Controlled Variables Selection for a Natural Gas to Liquids (GTL) process

Mehdi Panahi
Sigurd Skogestad

19.10.2011
AIChE Annual Meeting
Skogestad plantwide control procedure*

I  Top Down
   • Step 1: Identify degrees of freedom (MVs)
   • Step 2: Define operational objectives (optimal operation)
     – Cost function J (to be minimized)
     – Operational constraints
   • Step 3: Select primary controlled variables CV1s (Self-optimizing)
   • Step 4: Where set the production rate? (Inventory control)

II Bottom Up
   • Step 5: Regulatory / stabilizing control (PID layer)
     – What more to control (CV2s; local CVs)?
     – Pairing of inputs and outputs
   • Step 6: Supervisory control (MPC layer)
   • Step 7: Real-time optimization

Optimal Operation

Mode I: maximize efficiency
Mode II: maximize throughput

Self-optimizing control is when we can achieve acceptable loss with constant setpoint values for the controlled variables without the need to reoptimize the plant when disturbances occur.
Selection of CVs: Self-optimizing control procedure

Step 3-1: Define an objective function and constraints
Step 3-2: Degrees of freedom (DOFs)
Step 3-3: Disturbances
Step 3-4: Optimization (nominally and with disturbances)
Step 3-5: Identification of controlled variables (CVs) for unconstrained DOFs
Step 3-6: Evaluation of loss
Exact local method* for selection the best CVs

Exact local method gives the maximum loss imposed by each candidate CV set

The set with the minimum worst-case loss is the best

\[
\text{max. } \text{Loss} = \frac{1}{2} \bar{\sigma}(M)^2
\]

\[
M = J_{uu}^{1/2} G_y^{-1} (F W_d \ W_n)
\]

\[
F = G_y J_{uu}^{-1} J_{ud} - G_d^y
\]

F is optimal sensitivity of the measurements with respect to disturbances:

\[
F = \frac{\Delta y_{\text{opt.}}}{\Delta d}
\]

* I.J. Halvorsen, S. Skogestad, J.C. Morud and V. Alstad,

A simple flowsheet of GTL process*

CH₄ + CO + H₂ → (CH₂)ₙ

Process description

Synthesis gas unit

- Pre-reformer
- Auto-thermal reformer (ATR)
- Fired heater

CO₂ removal (optional)

Fischer-Tropsch (FT) reactor: slurry bubble column reactor

Fischer-Tropsch products separation
Detailed flowsheet of GTL process (UniSim)
Pre-reformer reactions
Converting higher hydrocarbons
than methane, For \( n \geq 2 \)
\[
C_nH_m + nH_2O \rightarrow (n + \frac{m}{2})H_2 + nCO
\]
Methanation
\[
CO + 3H_2 \leftrightarrow CH_4 + H_2O
\]
Shift Reaction
\[
CO + H_2O \leftrightarrow CO_2 + H_2
\]
Auto-thermal reformer (ATR) reactions
Oxidation of methane:
\[
CH_4 + \frac{3}{2}O_2 \leftrightarrow CO + 2H_2O
\]
Steam reforming of methane:
\[
CH_4 + H_2O \leftrightarrow CO + 3H_2
\]
Shift Reaction:
\[
CO + H_2O \leftrightarrow CO_2 + H_2
\]
Fischer-Tropsch (FT) reactions
\[
nCO + 2nH_2 \rightarrow (\text{-}CH_2\text{-})_n + nH_2O
\]
Fired heater

1. Preheating the following streams to 455°C:
   - fresh natural gas (pre-reformer feed)
   - recycle hydrocarbons from FT reactor (pre-reformer feed)

2. Generate super heated process steam (pre-reformer feed) and the super heated steam for driving the turbines in oxygen plant.

3. Preheating the outlet gas from the pre-reformer to 675°C

4. Preheating oxygen to 200°C

5. 10% of the total fired heater duty is assumed to be used to supply superheated steam for other mechanical equipment in the process.

The required fuel for the fired heater is supplied by the combustible components in the purge stream plus some fresh natural gas.
Fischer-Tropsch (FT) reactor

Simulation of a slurry bubble column reactor (SBCR)

Reactions: \( nCO + 2nH_2 \rightarrow (-CH_2-)_n + nH_2O \)

Kinetics (the model developed by Iglesia et al*): \( r_{CH_4} = \frac{1.08 \times 10^{-8} P_{H_2} P_{CO}^{0.05}}{1 + 3.3 \times 10^{-5} P_{CO}} \) \( \frac{mol_{CH_4}}{g\text{-atom surface metal. s}} \)
\( r_{CO} = \frac{1.96 \times 10^{-8} P_{H_2}^{0.6} P_{CO}^{0.65}}{1 + 3.3 \times 10^{-5} P_{CO}} \) \( \frac{mol_{CO}}{g\text{-atom surface metal. s}} \)

FT products distribution (ASF model):

\( w_n = n(1 - \alpha)^2 \alpha^{n-1} \)
\( \alpha^* = (0.2332 \frac{y_{CO}}{y_{CO} + y_{H_2}} + 0.633)[1 - 0.0039(T - 533)] \)

41 reactions: 21 reactions for \( C_nH_{2n+2} \) and 20 reactions for \( C_nH_{2n} \)

FT products: \( C_1, C_2, C_3-C_4 \) (LPG), \( C_5-C_{11} \) (Naphtha, Gasoline), \( C_{12}-C_{20} \) (Diesel), \( C_{21+} \) (wax)


FT Products distribution in our simulated reactor

![Graph showing FT Products distribution in a simulated reactor. The graph plots weight fraction against H2/CO ratio. Different lines represent various products: wt% CH4, wt% C2, wt% C3-C4, wt% C5-C11, wt% C12-C20, and wt% C21+. The y-axis represents weight fraction ranging from 0.00 to 1.00, and the x-axis represents H2/CO ratio ranging from 1.00 to 2.20.]
Mode I: Natural gas flowrate is given

Step 1: Define the objective function and constraints
Variables income = sales revenue – variable cost
Variable cost = cost of raw materials + cost of energy + cost of CO₂ removal

Inequality Constraints
1. Steam/Carbon ratio feed to the syngas unit ≥ 0.3 (soot free operation),
2. Inlet temperature of ATR (outlet of fired heater) ≤ 675°C (material constraint),
3. Outlet of ATR ≤ 1030°C. (soot free operation),
4. Purge ratio ≥ 2% (convergence issues),
5. In addition, there are capacity constraints on the variable units; fired heater (duty +40% compared to nominal), CO₂ recovery unit (+20% feedrate), oxygen plant (+20% oxygen flowrate).
Equality Constraints (Specs)

1. Fresh natural gas + recycle hydrocarbons temperature to pre-reformer is kept at 455°C,
2. Steam temperature to pre-reformer is kept at 455°C
3. Oxygen feed temperature to ATR is kept at 200°C,
4. Feed enters into syngas unit at 30 bar. Note that the pressure of the fresh streams are set in other units which are out of the our flowsheet boundary,
5. Fresh Syngas from ATR (after passing the boiler) is cooled down to 38°C for separation of water content,
6. Syngas enters into the FT reactor at 210°C,
7. Boling water pressure (cooling medium of FT reactor) is kept at 12.5 bar. This gives a gradient of 20°C between FT desired temperature (210°C) and the coolant (190°C).
8. FT products are cooled down to 30°C in a 3-phase separator to separate liquid fuels, water and tail gas,
9. Recycle tail gas to FT reactor is compressed to 27 bar,
Step 2: Identify degrees of freedom (DOFs) for optimization

1. \( \text{H}_2\text{O} \) (superheat steam) feedrate to pre-reformer (\( \text{H}_2\text{O}/\text{C} \)),

2. Superheat steam bypass stream flowrate,

3. Natural gas feedrate as fuel (make up) to the fired heater,

4. Natural gas + recycle hydrocarbons bypass stream flowrate,

5. Oxygen feedrate to ATR,

6. Oxygen bypass stream flowrate,

7. Separator duty for separation of water content in fresh syngas,
Step 2: Identify degrees of freedom (DOFs) for optimization

8. CO₂ recovery %,

9. Syngas pre-heater duty (the flow stream entering into the FT reactor),

10. Outlet medium pressure (MP) steam flowrate of steam drum,

11. 3-Phase separator duty for separation of FT products,

12. Tail gas recycle ratio to FT reactor and syngas unit,

13. Compressor II duty (the recycle tail gas flow to FT reactor),

14. Recycle tail gas purge ratio,

15. Compressor I duty (recycle tail gas to syngas).
Step 3: Identification of important disturbances

Natural gas flowrate,
Natural gas composition,
Natural gas price,
FT reactions kinetic parameter,
Change in active constraints value.
Step 4: Optimization

**MIXED method:** combines the advantage of global optimization of BOX and efficiency of SQP method

**Active constraints:**
1. the outlet temperature of the fired heater is active at the maximum (675°C),
2. the outlet temperature of the ATR is active at the maximum (1030°C),
3. purge ratio is active at the specified minimum, which is to purge 3%.

<table>
<thead>
<tr>
<th>Objective function (USD/hr)</th>
<th>Carbon Efficiency</th>
<th>H₂/CO into FT</th>
<th>CO₂ Recovery</th>
<th>H₂/CO fresh</th>
<th>Purge of tail gas</th>
<th>Recycle ratio to FT</th>
<th>H₂O/C</th>
<th>O₂/C</th>
<th>CO₂ Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>4929.30</td>
<td>74.59%</td>
<td>89.93%</td>
<td>96.92%</td>
<td>0.87</td>
<td>75.73%</td>
<td>73.79%</td>
<td>3%</td>
<td>2.1</td>
<td>2.03</td>
</tr>
</tbody>
</table>

15 degrees of freedom, 9 equality constraints and 3 active constraints:

**unconstrained degrees of freedom:** 15 – 9 – 3 = 3, which may be viewed as:

H₂O/C, CO₂ recovery, tail gas recycle ratio to FT reactor

MTU
Norwegian University of Science and Technology
Step 5. Identification of candidate controlled variables

18 candidate measurements including the three unconstrained degrees of freedom

\[
\binom{18}{3} = \frac{18!}{3!15!} = 816
\]

1- O\textsubscript{2}/C feed (y\textsubscript{1})
2- H\textsubscript{2}O/C feed (y\textsubscript{2})
3- CO\textsubscript{2} recovery% (y\textsubscript{3})
4- recycled tail gas ratio to FT reactor (y\textsubscript{4})
5- H\textsubscript{2}/CO in fresh syngas (y\textsubscript{5})
6- H\textsubscript{2}/CO in tail gas (y\textsubscript{6})
7- H\textsubscript{2}/CO into FT reactor (y\textsubscript{7})
8- H\textsubscript{2} mole fraction in fresh syngas (y\textsubscript{8})
9- CO mole fraction in fresh syngas (y\textsubscript{9})
10- CH\textsubscript{4} mole fraction in fresh syngas (y\textsubscript{10})
11- H\textsubscript{2} mole fraction in tail gas (y\textsubscript{11})
12- CO mole fraction in tail gas (y\textsubscript{12})
13- CH\textsubscript{4} mole fraction in tail gas (y\textsubscript{13})
14- H\textsubscript{2} mole fraction into FT reactor (y\textsubscript{14})
15- CO mole fraction into FT reactor (y\textsubscript{15})
16- fresh syngas flowrate (y\textsubscript{16})
17- tail gas flowrate to syngas unit (y\textsubscript{17})
18- tail gas flowrate to FT reactor (y\textsubscript{18})
Step 6. Selection of CVs

Exact local method for selection of the best CVs

a) Individual measurements
b) Combination of measurements

The set with the minimum worst-case loss is the best self-optimizing CV set

Applying a branch and bound algorithm
### a) Individual measurements (mode I)

#### worst-case loss for the best 5 individual measurement sets

<table>
<thead>
<tr>
<th>no.</th>
<th>Sets</th>
<th>Loss (USD/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$y_3$: CO$<em>2$ recovery, $y_9$: CO mole fraction in fresh syngas, $y</em>{12}$: CO mole fraction in tail gas</td>
<td>1393</td>
</tr>
<tr>
<td>2</td>
<td>$y_3$: CO$_2$ recovery, $y_2$: H$_2$/C, $y_6$: H$_2$/CO in tail gas</td>
<td>1457</td>
</tr>
<tr>
<td>3</td>
<td>$y_3$: CO$_2$ recovery, $y_2$: H$_2$/C, $y_5$: H$_2$/CO in fresh syngas</td>
<td>1698</td>
</tr>
<tr>
<td>4</td>
<td>$y_3$: CO$_2$ recovery, $y_6$: H$_2$/CO in tail gas, $y_5$: H$_2$/CO in fresh syngas</td>
<td>2594</td>
</tr>
<tr>
<td>5</td>
<td>$y_{10}$: CH$_4$ mole fraction in fresh syngas, $y_6$: H$_2$/CO in tail gas, $y_5$: H$_2$/CO in fresh syngas</td>
<td>2643</td>
</tr>
</tbody>
</table>
b) Combining of measurements (full \( H \) matrix)

\[ C = H y \]

The optimal \( H \) is obtained by solving the following optimization problem

\[
\min_H \|HY\|_F^2 \\
\text{s.t.} \quad HG^y = J_{uu}^{1/2}
\]

where \( Y = [F \ Wd \quad Wny] \)

An analytical solution is:

\[ H^T = (YY^T)^{-1} G^y (G^T (YY^T)^{-1} G^y)^{-1} J_{uu}^{1/2} \]

Applying a partial branch and bound algorithm

By combining 7 measurements the loss is almost zero from a practical point of view
Mode II: Natural gas feedrate is also a degree of freedom

Point A: oxygen flowrate saturates

1 extra DOF, 1 new active constraint

## Optimal values in: nominal point, saturation of oxygen flowrate and maximum throughput

<table>
<thead>
<tr>
<th></th>
<th>H$_2$/C</th>
<th>O$_2$/C</th>
<th>CO$_2$ recovery</th>
<th>Recycle ratio to FT</th>
<th>Purge of tail gas</th>
<th>H$_2$/CO fresh</th>
<th>H$_2$/CO into FT</th>
<th>CO conversion %</th>
<th>H$_2$ conversion %</th>
<th>α</th>
<th>Carbon efficiency</th>
<th>Objective function (USD/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>opt. nominal</td>
<td>0.6010</td>
<td>0.523</td>
<td>75.73%</td>
<td>73.79%</td>
<td>3%</td>
<td>2.1</td>
<td>2.03</td>
<td>85.74</td>
<td>95.50</td>
<td>0.87</td>
<td>74.59%</td>
<td>49293</td>
</tr>
<tr>
<td>max. oxygen</td>
<td>0.5357</td>
<td>0.516</td>
<td>76.80%</td>
<td>90%</td>
<td>3%</td>
<td>2.092</td>
<td>1.91</td>
<td>67.08</td>
<td>94.14</td>
<td>0.86</td>
<td>74.30%</td>
<td>59246</td>
</tr>
<tr>
<td>max. throughput</td>
<td>0.4084</td>
<td>0.504</td>
<td>76.04%</td>
<td>97.13%</td>
<td>3%</td>
<td>2.095</td>
<td>1.80</td>
<td>51.25</td>
<td>94.79</td>
<td>0.87</td>
<td>74.31%</td>
<td>59634</td>
</tr>
</tbody>
</table>

FT reactor volume is the bottleneck
a) Individual measurements (mode II)

worst-case loss for the best 5 individual measurement sets

<table>
<thead>
<tr>
<th>no.</th>
<th>Sets</th>
<th>Loss (USD/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$y_3$: CO$_2$ recovery</td>
<td>3022</td>
</tr>
<tr>
<td></td>
<td>$y_2$: H$_2$O/C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$y_7$: H$_2$/CO into FT reactor</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$y_3$: CO$_2$ recovery</td>
<td>3316</td>
</tr>
<tr>
<td></td>
<td>$y_2$: H$_2$O/C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$y_6$: H$_2$/CO in tail gas</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$y_3$: CO$_2$ recovery</td>
<td>3495</td>
</tr>
<tr>
<td></td>
<td>$y_2$: H$_2$O/C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$y_5$: H$_2$/CO in fresh syngas</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$y_3$: CO$_2$ recovery</td>
<td>4179</td>
</tr>
<tr>
<td></td>
<td>$y_2$: H$_2$O/C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$y_{17}$: tail gas flowrate to syngas unit</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$y_3$: CO$_2$ recovery</td>
<td>4419</td>
</tr>
<tr>
<td></td>
<td>$y_9$: CO mole fraction in fresh syngas</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$y_{15}$: CO mole fraction into FT reactor</td>
<td></td>
</tr>
</tbody>
</table>

b) In mode II, combination of 7 measurements results in almost zero loss
The third individual measurements set is common in modes I&II
the same setpoint for CO\textsubscript{2} recovery and H\textsubscript{2}/CO ratio,
setpoint for H\textsubscript{2}O/C decreases from 0.6 to 0.4 (throughput manipulator)

Operation in snowballing region should be avoided (max.
throughput in this case)

Saturation point of oxygen plant capacity is recommended for operation
Conclusions

• Self-optimizing method was applied for selection of the CVs for GTL
• There are 3 unconstrained DOFs in both modes of operation
• Combination of 7 measurements reduces the worst-case loss significantly, zero from engineering point of view
• There is one common set in the list of the best individual measurements in two modes, where two CVs (CO₂ recovery, H₂/CO in fresh syngas) have the same optimal setpoint value and the setpoint for the third one (H₂O/C) reduces from 0.6 to 0.4 as throughput increases
• Operation in Snowballing region should be avoided
• Saturation point of oxygen plant capacity is recommended for operation in practice

Thank you for your attention