

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

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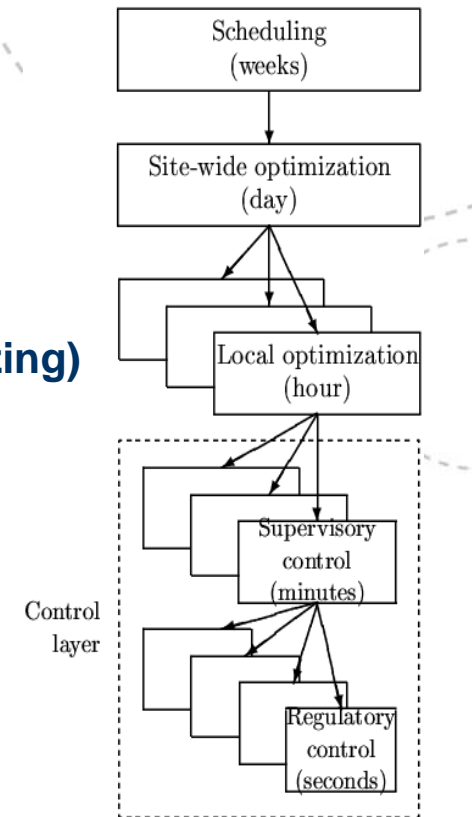
# Skogestad plantwide control procedure\*

## 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



\*Skogestad, S., 2004, Control Structure Design for Complete Chemical Plants, Computers and Chemical Engineering, 28, 219-234



# 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

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

$$M = J_{uu}^{1/2} G^{y-1} (F W_d \quad W_n)$$

$$F = G^y J_{uu}^{-1} J_{ud} - G_d^y$$

F is optimal sensitivity of the measurements with respect to disturbances;  $F = \frac{\Delta y^{\text{opt.}}}{\Delta d}$

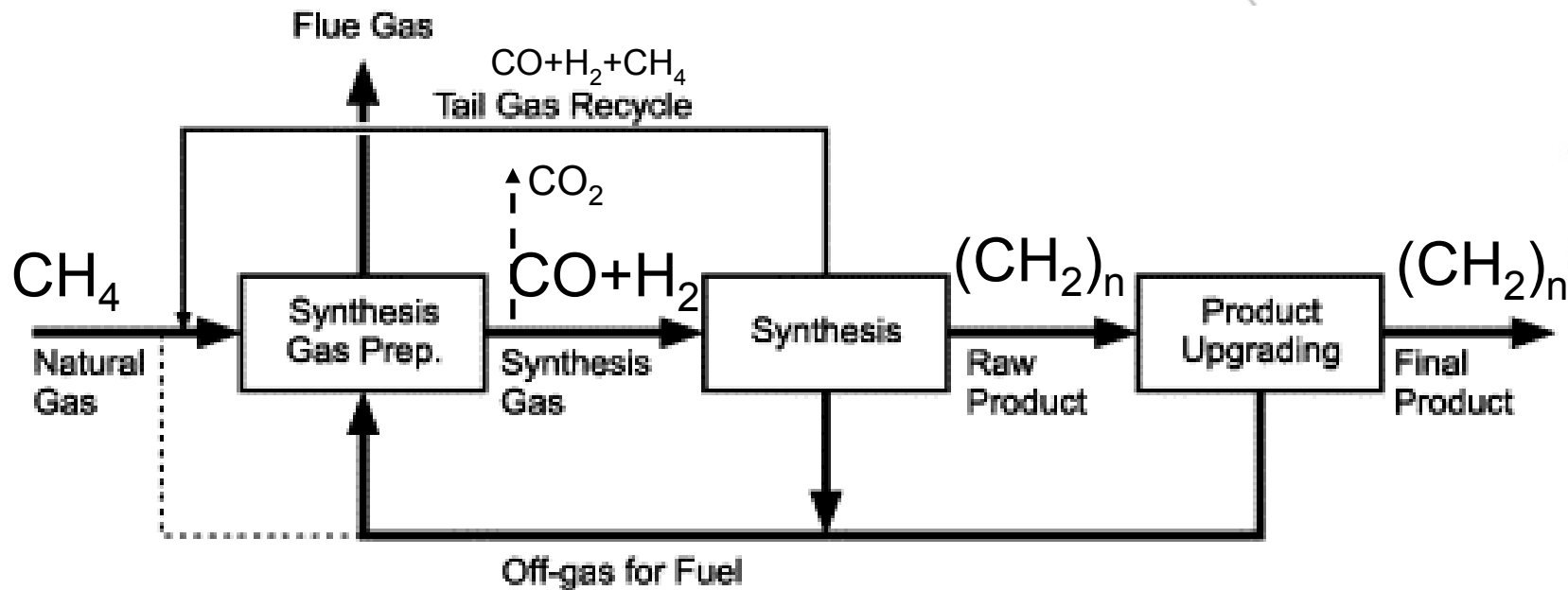
\* I.J. Halvorsen, S. Skogestad, J.C. Morud and V. Alstad,

'optimal selection of controlled variables' *Ind. Eng. Chem. Res.*, **42** (14), 3273-3284 (2003)



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## A simple flowsheet of GTL process\*



\* Rostrup-Nielsen, J., I. Dybkjaer, et al. (2000). "Synthesis gas for large scale Fischer-Tropsch synthesis." *American Chemical Society, Division of Petroleum Chemistry, Preprints* 45(2): 186-189



# Process description

## Synthesis gas unit

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

## CO<sub>2</sub> removal (optional)

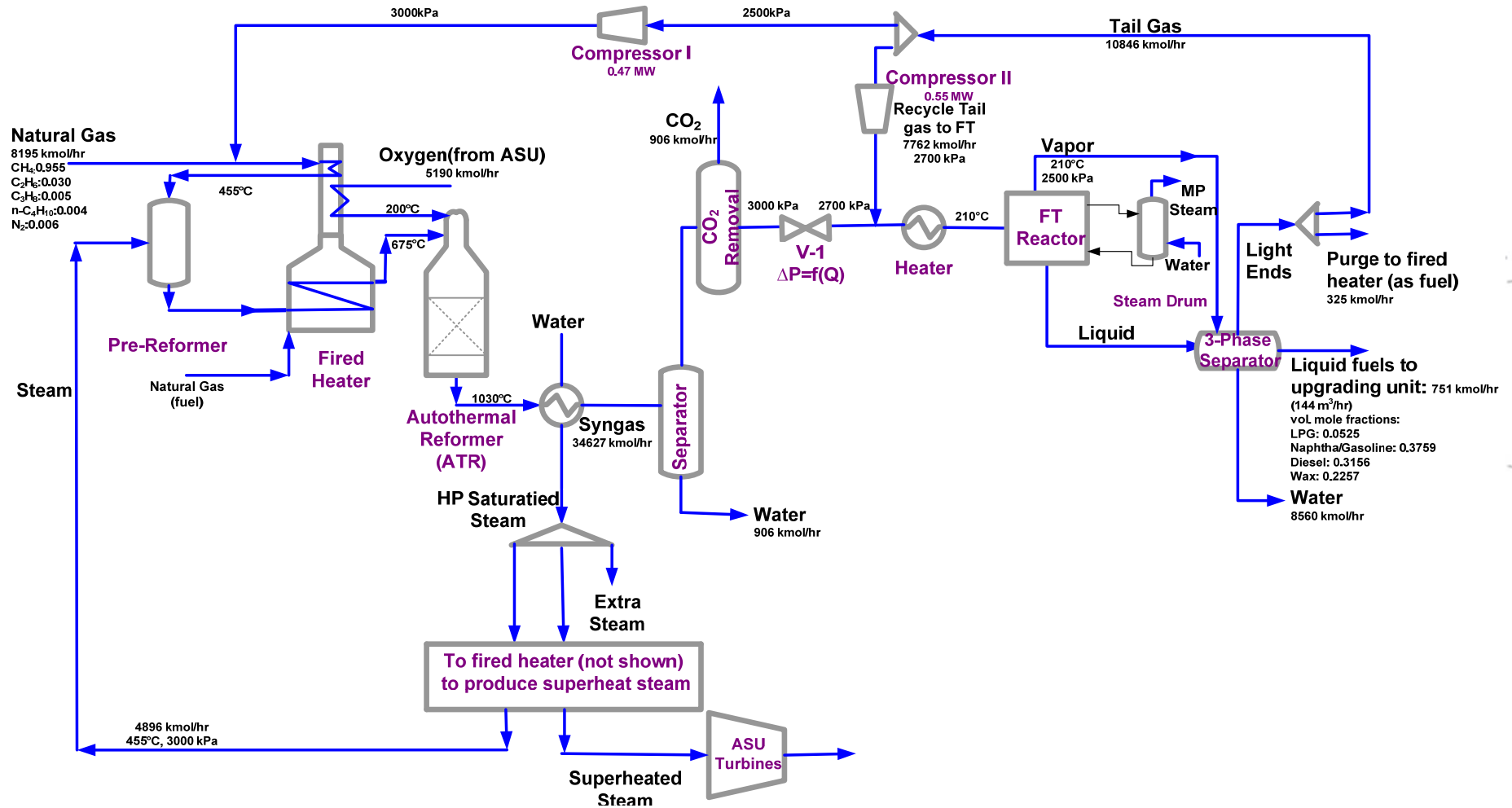
Fischer-Tropsch (FT) reactor: slurry bubble column reactor

Fischer-Tropsch products separation



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# Detailed flowsheet of GTL process (UniSim)



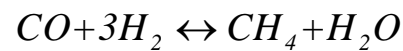


## Pre-reformer reactions

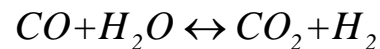
Converting higher hydrocarbons

than methane, For  $n \geq 2$   $C_nH_m + nH_2O \rightarrow (n + \frac{m}{2})H_2 + nCO$

Methanation



Shift Reaction



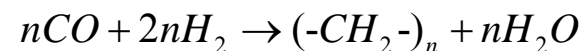
## Auto-thermal reformer (ATR) reactions

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



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# 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\*):

$$r_{CH_4} = \frac{1.08 \times 10^{-8} P_{H_2} P_{CO}^{0.05}}{1 + 3.3 \times 10^{-5} P_{CO}} \left( \frac{mol_{CH_4}}{g\text{-atom surface metal. s}} \right)$$
$$r_{CO} = \frac{1.96 \times 10^{-8} P_{H_2}^{0.6} P_{CO}^{0.65}}{1 + 3.3 \times 10^{-5} P_{CO}} \left( \frac{mol_{CO}}{g\text{-atom surface metal. s}} \right)$$

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)

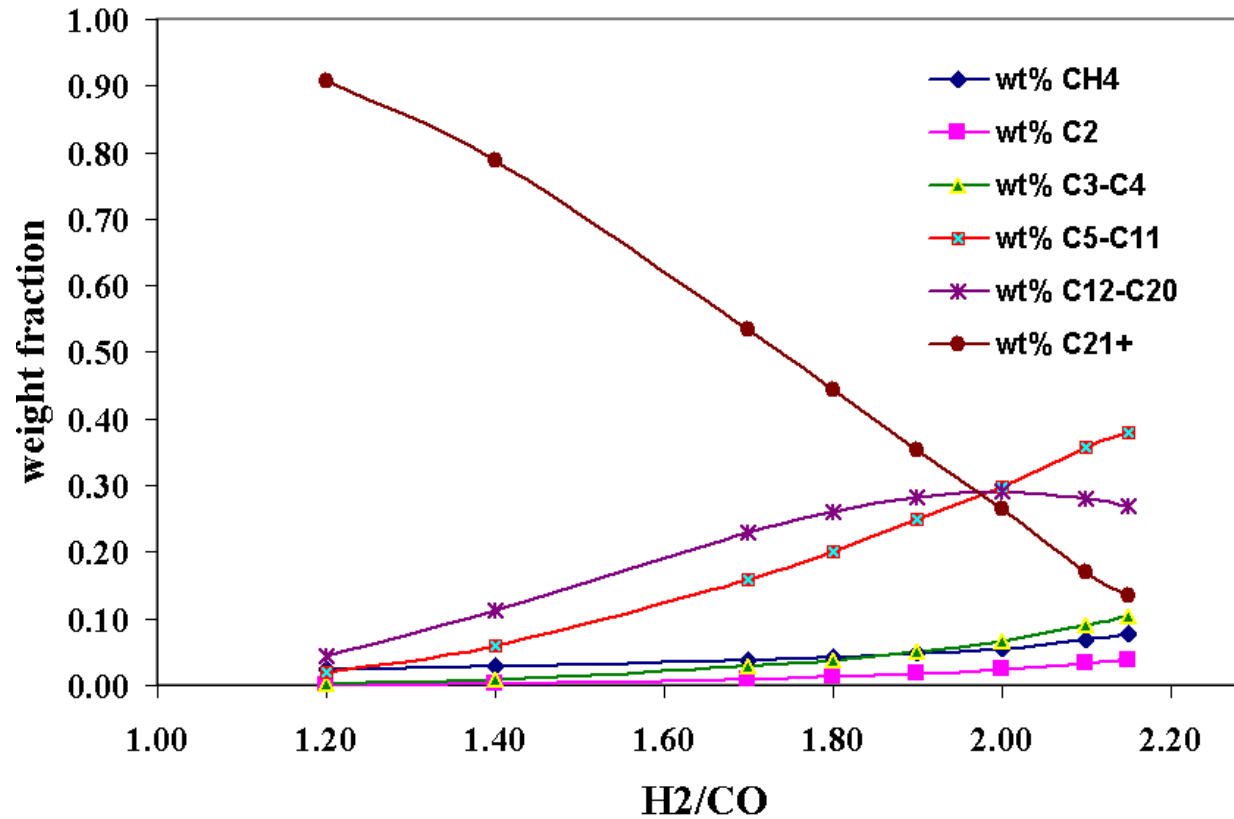
\*Iglesia, E.; Reyes, S. C.; Soled, S. L. Reaction-Transport selectivity models and the design of fischer-tropsch catalysts. Computer-aided design of catalysts, Becker R. E. ; Pereira. C. J. eds.,1993;199-257.

\*\*Song, H.-S.; Ramkrishna, D.; Trinh, S.; Wright, H. Operating strategies for Fischer-Tropsch reactors: A model-directed study. Korean Journal of Chemical Engineering 2004, 21, 2, 308-317



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# FT Products distribution in our simulated reactor



# 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 CO<sub>2</sub> removal

### Inequality Constraints

1. Steam/Carbon ratio feed to the syngas unit  $\geq 0.3$  (soot free operation),
2. Inlet temperature of ATR (outlet of fired heater)  $\leq 675^{\circ}\text{C}$  (material constraint),
3. Outlet of ATR  $\leq 1030^{\circ}\text{C}$ . (soot free operation),
4. Purge ratio  $\geq 2\%$  (convergence issues),
5. In addition, there are capacity constraints on the variable units; fired heater (duty +40% compared to nominal), CO<sub>2</sub> 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,



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## Step 2: Identify degrees of freedom (DOFs) for optimization

1. H<sub>2</sub>O (superheat steam) feedrate to pre-reformer (H<sub>2</sub>O/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. CO<sub>2</sub> 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).



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## Step 3: Identification of important disturbances

Natural gas flowrate,

Natural gas composition,

Natural gas price,

FT reactions kinetic parameter,

Change in active constraints value.



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## 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%.

### Optimal nominal values

H <sub>2</sub> O/C	O <sub>2</sub> /C	CO <sub>2</sub> Recovery	Recycle ratio to FT	Purge of tail gas	H <sub>2</sub> /CO fresh	H <sub>2</sub> /CO into FT	CO conversion		H <sub>2</sub> conversion		$\alpha$	Carbon Efficiency	Objective function (USD/hr)
							per pass	overall	per pass	overall			
0.6010	0.5233	75.73%	73.79%	3%	2.1	2.03	85.74%	95.50%	89.93%	96.92%	0.87	74.59%	49293

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

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

H<sub>2</sub>O/C, CO<sub>2</sub> recovery, tail gas recycle ratio to FT reactor



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## 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<sub>2</sub>/C feed (y<sub>1</sub>)
- 2- H<sub>2</sub>O/C feed (y<sub>2</sub>)
- 3- CO<sub>2</sub> recovery% (y<sub>3</sub>)
- 4- recycled tail gas ratio to FT reactor (y<sub>4</sub>)
- 5- H<sub>2</sub>/CO in fresh syngas (y<sub>5</sub>)
- 6- H<sub>2</sub>/CO in tail gas (y<sub>6</sub>)
- 7- H<sub>2</sub>/CO into FT reactor (y<sub>7</sub>)
- 8- H<sub>2</sub> mole fraction in fresh syngas (y<sub>8</sub>)
- 9- CO mole fraction in fresh syngas (y<sub>9</sub>)
- 10- CH<sub>4</sub> mole fraction in fresh syngas (y<sub>10</sub>)
- 11- H<sub>2</sub> mole fraction in tail gas (y<sub>11</sub>)
- 12- CO mole fraction in tail gas (y<sub>12</sub>)
- 13- CH<sub>4</sub> mole fraction in tail gas (y<sub>13</sub>)
- 14- H<sub>2</sub> mole fraction into FT reactor (y<sub>14</sub>)
- 15- CO mole fraction into FT reactor (y<sub>15</sub>)
- 16- fresh syngas flowrate (y<sub>16</sub>)
- 17- tail gas flowrate to syngas unit (y<sub>17</sub>)
- 18- tail gas flowrate to FT reactor (y<sub>18</sub>)



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## 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

no.	Sets			Loss (USD/hr)
1	$y_3$ :CO <sub>2</sub> recovery	$y_9$ : CO mole fraction in fresh syngas	$y_{12}$ : CO mole fraction in tail gas	1393
2	$y_3$ :CO <sub>2</sub> recovery	$y_2$ : H <sub>2</sub> O/C	$y_6$ : H <sub>2</sub> /CO in tail gas	1457
3	$y_3$ :CO <sub>2</sub> recovery	$y_2$ : H <sub>2</sub> O/C	$y_5$ : H <sub>2</sub> /CO in fresh syngas	1698
4	$y_3$ :CO <sub>2</sub> recovery	$y_6$ : H <sub>2</sub> /CO in tail gas	$y_5$ : H <sub>2</sub> /CO in fresh syngas	2594
5	$y_{10}$ :CH <sub>4</sub> mole fraction in fresh syngas	$y_6$ : H <sub>2</sub> /CO in tail gas	$y_5$ : H <sub>2</sub> /CO in fresh syngas	2643



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## b) Combining of measurements (full H matrix)

$$C = H y$$

The optimal H is obtained by solving the following optimization problem

$$\min_H \|HY\|_F^2$$

$$\text{s.t. } HG^y = J_{uu}^{1/2}$$

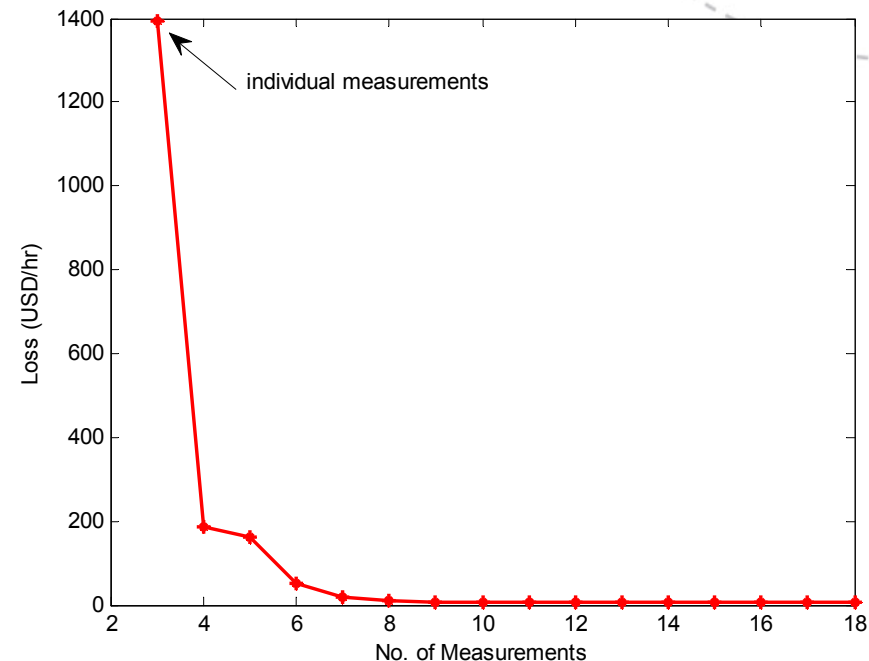
where  $Y = [F \ Wd \ \ Wny]$

An analytical solution is:

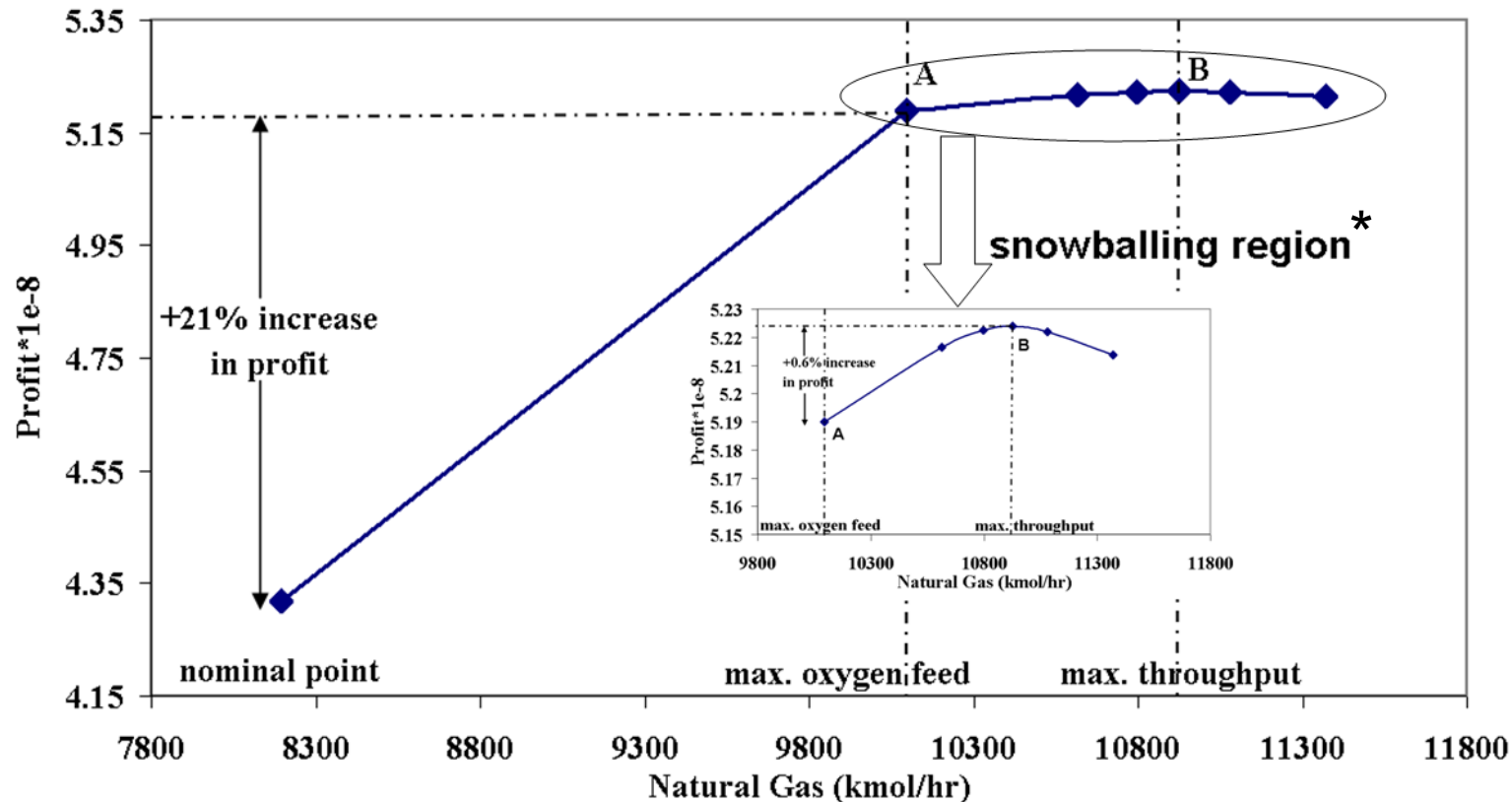
$$H^T = (YY^T)^{-1} G^y (G^{yT} (YY^T)^{-1} G^y)^{-1} J_{uu}^{1/2}$$

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

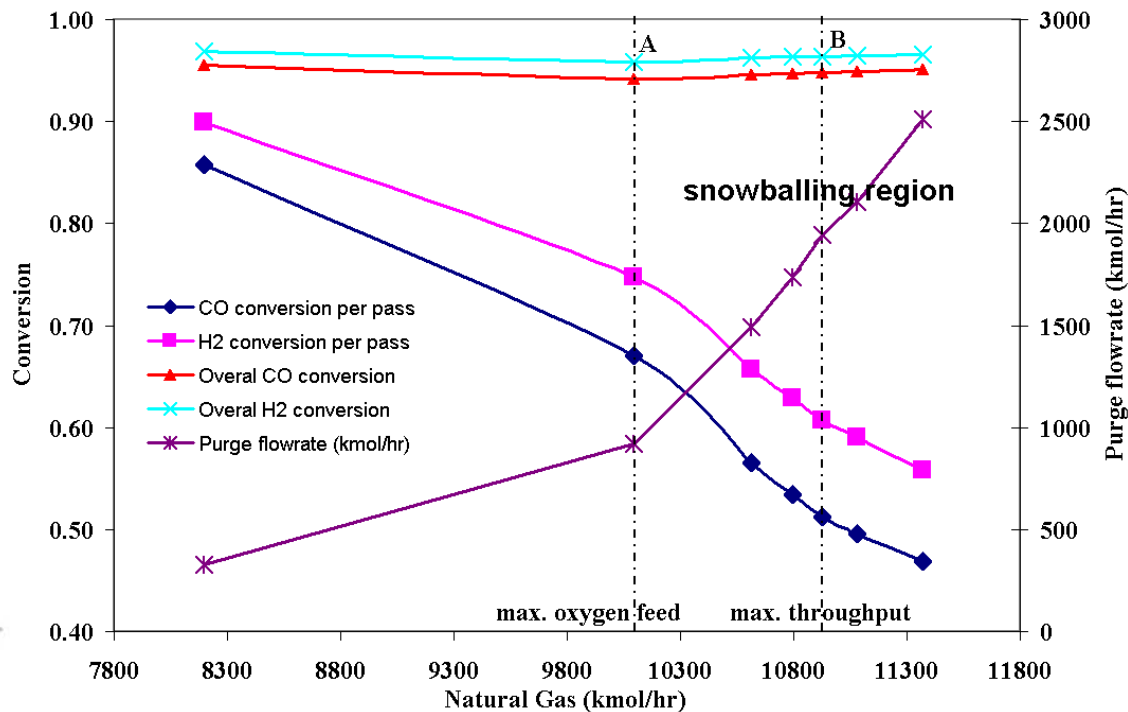
Luyben, W. L. (1994). "Snowball effects in reactor/separators processes with recycle." *Industrial & Engineering Chemistry Research* **33**(2): 299-305.



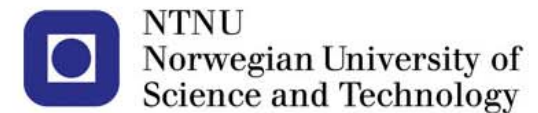
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## Optimal values in: nominal point, saturation of oxygen flowrate and maximum throughput

	H <sub>2</sub> O/C	O <sub>2</sub> /C	CO <sub>2</sub> recovery	Recycle ratio to FT	Purge of tail gas	H <sub>2</sub> /CO fresh	H <sub>2</sub> /CO into FT	CO conversion %		H <sub>2</sub> conversion %		$\alpha$	Carbon efficiency	Objective function (USD/hr)
								per pass	overall	per pass	overall			
opt. nominal	0.6010	0.523	75.73%	73.79%	3%	2.1	2.03	85.74	95.50	89.93	96.92	0.87	74.59%	49293
max. oxygen	0.5357	0.516	76.80%	90%	3%	2.092	1.91	67.08	94.14	74.705	95.88	0.86	74.30%	59246
max. throughput	0.4084	0.504	76.04%	97.13%	3%	2.095	1.80	51.25	94.79	60.69	96.39	0.87	74.31%	59634



**FT reactor volume is the bottleneck**





## a) Individual measurements (mode II)

worst-case loss for the best 5 individual measurement sets

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

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<sub>2</sub> recovery and H<sub>2</sub>/CO ratio,  
setpoint for H<sub>2</sub>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 ( $\text{CO}_2$  recovery,  $\text{H}_2/\text{CO}$  in fresh syngas) have the same optimal setpoint value and the setpoint for the third one ( $\text{H}_2\text{O}/\text{C}$ ) 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***



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