	8.1 million USD	140 USD/hr	[7,3]

Table S3: Other parameters for techno-economic analysis

Items	Price	Reference
Carbon dioxide	47 USD/tonne	[8]
Oxygen	40 USD/tonne	[6]
Deionized water	1.35 USD/tonne	[7]
Natural gas	265 USD/tonne	[1]
Storage tank investment	84 USD/kg of Hydrogen	[2]



Figure S3: Real-time and day-ahead electricity prices for Houston and Panhandle, TX for 2020. The average electricity price of day ahead market is slightly higher than that of the real time market. The standard deviation of real time market is around 40% higher than that of the day ahead market, which implies that real time market is more volatile. Panhandle has a cheaper electricity price than Houston does. Moreover, the negative price frequency of Panhandle real time market is up to 25%. In opposite, the negative price frequency of Houston real time market is only 0.9%. The average price of Houston real time market is 22.4 USD/MWh, which is 39% higher than the average price of Texas (16.1 USD/MWh in 2020) and 6% higher than the national average price (21 USD/MWh in 2020). The average price of the Panhandle real time market is 12.8 USD/MWh, which is closed to the average price in the middle of the US (Kansas, Oklahoma, South Dakota Nebraska). Because most of the methanol plants in the US are located in Texas, the electricity markets for a couple of locations in Texas were used for the case study.



Figure S4: Cumulative density function (CDF) of electricity prices. RTM and DAM of Panhandle have a high probability of having negative prices. RTM and DAM of Houston tend to shift toward right, which implied that the electricity prices are higher than that of the Panhandle region.

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