Integration of operation and design of solar fuel plants
A carbon dioxide to methanol case study

Huesman, Adrie

DOI
10.1016/j.compchemeng.2020.106836

Publication date
2020

Document Version
Accepted author manuscript

Published in
Computers and Chemical Engineering

Title

Integration of operation and design of solar fuel plants: A carbon dioxide to methanol case study

Author names and affiliations

Adrie Huesman*
Department of Chemical Engineering, Delft University of Technology, 2629 HZ Delft, The Netherlands
Shell Technology Center Amsterdam, Grasweg 31, 1031 HW Amsterdam, The Netherlands
*Correspondence: (adrie.huesman@shell.com)

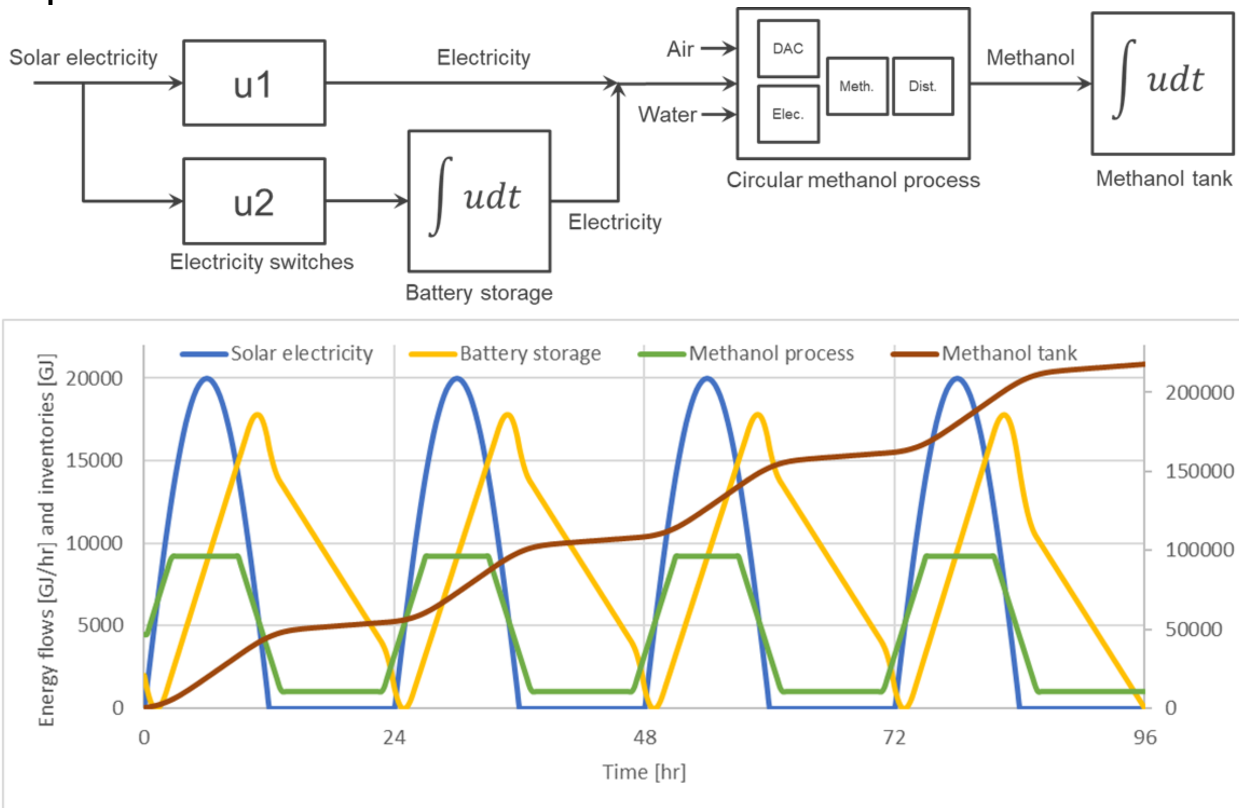
Highlights

- Solar fuel plants can be operated in a coupled or decoupled mode from the solar profile
- An extended optimal control framework determines the operation mode economically
- A simple dynamic model supports transparently key operational and design decisions
- For a cost structure by the year 2030 coupled operation is economically optimal
- An Operational Tipping Point marks the transition from coupled to decoupled operation

Abstract

Operation and design of solar fuel plants involves a decision about the degree of coupling between the solar electricity profile and the plant. Full decoupling needs large scale battery storage to ensure power availability during the night while full coupling requires high conversion capacity during the day to realize the required average methanol production. An extended optimal control framework is presented that determines economic optimal operation. Extended indicates that operational and design degrees of freedom are considered simultaneously. Using a simplified dynamic model of the plant, the framework minimizes total fuel cost for an estimated cost structure by the year 2030. The results show that full coupling is economically preferred and that limited operational flexibility increases the manufacturing cost of methanol from approximately 1000 to 1200 USD/ton. Analysis of the results reveals the cost structure determines an Operational Tipping Point that marks a clear transition from coupled to decoupled operation.

Graphical abstract



Keywords

Process operation and design; dynamic optimization; solar fuel plant

Acknowledgements

This research did not receive any specific grant from funding agencies in the public or not-for-profit sectors.

Nomenclature

Abbrevations	
AMPL	A Mathematical Programming Language
AIMMS	Advanced Interactive Multidimensional Modeling System
Capex	Capital expenditure
CONOPT	CONstrained OPTimizer
CPD	Conceptual Process Design
DAC	Direct Air Capture
Dist.	Distillation
Elec.	Electrolyser
GAMS	General Algebraic Modeling System
HHV	Higher Heating Value
IPOPT	Interior Point OPTimizer
Meth.	Methanol (synthesis)
NREL	National Renewable Energy Laboratory
Opex	Operational expenditure
OTP	Operational Tipping Point
SISO	Single Input Single Output

Symbols	
b, f, g, h	boundary condition(s) or constraint relation(s)
C1, C2, C3	cost factors [USD/GJ, USD/(GJ/hour)]
d	solar electricity
J	cost functional [USD]
P	production rate [ton/hr, GJ/hr]
Q	production amount [ton, GJ]
RR	Ramp Rate [(ton/hr)/hr, (GJ/hr)/hr]
s	Laplace variable
t, T	time [hr]
TR	Turndown Ratio [-]
u	operational degree(s) of freedom
v	design degree(s) of freedom
x	state variable(s)
y	algebraic variable(s)
z	decision variable(s)

Greek symbols	
η	efficiency [-]
τ	time constant [hr]

Subscripts	
c	conversion
f	final
max	maximum
min	minimum
req	required
s	storage

1. Introduction

The term solar fuel generally refers to a synthetic chemical fuel produced directly or indirectly from solar energy. Besides renewable energy also naturally occurring small molecules like water, carbon dioxide or nitrogen are needed as raw materials to produce dense energy carriers like methanol, hydrocarbons or ammonia. During use solar fuels are converted back into raw materials, so they can be produced in a circular way with a net zero carbon footprint. As demonstrated by Vázquez et al [1], the production of solar fuels via synthesis gas (indirect route) is technically already feasible. However, Michailos et al [2] and Tremel et al [3] point out that solar fuels are not cost competitive compared to fossil fuels. In the future this may change as the cost of renewable energy diminishes further and the cost of net carbon dioxide emissions from fossil fuels goes up.

Solar fuels serve a twofold purpose. First, these fuels can be used in applications where we already use fossil fuels. Although these will be gradually replaced by alternatives like batteries, in aviation applications this is difficult because of weight and volume requirements, see Berry et al [4]. Second, the production of renewable energy knows a diurnal but also a seasonal cycle. The shortage of renewable energy overnight can be addressed by large scale battery storage. However seasonal shortages require storage over months and dense energy carriers seem a better option as indicated by Gür [5] and Mulder [6].

There are many papers that focus on various aspects of solar fuel plants. For example, Herron et al [7] give a general process modelling framework to asses and compare different solar fuel technologies. Tountas et al [8] discuss various technologies at different scales to produce solar methanol and select the most viable technology. Smith et al [9] also examine solar methanol production but focus on the areas needed for solar PV, carbon dioxide air capture and carbon dioxide electrolysis for a 10000 ton/day plant. However, operation of solar fuel plants in these and other papers has received little attention. An exception is the recent paper of Shirazi et al [10]; the authors derive a dynamical model for the supercritical water gasification of microalgae followed by Fischer-Tropsch synthesis. The optimization is based on a genetic algorithm and aims to minimize the levelized cost of fuel. The optimization case and underlying model are quite specific and complex making it difficult to get insight in the operation of solar fuel plants. Powell, Hedengren and Edgar [11] describe the dynamic modelling and optimization of a hybrid solar thermal and fossil fuel system. Although the ‘product’ is (synthetic) hot oil rather than solar fuel their approach also deals with intermittency in a dynamic optimization setting. Looking at process operation from a general dynamic optimization perspective, then the work of the group of Pistikopoulos should be mentioned, see Burnak et al [12] for a recent overview. Their framework for integrated process design, scheduling and control is applied to Continuous Stirred Tank Reactor systems and a residential Combined Heat and Power unit. The starting point of their framework is a high-fidelity dynamic model which in case of a solar fuel plant is not easy to obtain. In addition, it may be easier to derive valuable insight in the operation of solar fuel plants from a simple dynamic model.

As a subject, operation of solar fuel plants, is important for several reasons:

- Douglas [13] points out one of the first decisions of a Conceptual Process Design (CPD) is the selection of operation mode. This is done at the beginning of a conceptual design (see figure 1) since it affects both process and control design.

- The selection of a specific operation mode is not trivial for a solar fuel plant. In conventional operation modes like continuous, discontinuous or batch it is assumed that raw materials and utilities are always available while renewable energy is only available on an intermittent basis.
- In Life Cycle Analysis of any plant, operation represents the longest period, typically at least 20 years. Furthermore, it is only during operation that a plant generates value for its stakeholders (society, investors and company).

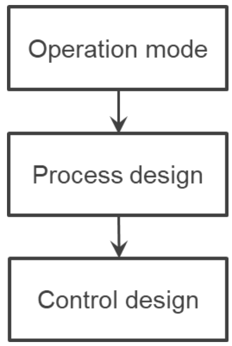


Figure 1 The three stages of Conceptual Process Design.

In this work the focus will be on the operation of solar fuel plant. To be more precise, we seek to answer the following questions:

1. How to frame operation mode selection of a solar fuel plant that uses intermittent power?
2. How to determine the best operation mode for a solar fuel plant?
3. Which factors determine/influence the operation of a solar fuel plant?

Rather than being precise for a very specific case the idea is to obtain general insight in the operation of solar fuel plants. The focus will be on the diurnal rather than the seasonal cycle since the diurnal cycle introduces the fastest dynamics. The indirect route to methanol via the hydrogenation of carbon dioxide will serve as a case study.

The rest of this paper is organized as follows. First a solar methanol plant is introduced followed by a discussion on process operation and how this relates to process economics. Then an extended optimal control framework is introduced that can determine optimal operation from an economic perspective. The word extended is used to indicate that this framework considers both operational and design degrees of freedom. The section ‘Results and discussion’ examines the influence of required operational flexibility and how cost structure determines operation. The last section summarizes the conclusions and suggests possible further work.

2. Process operation and economics

Figure 2 shows a simplified flow scheme of a solar fuel plant. It is assumed that the product methanol is produced via the hydrogenation of carbon dioxide:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad (1)$$

Carbon dioxide is obtained from air via Direct Air Capture (DAC), while hydrogen is produced via electrolysis of water. Methanol is separated from the byproduct water, via distillation. The plant can store both electricity and methanol. The battery storage allows for dynamic decoupling from the solar electricity profile, in other words the methanol process can be maintained for some time even if there is little or no solar electricity available (e.g. overnight).

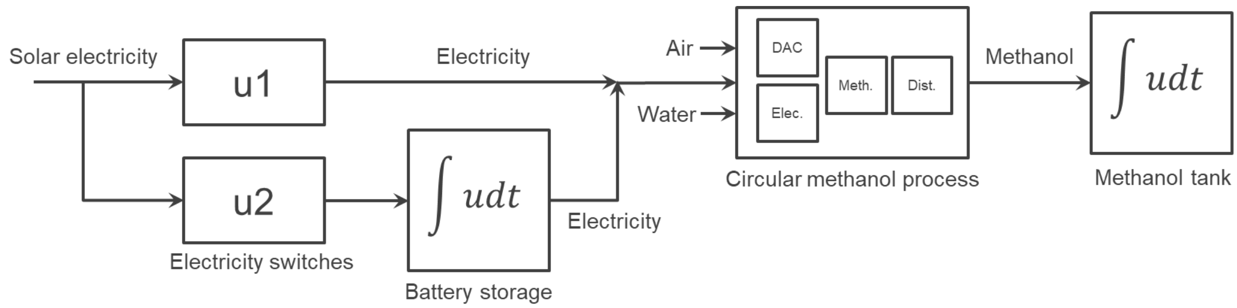


Figure 2 A block flow scheme of a solar fuel plant. Solar electricity is routed directly or via battery storage to a circular methanol process that consist of four units: Direct Air Capture (DAC) of carbon dioxide, water electrolyser (Elec.), methanol synthesis (Meth.) and distillation (Dist.).

The major part of the power supplied to the circular methanol process is used for water electrolysis. However also DAC and rotating equipment like pumps and compressors need power. The energy required for distillation may be provided by heat integration with the methanol synthesis section since reaction (1) is exothermic (also see appendix A).

This solar fuel plant may be operated in many ways, but two extremes can be identified:

1. The methanol process is dynamically fully decoupled from the solar electricity profile. The methanol process runs basically in steady state at the required average production rate. Clearly this requires substantial battery storage to maintain production overnight.
2. The methanol process is dynamically fully coupled with the solar electricity profile. In this case the methanol process will operate in a highly dynamic way and shut down overnight. The result is that no battery storage is needed.

Besides the impact on battery storage both modes have other pros and cons as well, see table 1.

Table 1 The advantages and disadvantages of fully decoupled and fully coupled operation.

	Pros	**Cons**
Fully decoupled	● Known operation mode ● High process equipment utilization: Design capacity/average capacity → 1	● Battery storage needed ● Lower overall efficiency: (Dis)charge efficiencies < 100% Voltage during discharge lower
Fully coupled	● No battery storage needed ● Higher overall efficiency	● Unknown operation mode ● Lower process equipment utilization: Design capacity/average capacity > 2

In industry it is well known how to design a process of more than 5-10 unit operations for steady state operation. However, the design of such a process for highly dynamic operation that needs significant operational flexibility in terms of high Turndown Ratios (*TRs*) and steep Ramp (up and down) Rates (*RRs*) is an academic research topic. If the production rate is indicated by *P* (e.g. in ton/hour) then *TR* and *RR* are defined as:

$$TR = P_{max}/P_{min} \tag{2}$$

$$RR = dP/dt \tag{3}$$

Where *t* is time. Figure 3 depicts things in a graphical way.

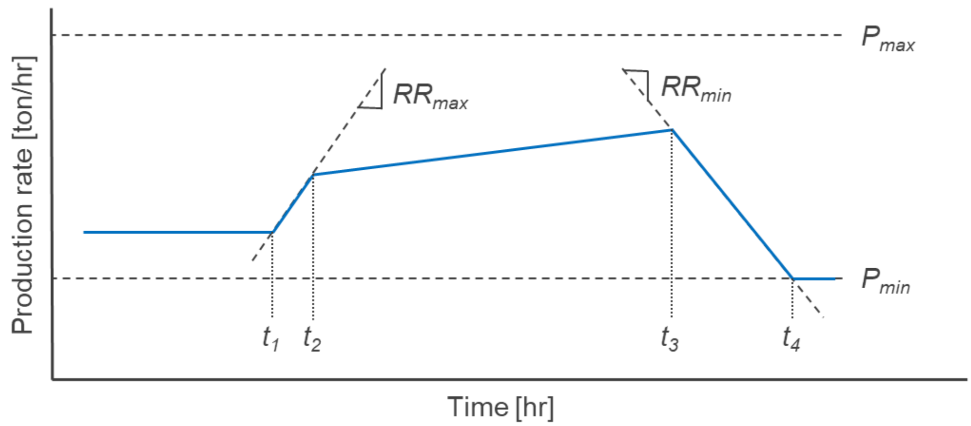


Figure 3 Operational flexibility. Initially the plant is operated in steady state. At t_1 production rate is ramped up according RR_{max} until t_2. Then production rate is ramped up at a slower pace. At t_3 the plant is ramped down according RR_{min}. From t_4 onwards production is maintained at P_{min}.

For conventional continuous processes *TR* is typically 2 or less. Values for normalized maximum ramp rates (RR_{max}/P_{max}) are much less known or reported. Power plants are an exception, for example Feldmüller [14] reports a range of 1 – 15%/minute. Conventional process plants have little need for high *RRs* as tankage on feed and product side offers one to a few weeks of storage. Furthermore, process plants are more complex than power plants in terms of number of unit operations and the presence of recycles. So, we may expect values well below 1%/minute from conventional designs methods.

Table 1 mentions process equipment utilization. Given a required average capacity the design capacity for coupled operation will be at least twice that of decoupled operation. So, Capital expenditure (Capex) of the methanol process part will be significantly higher for coupled operation. On the other hand, coupled operation avoids battery Capex and lowers via a higher efficiency the electricity consumption in other words Operational expenditure (Opex). In other words, there is an intricate economic trade-off between various costs and the most attractive operation mode can be determined by the formulation of an optimization problem.

3. An extended optimal control formulation

An attractive starting point is an optimal control formulation, since this allows for the inclusion of all relevant plant dynamics. However, such a formulation typically only considers operational degrees of freedom that relate to Opex. From the discussion in the previous section it is clear that also Capex, so design degrees of freedom must be considered:

$$\min_{u,v} J(x,y,u,v)$$
$$s.t. \begin{cases} dx/dt = f(x,y,u,v), b\left(x(0), x(T_f)\right) = 0 \\ g(x,y,u,v) = 0, h(x,y,u,v) \geq 0 \end{cases} \tag{4}$$

Where *x* are the state variables, *y* the algebraic variables, *u* the operational degrees of freedom, *v* the design degrees of freedom, *J* the cost functional, *f* the dynamic constraints, *b* the boundary conditions, and *g* and *h* the algebraic constraints.

The solar fuel plant shown in figure 2 can be simplified in two steps:

A. By viewing the solar fuel plant as an energy storage and conversion network. The arrows are now signals representing equivalent energy flows (electricity or methanol).
B. By lumping the storage and conversion dynamics of the equivalent energy flows performed by the blocks as Single Input Single Output (SISO) energy transfer functions.

Figure 4 shows the result of this simplification. In plantwide control terms, see Buckley [15], figure 4 is a 'material balance control system': It shows how production rate changes are initiated and propagated through the solar fuel plant. Storage is modelled as an integrator while the conversion by the circular methanol process is modelled as a third order process. The idea behind the latter is that the methanol process consists of three sections; (i) synthesis gas preparation (DAC and electrolyser), (ii) methanol synthesis and (iii) distillation. Let's assume that the dynamics of each section is adequately described by one dominant time constant[1], then the overall dynamics is a third order transfer function (the sections are connected in series). If the time constants of the sections were very different then the order could be reduced by leaving out the smallest time constant. Therefore, the three time constants were assumed to be equal. Note that the other part of the plantwide control system, the 'quality control loops' or unit operations control schemes, should be designed to support the required operational flexibility, especially the minimum and maximum ramp rates.

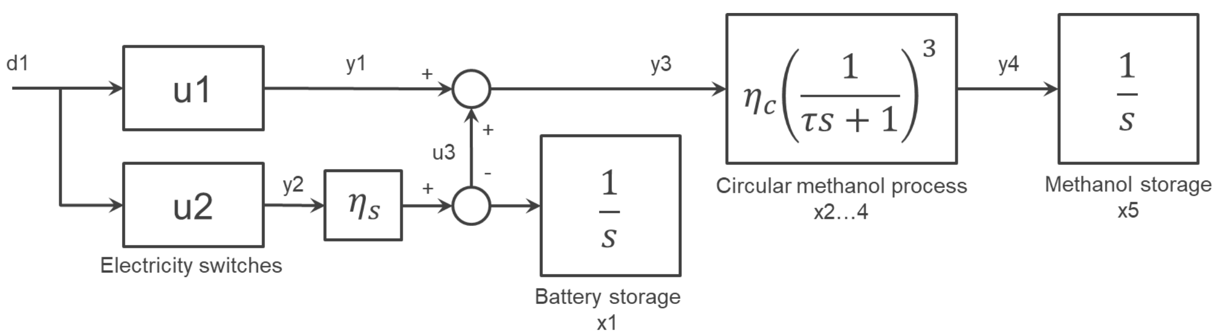


Figure 4 A block signal diagram of a solar fuel plant. The parameters η_s and η_c are efficiencies. Five states (*x1 – x5*) are used to describe the plant dynamics.

The proposed simplification reduces the size of the dynamic model considerably. A detailed model can easily have hundreds of states and even more algebraic variables. However, such a detailed model is harder to use in an optimal control setting and the results are more difficult to analyze. Moreover, the questions formulated at the end of the introduction were placed in the context of CPD and typically at this design stage no detailed model is available. Still the simplified model shown in figure 4 has all the important characteristics required to support the economic trade-off between expenditure for electricity, battery storage and methanol production. In addition, the model captures the essence of the operational flexibility regarding production rate changes[2].

---

[1] A first order process, for example an intermediate process inventory under proportional control.

[2] Conventional continuous (semi steady state) operation has limited operational flexibility. Batch operation offers flexibility in terms of product changes, in other words making different products.

The best operation mode is now the solution of the following optimal control problem:

$$\min_{u,v}(Capex\ battery\ storage + Capex\ methanol\ process + Opex)$$
$$s.t. \begin{cases} model\ equations \\ x5(T_f) = Q_{req}, d1(t) \geq y1(t) + y2(t), operational\ constraints \end{cases} \quad (5)$$

So, the total of Capex and Opex is minimized while a certain amount of methanol $x5(T_f)$ must be produced over the period T_f. Another constraint is the limited availability of solar electricity $d1(t)$ and operational constraints like $y3(t) \geq P_{min}$ to stay within the operating window. The idea here is to avoid shut down overnight and consequently a long cold start up every morning.

This problem has five degrees of freedom:

1. The flow of electricity directly routed to the solar methanol plant *y1* (set via switch *u1*).
2. The flow of electricity routed to electricity storage *y2* (set via switch *u2*).
3. The flow of electricity coming from electricity storage and going to the methanol process *u3*.
4. The size of the battery storage. This is the maximum of state *x1(t)* and directly related to the required Capex for battery storage.
5. The size of the methanol process. This is the maximum of input *y3(t)* and directly related to the required Capex for the methanol process.

Note that the first three degrees of freedom are operational degrees of freedom *u*, while the last two are design degrees of freedom *v*.

From the discussion above follows that the cost functional in formulation (5) can be written as:

$$\min\left(C1 \max x1(t) + C2 \max y3(t) + C3 \int_0^{T_f} [y1(t) + y2(t)]dt\right) \quad (6)$$

Where *C1, C2* and *C3* are appropriate cost factors, their values are derived in appendix A. The same goes for the efficiencies η_s and η_c. Formulation (6) is a minimax problem. To ensure convergence the problem was reformulated. This is easily explained by means of an example; consider the following minimax problem:

$$\min \max(x(t1), x(t2), x(t3), \ldots, x(tn))$$
$$s.t.\ \ g(x) = 0\ and\ h(x) \geq 0 \quad (7)$$

This can be reformulated as:

$$\min z$$
$$s.t. \begin{cases} g(x) = 0\ and\ h(x) \geq 0 \\ z \geq x(t1), z \geq x(t2), z \geq x(t3), \ldots, z \geq x(tn) \end{cases} \quad (8)$$

So, by the introduction of one extra decision variable *z* and *n* extra inequalities minimax problem (7) becomes a minimization problem. It should be noted that in the reformulation of (6) two extra decision variables were introduced, one for *x1(t)* and one for *y3(t)*. A complete full mathematical problem formulation can be found in appendix B in the form of an AMPL model.

From a CPD point of view the sequential approach has become an integrated simultaneous search through a high dimensional Operation – Design – Control space, see figure 5.

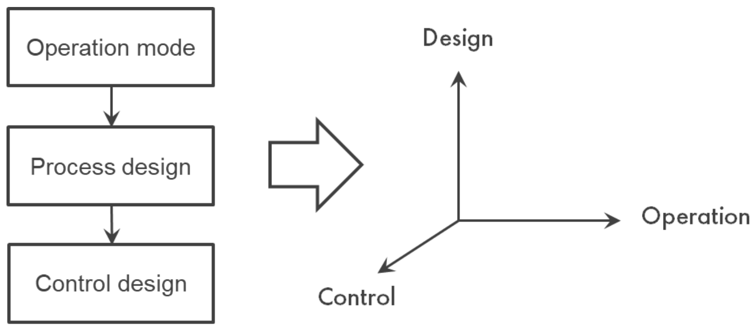


Figure 5 The sequential CPD approach (left) and the extended optimal control framework (right).

4. Results and discussion

For a proper understanding of the results the set-up needs to be explained in some detail:

- The solar profile is based on data made available by the National Renewable Energy Laboratory (NREL) [16]. From the set Actual_32.55_-117.05_2006_DPV_13MW_5_Min.csv (available under California) 12 April 2006 was selected because of clear weather and a daylight period of approximately 12 hours. To ensure the required methanol production (see below) the solar profile was scaled to have a maximum value of 20000 GJ/hr. The sample period used in the NREL data set (5 minutes) captures the solar profile dynamics well and supports the time step used for solving the differential equations (15 minutes).
- All flows are expressed as energy flows and given in GJ/hour. Storage is expressed as energy and given in GJ. Besides simplification this improves numerical conditioning.
- Switches $u1$ and $u2$ can be manipulated freely but $u1 + u2 \leq 1$. In other words, the total renewable energy to methanol process and battery storage cannot exceed the supply.
- All calculations cover four days. This is long enough to demonstrate periodic operation yet the calculation times (a few seconds) allow to wait for the results and set up another run. To support four days the solar profile mentioned above was repeated four times.
- The initial condition for $x1$ was set at 2000. This proved to be enough to maintain operation above P_{min} = 1000 until solar power production was high enough to take over. The initial conditions for $x2$ – $x4$ were set at 1000, this is well above P_{min} times the conversion efficiency. There are no final conditions for $x1$ – $x4$, so these are decision variables. The initial condition of $x5$ was set at 0 implying starting with an empty methanol tank. The final condition for $x5$ is 217920 representing the totalized required average methanol production over four days.
- The average required methanol production is 100 ton/day. To put this in perspective, a large-scale methanol facility produces 1e6 – 2e6 ton/year or 114 – 228 ton/hour. The average required methanol production converts to 2270 GJ/hour since the Higher Heating Value (HHV) of methanol is 22.7 MJ/kg.
- The required methanol production Q_{req} over four days equals $2270 \times 24 \times 4 = 217920$ GJ. With a η_c of 0.5 the average value of $y3$ should be approximately 4540 GJ/hour. Given this average value, $y3_{min}$ was set at 1000 GJ/hour. Based on engineering experience the time constant in the third order transfer function was set to 0.5 hour.

The reformulated extended optimal control problem was solved using dynamic optimization, the so-called simultaneous approach, see Biegler [17]. The simultaneous method offers besides speed also excellent state constraint handling. The differential equations were transcribed using an implicit Euler scheme. The resulting optimization problem can easily be programmed in an algebraic language like GAMS, AMPL or AIMMS and solved by an adequate solver e.g. CONOPT or IPOPT. The first runs revealed the presence of non-unique solutions; implying a problem formulation that allows for a multitude of equivalent solutions. For that reason, the term $0.000001.(y2(t))^2 + 0.000001.(y3(t))^2$ was added to cost functional (6) and Non-Linear Program solvers were used. Solutions were accepted based on apparent 'smoothness' of the optimal profiles rather than mathematical rigor (conditioning of the Hessian matrix of the Lagrangian).

Figures 6a and 6b show the solution for the reference case. The constraints related to operational flexibility are given in the caption. Numerical results for the reference and other cases are given in table 2.

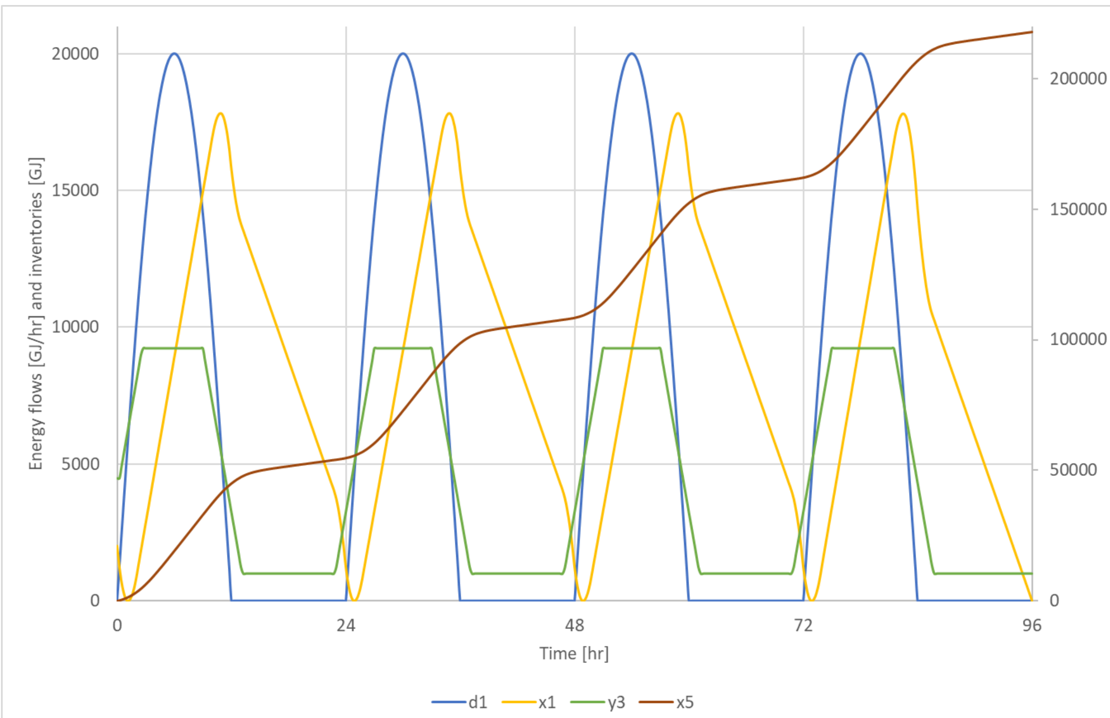


Figure 6a Selected optimal trajectories for the reference case (P_{min} = 1000, RR_{min} = -2000 and RR_{max} = 2000). First sunrise occurs at t = 0, only variable $x5$ correspond to the right axis.

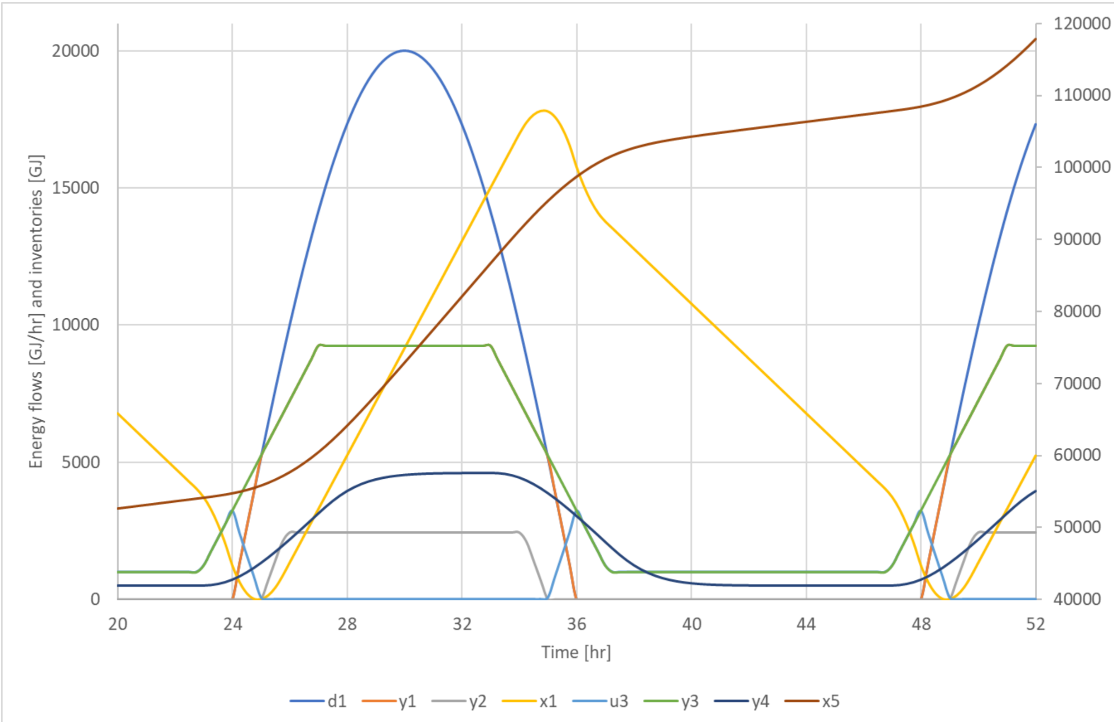


Figure 6b All optimal trajectories for the reference case (P_{min} = 1000, RR_{min} = -2000 and RR_{max} = 2000). The graph zooms in on the 2nd day. Only variable *x5* correspond to the right axis.

Table 2 Selected numerical results for the reference and other cases. The shaded rows are enforced operational constraints, NA means that the indicated constraint was absent.

Case	**Reference**	**Fast**	**Slow**	***TR* = 1**	***TR* = 4**
P_{min} [GJ/hour]	1000	1000	1000	1000	1000
***TR* [-]**	NA	NA	NA	1	4
RR_{min} [(GJ/hour)/hour]	-2000	-4000	-500	-2000	-2000
RR_{max} [(GJ/hr)/hour]	2000	4000	500	2000	2000
Capex battery storage [USD]	1.92E06	1.41E06	4.44E06	6.37E06	3.57E06
Capex methanol process [USD]	4.13E06	4.22E06	2.93E06	2.05E06	3.30E06
Opex [USD]	3.74E06	3.70E06	3.93E06	4.12E06	3.87E06
Total Capex and Opex [USD]	9.79E06	9.33E06	1.13E07	1.25E07	1.07E07
Capex battery storage [%]	19.63	15.09	39.26	50.82	33.24
Capex methanol process [%]	42.21	45.28	25.96	16.34	30.70
Opex [%]	38.16	39.63	34.78	32.84	36.07
Min *y3* [GJ/hour]	1000.00	1000.00	1000.00	4580.32	1842.31
Max *y3* [GJ/hour]	9236.43	9439.25	6556.08	4580.32	7369.24
***TR* [-]**	9.24	9.44	6.56	1.00	4.00
Overall efficiency [%]	48.41	48.93	46.02	43.91	46.70
Manuf. cost methanol [USD/ton]	1019.90	971.62	1177.03	1306.45	1118.75

Figure 6a shows that the methanol process largely follows the solar profile. In other words, there is high degree of coupling and operation is very dynamic. Still during the day, the process settles in a steady state and the same happens overnight at P_{min}. The latter means that battery storage is completely discharged around sunrise. The resulting *TR* is 9.24, a very high value compared to conventional operation. Figure 6b reveals that the methanol process is ramped up a bit before sunrise suggesting that RR_{max} poses a dynamic limitation. The result of other values for RR_{min} and

RR_{max} is displayed in figure 7. Indeed, for a wide *RR* range (fast case) the methanol process trajectory *y3* coincides during ramp up and down perfectly with the solar profile *d1*. However, in the case of a narrow *RR* range (slow case) the methanol process is already ramped up in the middle of the night and it never reaches a steady state during the night. Furthermore, going from the fast to slow case the required battery storage size more than triples.

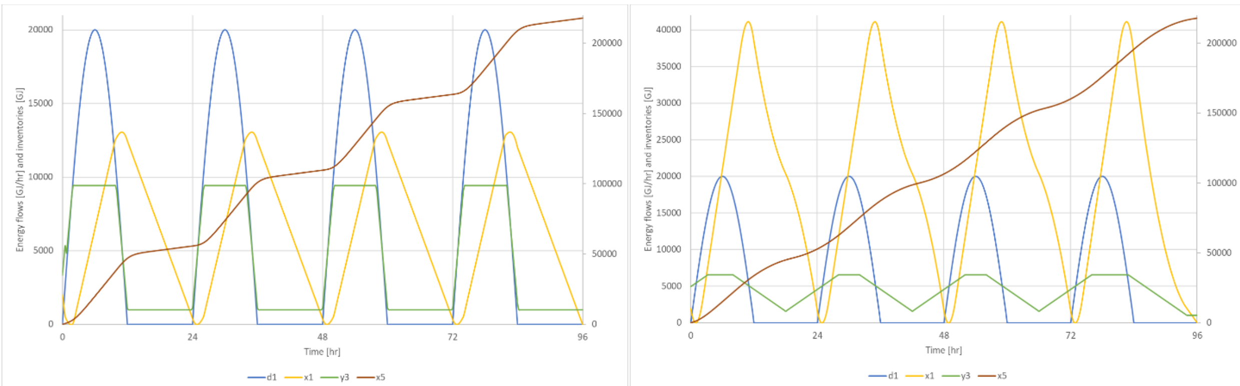


Figure 7 Selected optimal trajectories for the fast case, shown left (P_{min} = 1000, RR_{min} = -4000 and RR_{max} = 4000) and the slow case, shown right (P_{min} = 1000, RR_{min} = -500 and RR_{max} = 500). First sunrise occurs at t = 0, only variable *x5* correspond to the right axis.

The next operational constraint to change is *TR*. Since the *TR* of the reference case is already high, two cases are shown in figure 8 for lower *TR* values. The *RR* range is, compared to the reference case, unchanged.

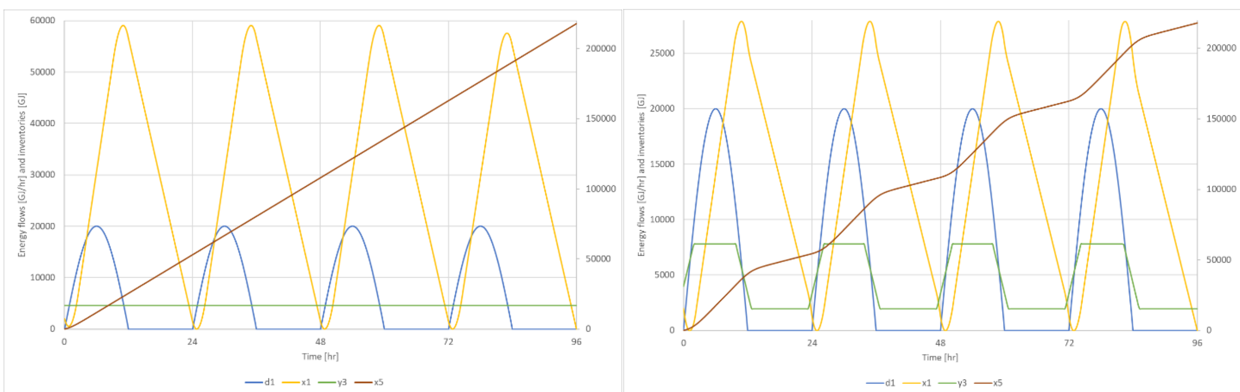


Figure 8 Selected optimal trajectories for the *TR* = 1 case, shown left (P_{min} = 1000, RR_{min} = -2000 and RR_{max} = 2000) and the *TR* = 4 case, shown right (P_{min} = 1000, RR_{min} = -2000 and RR_{max} = 2000). First sunrise occurs at t = 0, only variable *x5* correspond to the right axis.

The case *TR* = 1 enforces steady state operation. From a cost point of view this case is characterized by the highest Capex for battery storage, the lowest Capex for methanol processing and the highest manufacturing cost of methanol (see table 2). Clearly full decoupled operation is not attractive for the assumed cost structure (the values of *C1*, *C2* and *C3*). The case *TR* = 4 is economically more attractive than the *TR* = 1 case and seems more within our technical reach than the reference case with a *TR* of 9.24.

Figure 9 summarizes 25 optimizations for various combinations of *TRs* and *RR* ranges. From this graph the following can be concluded:

- Just economically speaking full coupling, enabled by high *TR*s and wide *RR* ranges, is the optimal operation mode.
- Limited operational flexibility, meaning lower *TRs* and narrow *RR* ranges increases methanol cost. The maximum impact is around 20%.
- Just increasing *TR* or *RR* range in isolation has a limited impact. To maximize impact both, must be increased in a balanced way.

There are two reasons why the impact of limited operational flexibility is limited to 20%. First, almost a fixed and economically significant amount of renewable energy so Opex is needed to produce methanol (see table 2). Second, there is a Capex compensation; increasing the battery size increases production overnight but lowers the required conversion capacity during the day. With respect to increasing *TR* or *RR* range in a balanced way consider the following example. Suppose we have a slow process and the *TR* is increased. Then it can be expected that no full use can be made of this higher *TR* since there is only a limited amount of time available to ramp up or down. So narrow *RR* ranges limit the effective *TR* dynamically.

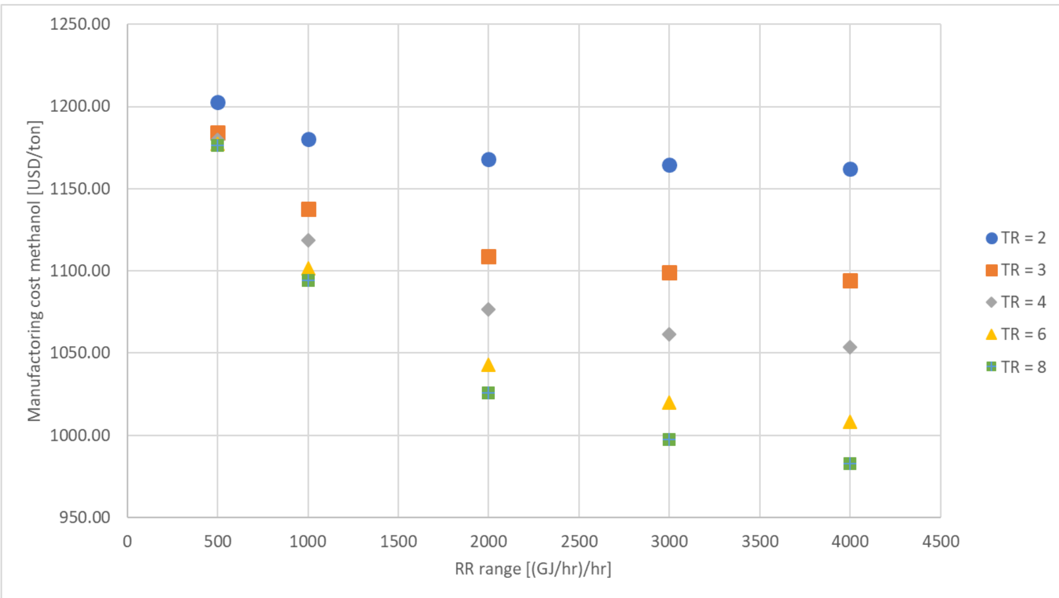


Figure 9 The manufacturing cost of methanol as a function of *TR* and *RR* range. A *RR* range of e.g. 1000 implies R_{min} = -1000 and R_{max} = 1000.

In the last part of this section the focus is on cost structure and its impact on operation. Figure 6a shows that the input of the methanol process cycles between $y3_{max}$ and $y3_{min}$. The day production determines via $y3_{max}$ the size of the methanol process while the night production determines via $y3_{min}$ the size of the battery storage. To simplify analysis the trapezoidal waveform is approximated by a square wave with a day and night period of 12 hours each. The manufacturing cost of methanol for both periods is then given by:

Day period

Production: $y3_{max}$ [GJ/hr] × 12 [hr] × η_c [-]/22.7 [GJ/ton] (9)

Cost: $y3_{max}$ [GJ/hr] × *C2*/4 [USD/GJ/hr] + $y3_{max}$ [GJ/hr] × 12 [hr] × *C3* [USD/GJ] (10)

Manufacturing cost, divide equation (10) by (9): $(22.7/\eta_c) \times (C2/48 + C3)$ [USD/ton] (11)

Night period

Production: $y3_{min}$ [GJ/hr] × 12 [hr] × η_c [-]/22.7 [GJ/ton] (12)

Cost: $y3_{min}$ [GJ/hr] × 12 [hr] × $C1/4$ [USD/GJ] + $y3_{min}/\eta_s$ [GJ/hr] × 12 [hr] × $C3$ [USD/GJ] (13)

Manufacturing cost, divide equation (13) by (12): $(22.7/\eta_c) \times (C1/4 + C3/\eta_s)$ [USD/ton] (14)

The value 22.7 corresponds to the LHV of methanol. In appendix A, *C2* is calculated for 4 days, for that reason C2 is divided by 4 in equations (10) and (13). Now if η_s is assumed to be 1 and equation (11) is set equal to equation (14) then cost equilibrium is obtained for:

$C2/C1 = 12$ [hr] (15)

Equation (15) describes an Operational Tipping Point (OTP). If $C2/C1 < 12$ then coupled operation is economically preferred while $C2/C1 > 12$ favors decoupled operation.

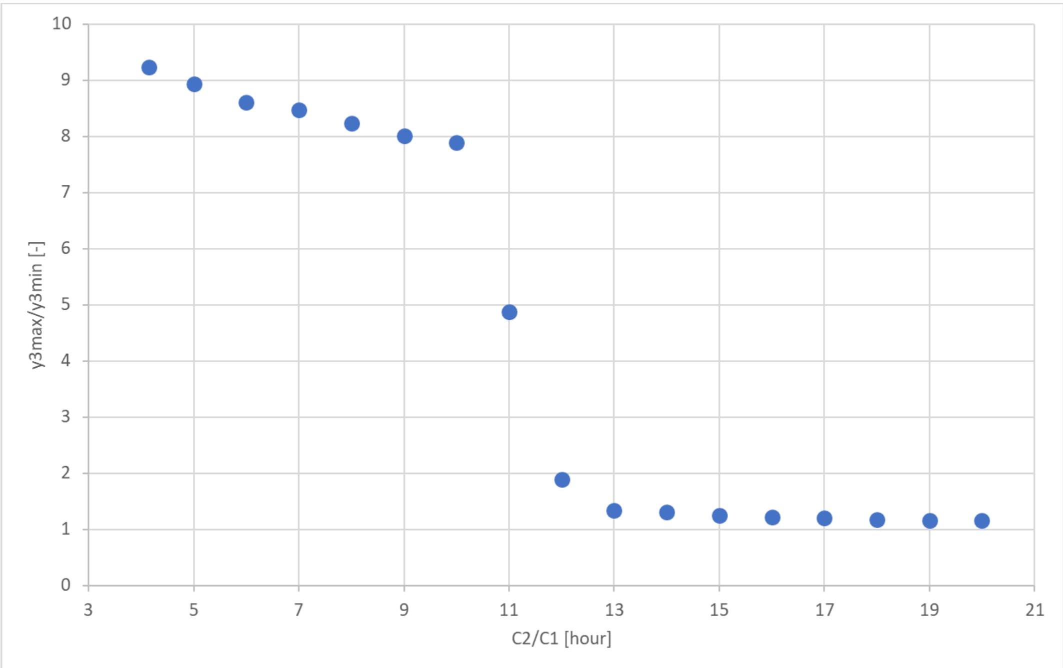


Figure 10 The *TR* ($y3_{max}/y3_{min}$) as function of relevant cost structure (*C2/C1*).

This analysis above was verified by plotting $y3_{max}/y3_{min}$, so *TR* as function of *C2/C1*, see figure 10. This figure clearly shows that indeed there is a rather sharp transition, however it occurs at C2/C1 ≈ 11 rather than 12. This is to be expected; the analysis was based on simplifying assumptions. It should be noted that the leftmost point in figure 10 corresponds to the reference case. This means that considerable changes in cost structure would be needed to cross the OTP to decoupled operation. Figure 10 also indicates that for high *C2/C1* values the *TR* stays above 1. This is caused by a round trip battery storage efficiency below 100% ($\eta_s = 0.8$). So, methanol production during the night requires more electrical energy than during the day and as a result production rate is increased slightly during the day.

5. Conclusions and further work

The major conclusions are:

- Solar fuel plants can be operated decoupled from or coupled with the solar profile. Decoupled means that the process runs basically in steady state at the required average production rate. This requires substantial battery storage to maintain production overnight. Coupled implies highly dynamic operation, so little battery storage is needed but the production rate during the day must be well above the required average production rate. In other words, there is an intricate economic trade-off between various costs.
- Dynamic operation must be supported by adequate operational flexibility. The latter translates in specifications for Turndown Ratio and Ramp up and down Rates.
- An extended optimal control framework is proposed that can determine optimal operation from an economic point of view. The word extended means that besides operational also design degrees of freedom are considered.
- The framework makes use of a simplified dynamic model that is essentially an energy network capturing the essence of storage and conversion. Because of its simplicity the model supports in a transparent way key operational and design decision.
- The framework is used to determine optimal operation of a solar methanol plant with an estimated cost structure by the year 2030. The optimization results show that coupled operation is economically preferred and that limited operational flexibility increases the manufacturing cost of methanol from ≈1000 to ≈1200 USD/ton.
- The cost structure determines an Operational Tipping Point that marks a clear transition from coupled to decoupled operation.

Further work may include:

- The work shows the value of operational flexibility (≈200 USD/ton). However high operational flexibility comes at additional cost. It seems logical to make these costs part of the framework by focusing on the limiting factor(s) for operational flexibility.
- Switching to hot standby, e.g. total reflux operation for a distillation column, is an alternative for operation at minimal production rate overnight. This alternative could be added to the framework. Switching implies discontinuity, so the result would be a Mixed Integer problem.
- Besides electricity both hydrogen and carbon dioxide can, in principle, be stored as well. Adding this to the framework would be quite straightforward. It could make sense to combine this with the possibility to switch to hot standby.
- As stated in the introduction this work focused on the diurnal cycle. It would be valuable to include the seasonal cycle. This can be done by extending the time horizon and including seasonal changes in the solar electricity profile.
- The current approach is completely deterministic: The solar profile is known beforehand. But in real life, there is uncertainty in the form of cloud coverage. The effects of uncertainty could be mitigated via robust optimization possibly combined with the sizing of the solar PV field.
- This work makes use of a simplified dynamic model. It would valuable to investigate how the characteristics of this model influence the results. The results presented in this paper may apply to a range of dynamics.

6. literature

1. Vázquez, F. V., Koponen, J., Ruuskanen, V., Bajamundi, C., Kosonen, A., Simell, P., Ahola, J., Frilund, C., Elfving, J., Reinikainen, M., Heikkinen, N., Kauppinen, J., Piermartini, P.

(2018). Power-to-X technology using renewable electricity and carbon dioxide from ambient air: SOLETAIR proof-of-concept and improved process concept. Journal of CO2 Utilization, 28, 235-246. https://doi.org/10.1016/j.jcou.2018.09.026

2. Michailos, S., McCord, S., Sick, V., Stokes, G., Styring, P. (2019). Dimethyl ether synthesis via captured CO2 hydrogenation within the power to liquids concept: A techno-economic assessment. Energy conversion and management, 184, 262-276. https://doi.org/10.1016/j.enconman.2019.01.046
3. Tremel, A., Wasserscheid, P., Baldauf, M., Hammer, T. (2015). Techno-economic analysis for the synthesis of liquid and gaseous fuels based on hydrogen production via electrolysis. International Journal of Hydrogen Energy, 40(35), 11457-11464. https://doi.org/10.1016/j.ijhydene.2015.01.097
4. Berry, A. M., Murphy, A., Seven, J., Arts, K., van Dijk, M., Carter, M., & Harrison, P. (2019). Long-term aviation fuel decarbonization: Progress, roadblocks, and policy opportunities. https://theicct.org/sites/default/files/publications/Alternative_fuel_aviation_briefing_20190109.pdf
5. Gür, T. M. (2018). Review of electrical energy storage technologies, materials and systems: challenges and prospects for large-scale grid storage. Energy & Environmental Science, 11(10), 2696-2767. https://doi.org/10.1039/C8EE01419A
6. Mulder, F. M. (2014). Implications of diurnal and seasonal variations in renewable energy generation for large scale energy storage. Journal of Renewable and Sustainable Energy, 6(3), 033105. https://doi.org/10.1063/1.4874845
7. Herron, J.A., Kim J., Upadhye A.A., Huber G.W., Maravelias, C.T. (2015). A general framework for the assessment of solar fuel technologies, Energy Environ. Sci., 8, 126–157. https://doi.org/10.1039/c4ee01958j
8. Tountas, A.A., Peng, X., Tavasoli, A.V., Duchesne, P.N., Dingle, T.L., Dong, Y., Hurtado, L., Mohan, A., Sun, W., Ulmer, U., Wang, L., Wood, T.E., Maravelias, C.T., Sain, M.M., Ozin, G.A. (2019). Towards Solar Methanol: Past, Present, and Future, Adv. Sci. 6, 1801903. https://doi.org/10.1002/advs.201801903
9. Smith, W.A., Burdyny, T., Vermaas, D.A., Geerlings H. (2019). Pathways to Industrial-Scale Fuel Out of Thin Air from CO2 Electrolysis, Joule 3, 1822-1834. https://doi.org/10.1016/j.joule.2019.07.009
10. Shirazi, A., Rahbari, A., Asselineau, C.A., Pye, J. (2019). A solar fuel plant via supercritical water gasification integrated with Fischer–Tropsch synthesis: System-level dynamic simulation and optimization, Energy Conversion and Management 192, 71–87. https://doi.org/10.1016/j.enconman.2019.04.008
11. Powell, K.M., Hedengren, J.D., Edgar, T.F. (2014). Dynamic optimization of a hybrid solar thermal and fossil fuel system, Solar Energy 108, 210–218. http://dx.doi.org/10.1016/j.solener.2014.07.004
12. Burnak, B., Diangelakis, N.A., Katz, Pistikopoulos, E.N. (2019). Integrated process design, scheduling, and control using multiparametric programming, Computers and Chemical Engineering 125, 164–184. https://doi.org/10.1016/j.compchemeng.2019.03.004
13. Douglas, J.M. (1988). Conceptual Design of Chemical Processes, New York.
14. Feldmüller, A. (2017). Flexibility of coal and gas fired power plants, Advanced Power Plant Flexibility Campaign. http://www.cleanenergyministerial.org/sites/default/files/2018-01/Andreas%20Feldmueller%20Siemens.pdf (accessed 12 September 2019).
15. Buckley, P.S. (1964). Techniques of process control, New York.
16. [dataset] National Renewable Energy Laboratory (NREL). Solar Power Data for Integration Studies. https://www.nrel.gov/grid/solar-power-data.html.

17. Biegler, L.T. (2007). An overview of simultaneous strategies for dynamic optimization, Chemical Engineering and Processing 46, 1043–1053. https://doi.org/10.1016/j.cep.2006.06.021

Appendix A: Estimation of efficiencies and cost factors

Steilen and Jörissen [A1] give round trip efficiencies for various secondary battery technologies that range from 70 to 95%. In the calculations 80% is assumed (η_s = 0.8).

Smith et al [A2] give the energy requirements for a solar methanol plant:

- CO_2 Capture: 13 kJ/mol CO_2.
- Bipolar Membrane Electrodialysis: 215 kJ/mol CO_2.
- H_2O Electrolyzer: 1224 kJ/mol CO_2 (the hydrogenation of CO_2 requires 3 mol H_2/mol CO_2).
- Reactor and Distillation: ≈ 0 kJ/mol CO_2, van der Ham et al [A3] show that high heat integration is well possible.

So, the total energy demand is 1452 kJ/mol CO_2. Since the higher heating value of methanol is 726 kJ/mol, the overall conversion efficiency equals 726/1452 × 100% = 50% (η_c = 0.5).

In the cost factor estimations below the idea is to aim for a reasonable and consistent cost structure (values of *C1*, *C2* and *C3*) in the year 2030. Schmidt et al [A4] mention that regardless of technology, capital costs are on a trajectory towards 340 ± 60 USD/kWh for installed stationary systems and 175 ± 25 USD/kWh for battery packs once 1TWh of capacity is installed for each technology. Furthermore, they state that bottom-up assessment of material and production costs indicates this price range is not infeasible. We will assume 340 USD/kWh which can be converted to 9.444E4 USD/GJ. If we assume a lifespan of 10 years than 4 days (the calculations span 4 days) amounts to 4/(10 × 350[3]) × 94444.4 USD/GJ = 107.9 USD/GJ. (*C1* = 107.9).

In the methanol process, the following overall reaction takes place:

$$3H_2 \text{ (6.05 ton)} + CO_2 \text{ (44.01 ton)} \rightarrow CH_3OH \text{ (32.04 ton)} + H_2O \text{ (18.02 ton)} \qquad \text{(A1)}$$

So, the production of 100 ton/hour (8.400E05 ton/year) of methanol requires 18.88 ton/hour (1.586E+05 ton/year) of hydrogen and 137.36 ton/hour (1.154E06 ton/year) of carbon dioxide. The total Capex is the sum of electrolyser, Direct Air Capture (DAC) and methanol process:

- Saba et al [A5] mention a future Capex range (through 2030) of 397 - 955 €/kW_{HHV} for alkaline and PEM electrolysers. Assuming 500 €/kW_{HHV} gives after conversion[4] 2343 USD/(ton H_2/year). So, the Capex for the electrolyser is 1.586E05 ton/year × 2343 USD/(ton/year) = 3.716E08 USD.
- In their paper Fasihi, Efimova and Breyer [A6] give an overview of the economics of DAC. For the various technologies the Capex range is 41 – 2350 €/(ton CO_2/year), this range is also broadened by the fact that it includes the past, the mid and long term future. We will assume 1000 USD/(ton CO_2/year). So, the Capex related to DAC is then 1.154E06 ton/year × 1000 USD/(ton/year) = 1.154E09 USD.
- Finally, Turaga [A7] performs some statistics on recent (intended) methanol plant investments. He arrives at an average 532 USD/(ton CH_3OH/year). Since this includes steam methane reforming we will assume a lower 300 USD/(ton CH_3OH/year). So, the Capex for the methanol part is 8.400E05 ton/year × 300 USD/(ton/year) = 2.520E08 USD.

[3] 350 operational days per year.

[4] The Higher Heating Value of hydrogen equals 141.7 MJ/kg and the exchange rate of USD to € is set to 1.

Taking all Capex together gives 1.777E09 USD. Expressed in terms of average input *y3*[5] this is 1.777E09 USD/(4540 GJ/hour) = 3.915E05 USD/(GJ/hour). Assuming a lifespan of 10 years, 4 days amounts to 4/(10 × 350) × 3.915E05 USD/(GJ/hour) = 447.4 USD/(GJ/hour). (*C2* = 447.4).

In a recent report from the International Renewable Energy Agency [A8] the levelized cost of electricity from utility-scale solar PV projects over the period 2010 – 2018 are presented. Some projects in 2018 were at a price level of 0.05 USD/kWh. In the calculations 0.03 USD/kWh is assumed. This can be converted to 8.3 USD/GJ (*C3* = 8.3).

References

A1 Steilen, M., Jörissen, L. (2015). Hydrogen Conversion into Electricity and Thermal Energy by Fuel Cells: Use of H2-Systems and Batteries, in:, Moseley, P.T., Garche, J. (Eds.), Electrochemical Energy Storage for Renewable Sources and Grid Balancing, Elsevier, 143-158. https://doi.org/10.1016/B978-0-444-62616-5.00010-3

A2 Smith, W.A., Burdyny, T., Vermaas, D.A., Geerlings H. (2019). Pathways to Industrial-Scale Fuel Out of Thin Air from CO2 Electrolysis, Joule 3, 1822-1834. https://doi.org/10.1016/j.joule.2019.07.009

A3 Van der Ham L. G. J., Van den Berg H., Benneker A., Simmelink G., Timmer J., Van Weerden S. (2012). Hydrogenation of carbon dioxide for methanol production, Chemical Engineering Transactions, 29, 181-186.

A4 Schmidt O., Hawkes A., Gambhir A. and Staffell I. (2017). The future cost of electrical energy storage based on experience rates, Nature Energy 2, 17110. https://doi.org/10.1038/nenergy.2017.110

A5 Saba, S. M., Müller, M., Robinius, M., Stolten, D. (2018). The investment costs of electrolysis—A comparison of cost studies from the past 30 years, Int J Hydrogen Energy 43, 1209-1223. https://doi.org/10.1016/j.ijhydene.2017.11.115

A6 Fasihi, M.; Efimova, O.; Breyer, C. (2019). Techno-economic assessment of CO2 direct air capture plants, Journal of Cleaner Production 224, 957-980. https://doi.org/10.1016/j.jclepro.2019.03.086

A7 Gas processing and LNG. (2015). Small-scale methanol technologies offer flexibility, cost effectiveness. http://www.gasprocessingnews.com/features/201510/small-scale-methanol-technologies-offer-flexibility,-cost-effectiveness.aspx (accessed 25 September 2019)

A8 International Renewable Energy Agency. (2019). Renewable Power Generation Costs in 2018, IRENA, ISBN 978-92-9260-126-3. https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2019/May/IRENA_Renewable-Power-Generations-Costs-in-2018.pdf

[5] An average methanol production of 100 t/h converts to 2270 GJ/h (Higher Heating Value of methanol is 22.7 MJ/kg). Given a η_c = 0.5 the average value of *y3* is therefore 4540 GJ/h.

Appendix B: A complete full mathematical problem formulation

```
# SP1.mod - Solar fuel plant problem in AMPL format
# Adrie Huesman 17 September 2019

# SETS
# no set declaration necessary

# PARAMETERS
param Ng > 0 integer; # number of grid points
param Dt > 0; # time step [hr]
param Etas > 0; # round trip efficiency battery storage [-]
param Etac > 0; # overall electricity to methanol efficiency conversion [-]
param Tau > 0; # time constant [hr]
param Rc > 0; # ramp constraint [(GJ/hr)/hr]
param TDc > 0; # Turn Down ratio constraint [-]
param d1{1..Ng} >= 0; # solar profile [GJ/hr]
param C1 > 0; # battery storage cost (capex) [$/GJ]
param C2 > 0; # methanol process cost (capex) [$/GJ/hr]
param C3 > 0; # electricity cost (opex) [$/GJ]

# VARIABLES
var y3{1..Ng} >= 1000, :=2200, <= 25000; # electricity to methanol process [GJ/hr]
var x1{1..Ng} >= 0, :=10000, <= 100000; # charge state battery storage [GJ]
var x2{1..Ng} >= 0, := 2200, <= 25000; # intermediate state methanol process [GJ]
var x3{1..Ng} >= 0, := 2200, <= 25000; # intermediate state methanol process [GJ]
var x4{1..Ng} >= 0, := 2200, <= 25000; # intermediate state methanol process [GJ]
var x5{1..Ng} >= 0, := 100000, <= 400000; # level state methanol tank [GJ]
var y1{1..Ng} >= 0, := 2200, <= 50000; # electricity directly to methanol plant
[GJ/hr]
var y2{1..Ng} >= 0, := 2200, <= 50000; # electricity to battery storage  [GJ/hr]
var u3{1..Ng} >= 0, := 2200, <= 50000; # electricity from battery storage to methanol
process [GJ/hr]
var y4{1..Ng} >= 0, := 2200, <= 50000; # methanol flow to tank [GJ/hr]
var u1{1..Ng} >= 0, := 0.5, <= 1; # switch electricity directly to methanol process [-
]
var u2{1..Ng} >= 0, := 0.5, <= 1; # switch electricity to battery storage [-]
var CapS >= 0, := 10000, <= 100000; # maximum capacity battery storage [GJ]
var CapC >= 0, := 50000, <= 200000; # maximum capacity methanol process [GJ/hr]
var LowC >= 0, := 50000, <= 200000; # minimum capacity methanol process [GJ/hr]

# OBJECTIVE
minimize cost: C1*CapS + C2*CapC + C3*sum {j in 1..Ng} Dt*(y1[j] + y2[j] +
0.000001*y2[j]*y2[j] + 0.000001*y3[j]*y3[j]); # total of capex and opex

# CONSTRAINTS
s.t. eq1 {j in 1..Ng}: y1[j] = u1[j]*d1[j]; # via switch u1, y1 is set
s.t. eq2 {j in 1..Ng}: y2[j] = u2[j]*d1[j]; # via switch u2, y2 is set
s.t. eq3 {j in 1..Ng}: u1[j] + u2[j] <= 1; # y1 + y2 should not exceed d1
s.t. eq4 {j in 1..Ng-1}: (x1[j+1] - x1[j])/Dt = Etas*y2[j+1] - u3[j+1]; # implicit
Euler approximation for batterry storage
s.t. eq5: x1[1] = 2000; # initial condition
s.t. eq6 {j in 1..Ng}: y3[j] = y1[j] + u3[j];
s.t. eq7 {j in 1..Ng-1}: (x2[j+1] - x2[j])/Dt = 1/Tau*(-x2[j+1] + Etac*y3[j+1]); #
implicit Euler approximation methanol process
s.t. eq8: x2[1] = 1000; # initial condition
s.t. eq9 {j in 1..Ng-1}: (x3[j+1] - x3[j])/Dt = 1/Tau*(-x3[j+1] + x2[j+1]); # implicit
Euler approximation methanol process
s.t. eq10: x3[1] = 1000; # initial condition
s.t. eq11 {j in 1..Ng-1}: (x4[j+1] - x4[j])/Dt = 1/Tau*(-x4[j+1] + x3[j+1]); #
implicit Euler approximation methanol process
s.t. eq12: x4[1] = 1000; # initial condition
s.t. eq13 {j in 1..Ng}: y4[j] = x4[j];
```

```
s.t. eq14 {j in 1..Ng-1}: (x5[j+1] - x5[j])/Dt = y4[j+1]; # implicit Euler
approximation for methanol tank
s.t. eq15: x5[1] = 0; # initial condition
s.t. eq16: x5[Ng] = 217920; # required methanol production
s.t. eq17 {j in 1..Ng-1}: y3[j+1] - y3[j] >= -Rc*Dt; # max negative ramp
s.t. eq18 {j in 1..Ng-1}: y3[j+1] - y3[j] <= Rc*Dt; # max positive ramp
s.t. eq19 {j in 1..Ng}: CapS >= x1[j]; # replaces (max {j in 1..Ng} x1[j]) in the
objective
s.t. eq20 {j in 1..Ng}: CapC >= y3[j]; # CapS and CapC are pushed down by cost
s.t. eq21 {j in 1..Ng}: LowC <= y3[j]; # determine LowC, LowC is pushed up by eq22
s.t. eq22: CapC/LowC <= TDc; # limit turndown ratio

# DATA
data;
param Etas := 0.8; # 0.8
param Etac := 0.5; # 0.5
param Tau := 0.5; # 0.5

param C1 := 107.9; # 107.9
param C2 := 447.4; # 447.4
param C3 := 8.3; # 8.3

param Rc := 2000; # 2000
param TDc := 10; # 10

param Ng := 385; # this is 4 days (Ng - 1)*0.25
param Dt := 0.25;
param d1 :=
1      0
2      1308.050048
3      2610.498931
4      3901.769473
5      5176.332358
6      6428.72982
7      7653.599002
8      8845.694926
9      9999.912954
10     11111.31064
11     12175.1289
12     13186.81239
13     14142.02901
14     15036.68846
15     15866.95973
16     16629.28754
17     17320.40756
18     17937.36036
19     18477.5041
20     18938.52586
21     19318.45149
22     19615.65413
23     19828.86115
24     19957.15956
25     20000
26     19957.19901
27     19828.93986
28     19615.77179
29     19318.60757
30     18938.71971
31     18477.73489
32     17937.62709
33     17320.7091
34     16629.62259
35     15867.32685
```

```
    15037.08609
    14142.45545
    13187.2658
    12175.60735
    11111.81207
    10000.43523
    8846.235802
    7654.156165
    6429.300884
    5176.914879
    3902.360955
    2611.096843
    1308.651828
    0.603071796
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
    0
# repeat sequence d[1] - d[96] three times
```