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NLP optimization of gas turbine including experimental catalyst conversion data in methanol plant

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Abstract

This paper presents a study on experimentally measured degrees of conversion in successive catalyst bed levels which can be included in simultaneous optimization using nonlinear programming (NLP) algorithm. The NLP model is including equations of structural and parametric optimization of: existing catalyst model, recycled gas stream, reactor, gas turbine, heat exchangers, flash, compressors, splitter and CO_2 reuse. The optimization approach is illustrated by a complex low-pressure Lurgi methanol process, giving an additional profit of 3,5 MUSD/a.

Keywords: catalyst, degree of conversion, NLP model, CO_2 reuse, methanol.

1. Introduction

Several research studies have been published on catalyst selectivity for methanol production. Lange presented a review of methanol synthesis technologies [1]. Moreover, several studies were reported on the kinetic modelling of methanol synthesis [2, 3] and deactivation models regarding the effects of temperature and gas composition [4, 5]. Kordabadi and Jahanmiri [6] presented a mathematical model on the heterogeneous catalysis of a methanol synthesis reactor along with its temperature profile, using genetic algorithm.

2. The catalysis

Catalysis increases the rate of reaction. Although the catalyst remains unchanged at the end of the process, the material takes part in the reaction. In fact, theories of catalyst activity postulate that the material does actively participate in the reaction. The mechanism of catalysis is based on lowering the free energy of activation by the presence of a catalytic material. The catalyst is effective in increasing the rate of reaction because it makes an alternative mechanism possible, each step of gas conversion having a lower free energy of activation than that for the uncatalyzed process.

This paper presents mathematical prediction calculation for experimentally determined degrees of conversion after each catalyst bed level (see case study).

3. Case study

The proposed calculation, using the degree of conversion data of the catalyst bed levels was tested for a complex, low-pressure Lurgi methanol process [7]. The simplified flow sheet of the methanol process is presented in Figure 1.
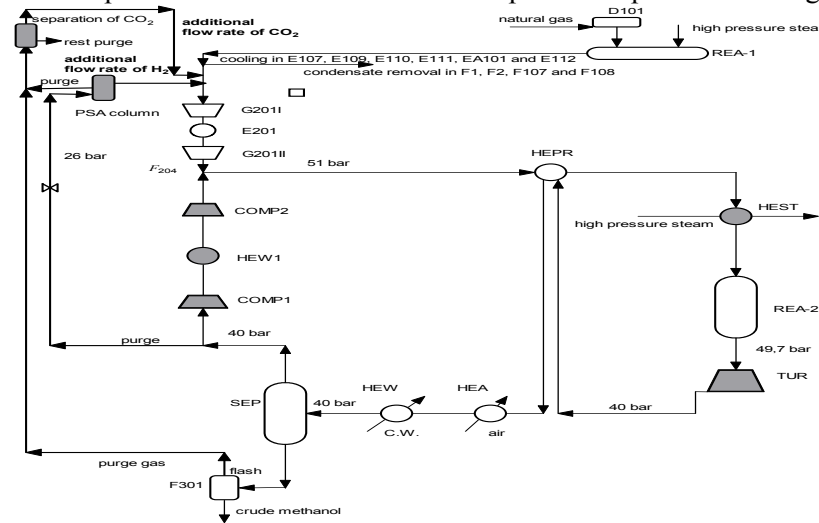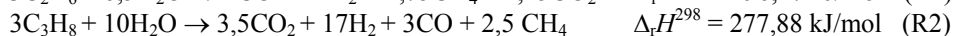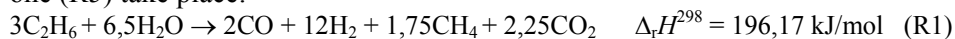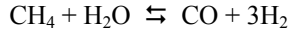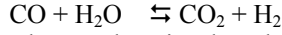

Figure 1: Simplified flow sheet of the methanol plant.

In the first subsystem, natural gas is desulphurized (D101) and heated in a steam reformer (REA-1) to 825 ^{o}C and 17,5 bar pressure, and synthesis gas (a mixtures of CO, CO_2, CH_4 and H_2) is produced from the natural gas and steam on the NiO catalyst. Four endothermic reactions (R1–R4) and an exothermic one (R5) take place:

$3C_2H_6 + 6,5H_2O \rightarrow 2CO + 12H_2 + 1,75CH_4 + 2,25CO_2$ $\Delta_rH^{298} = 196,17$ kJ/mol (R1)

$3C_3H_8 + 10H_2O \rightarrow 3,5CO_2 + 17H_2 + 3CO + 2,5\,CH_4$ $\Delta_rH^{298} = 277,88$ kJ/mol (R2)

$3C_4H_{10} + 13,5H_2O \rightarrow 4,75CO_2 + 22H_2 + 4CO + 3,25\,CH_4$ $\Delta_rH^{298} = 361,48$ kJ/mol (R3)

$$CH_4 + H_2O \leftrightarrows CO + 3H_2 \qquad\qquad \Delta_rH^{298} = 206{,}08 \text{ kJ/mol (R4)}$$

$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad\qquad \Delta_rH^{298} = -41{,}17 \text{ kJ/mol (R5)}$$

The catalyst is placed in 7 beds ($i = 7$). The length fractions of the shell tube, temperatures and amount fractions of components in the reformer at each bed level outlet are known (Table 1).

Table 1: Length fraction of shell tube, temperature, and amount fraction of components in reformer after catalyst bed levels.

Level i	Length fraction of tube	Temperature; $\vartheta/°C$	Amount fraction of components (x_k)					
			CH$_4$	H$_2$	CO	CO$_2$	H$_2$O	N$_2$
Inlet	0,000	433,0	0,275	0,017	0,000	0,001	0,702	0,002
1	0,114	613,8	0,239	0,121	0,002	0,027	0,610	0,002
2	0,229	668,5	0,171	0,277	0,017	0,054	0,478	0,002
3	0,343	722,1	0,121	0,379	0,042	0,062	0,394	0,002
4	0,457	760,5	0,088	0,441	0,064	0,061	0,344	0,002
5	0,571	790,4	0,066	0,480	0,081	0,058	0,313	0,002
6	0,686	814,9	0,050	0,507	0,094	0,054	0,292	0,002
7	0,800	836,6	0,039	0,526	0,105	0,051	0,277	0,002
outlet	1,000	855,2	0,030	0,541	0,114	0,049	0,266	0,002

The reactions from R1 to R3 take place with 100 % conversion at the inlet of the reactor [7]. Reactions R4 and R5 take place in each catalyst bed level with increasing degrees of conversion. The key components are CH$_4$ and H$_2$O (k = CH$_4$, H$_2$O). The amount ratio between catalyst bed levels $i − 1$ and i ($f_{k,i-1,i}$) can be calculated from the amount fractions x_i of the key components k:

$$f_{k,i-1,i} = x_{k,i-1} / x_{k,i} \quad k \in CH_4, H_2O \quad i \in 1, \ldots, 7 \tag{3.1}$$

The amount flow rate ($F_{k,i}$) of methane and water in the bed level i can be estimated by the division of the amount flow rate ($F_{k,i-1}$) in the bed level $i − 1$, and the amount ratio ($f_{k,i-1,i}$):

$$F_{k,i} = F_{k,i-1} / f_{k,i-1,i} \quad k \in CH_4, H_2O \quad i \in 1, \ldots, 7 \tag{3.2}$$

The amount flow rate change ($\Delta F_{CH4,i}$) of methane reacting in bed level i is given by the equation:

$$\Delta F_{CH4,i} = F_{CH4,i-1} - F_{CH4,i} \quad i \in 1, \ldots, 7 \tag{3.3}$$

With equation 3.4 the reacted amount flow rate change of H$_2$O after reactions R4 and R5 in level i ($\Delta F_{H2O,i}$) can be calculated:

$$\Delta F_{H2O,i} = F_{H2O,i-1} - F_{H2O,i} \quad i \in 1, \ldots, 7 \tag{3.4}$$

The amount flow rate of the methane reaction is the same as the amount flow rate change of the water after reaction R4 in level i ($\Delta FR4_{H2O,i}$):

$$\Delta F_{CH4,i} = \Delta FR4_{H2O,i} \quad i \in 1, \ldots, 7 \tag{3.5}$$

The amount flow rate change of the water after reaction R5 in level i ($\Delta FR5_{H2O,i}$) is:

$$\Delta FR5_{H2O,i} = \Delta F_{H2O,i} - \Delta FR4_{H2O,i} \quad i \in 1, \ldots, 7 \tag{3.6}$$

With the above-mentioned equations, the degrees of conversion (X) for reactions R4 and R5 in the bed levels can be estimated (eq. 3.7 in 3.8), the reacted methane being the key component for reaction R4, and the reacted water the key component for both reactions (Table 2):

$$X_{R4,i} = \Delta F_{CH4,i} / F_{CH4,i-1} \quad i \in 1, \ldots, 7 \tag{3.7}$$

$$X_{R5,i} = \Delta FR5_{H2O,i} / (F_{H2O,i-1} - \Delta FR4_{H2O,i}) \qquad i \in 1, \dots, 7 \tag{3.8}$$

The calculated amount ratio for methane is in good agreement with the experimental measurements (Table 2). The calculated amount ratio for water is too low. The disagreement in levels 1 to 4 is from 6,1 % to 5,3 % and in levels 5, 6 and 7 it is from 3,6 % to 2 %. The corrections are made after comparing the composition of the components in the outlet stream. The flow rate of water as a raw material in the reformer is changing, and the amount ratio f for water is fluctuating with it. The degree of conversion for reaction R4 at first bed level is 0,13; then it increases in the second and third bed level from 0,284 to 0,292; then decreases from the fourth to seventh bed level from 0,27 to 0,21. The degree of conversion for reaction R5 at the first bed level is 0,023; then it increases at the second bed level to 0,067, and decreases in the third to seventh bed levels, from 0,031 to 0,0002.

Table 2: The amount ratios (f) and degrees of conversion (X) of reactions R4 and R5.

i level	$\vartheta/°C$	$f_{CH4,i}$ case	$f_{CH4,i}$ calculated	$f_{H2O,i}$ case	$f_{H2O,i}$ calculated	$X_{R4,i}$	$X_{R5,i}$
inlet	433,0						
1	613,8	1,15	1,15	1,15	1,08	**0,130**	**0,0230**
2	668,5	1,39	1,39	1,27	1,20	**0,284**	**0,0670**
3	722,1	1,41	1,41	1,21	1,14	**0,292**	**0,0310**
4	760,5	1,37	1,37	1,14	1,08	**0,270**	**0,0030**
5	790,4	1,33	1,33	1,09	1,05	**0,240**	**0,0010**
6	814,9	1,32	1,32	1,07	1,04	**0,240**	**0,0003**
7	836,6	1,28	1,28	1,05	1,03	**0,210**	**0,0002**
outlet	855,2						

The hot stream of the synthesis gas is cooled in the boiler E107, in heat exchangers (E109–E111), in the air cooler EA101 and in the water cooler E112. The condensate expands in flash separators: F1, F2, F107 and F108. The synthesis gas is compressed in a two-stage compressor G201-I and G201-II. In the second subsystem, methanol is produced by catalytic hydrogenation of carbon monoxide and/or carbon dioxide in the reactor REA-2. The second reactor is operated at 51 bar pressure. The outlet stream of REA-2, crude methanol is cooled with its inlet stream in the heat exchanger HEPR. The methanol is flashed in F301. In the third subsystem, crude methanol is refined to pure methanol by distillation in the purification section of the process, to remove water and a variety of other impurities.

The high-pressure reactor REA-2 is operated within the existing parameters and unconverted gas is recycled. The high recycle ratio and operating pressure of the reactor are exploited to produce electricity, using a gas turbine (TUR) placed downstream the reactor. The turbine uses REA-2 outlet gas as a working fluid. The inlet stream of the reactor is heated by a process stream (HEPR) or by high-pressure steam (HEST) or a combination of both. The stream leaving the turbine is cooled using air (HEA) and water (HEW) coolers before entering the flash (SEP). The liquid stream of the separation is the product and the recycled gas stream is compressed to 51 bar in a new, two-stage compressor (COMP1, 2) with intermediate water cooling (HEW1). The purge gas is separated from the

crude methanol in the flash F301. The high-pressure purge gases from separators SEP and F301 can be mixed and then CO_2 can be separated, before the gas is burnt in the furnace (REA-1), by using membrane, absorption, or adsorption system. The producer has to decide on the choice. The producer can utilize an existing, inactive pressure swing adsorption (PSA) column for H_2 to separate additional H_2 flow rate, or use another adsorbent as mesoporous molecular sieve MCM-41 for CO_2 separation. In the retrofitted methanol process, the recycled CO_2 can be reused as the reactant, and CO_2 emission can be reduced. The methanol process parameters are optimized using a nonlinear programming (NLP) model [7]. The mathematical model is applied, including integration of heat flows, generation of electricity, CO_2 reuse, increased production, existing catalyst model and decreased CO_2 emissions. Simultaneous optimization is promising additional annual profit, which is strongly influenced by the flow rate of CO_2 in the process. The CO_2 flow rate depends very much on the degrees of conversion in reactors REA-1 and REA-2, and catalyst selectivity in REA-1. The parameters in the retrofitted model of the process units [7] were simultaneously optimized using the GAMS/MINOS [8]. This NLP can be solved with a large-scale reduced gradient method (e. g. MINOS). The model is non-convex, it does not guarantee a global optimization solution but it quickly gives good results for non-trivial, complex processes. The NLP model has variable heat capacity flow rate for all the streams and the structure can also be varied by using them. The NLP model contains equations for structural and parametric optimization.

The retrofitted methanol process (Fig. 2) with the maximum additional CO_2 flow rate of 640 kg/h from purge gas to be reused, electricity generation using gas turbine pressure drop from 49,7 bar to 37 bar, and outlet temperature, $T_{tur, out}$ = 110 ^{o}C were selected as a starting flow sheet. The flow rate of CO_2 is separated from the purge gas in the PSA and re-injected before the G201I compressor. The existing PSA column is not used for the purification of H_2, as the additional H_2 is not needed because of the catalyst selectivity in reactor REA-1. Therefore the PSA with a new adsorbent can be better used for CO_2 separation from purge gas. The total additional annual methanol production (including all the effects of the additional flow rates of CO_2 and reduced flow rate of steam) is estimated to be 10 mol/s. The structure enables 20 MW of electric power to be generated. The steam exchanger (HEST) needs 25 MW of heat flow rate. The integrated process stream exchanges 6 MW of heat flow rate in HEPR. Additional annual depreciation of the gas turbine, new heat exchangers (HEST, HEW1) and the new two-stage compressor, is estimated to be 3,04 MEUR/a. The cost of the high-pressure steam used in HEST will be 2,64 MEUR/a, the CO_2 purification cost from purge gas in the existing PSA column and inlet injection cost in the recycle are estimated to be 0,4 MEUR/a. In the depreciation account for retrofit we included 0,35 MEUR/a for the contingency. The annual income from the additional production of electricity will be 8,7 MEUR/a, and that of the methanol 1,06 MEUR/a. The

steam flow rate can be reduced by 9 192 t/a giving additional annual savings of 0,06 MEUR/a. The emission tax for CO_2 is reduced by 0,11 MEUR/a.
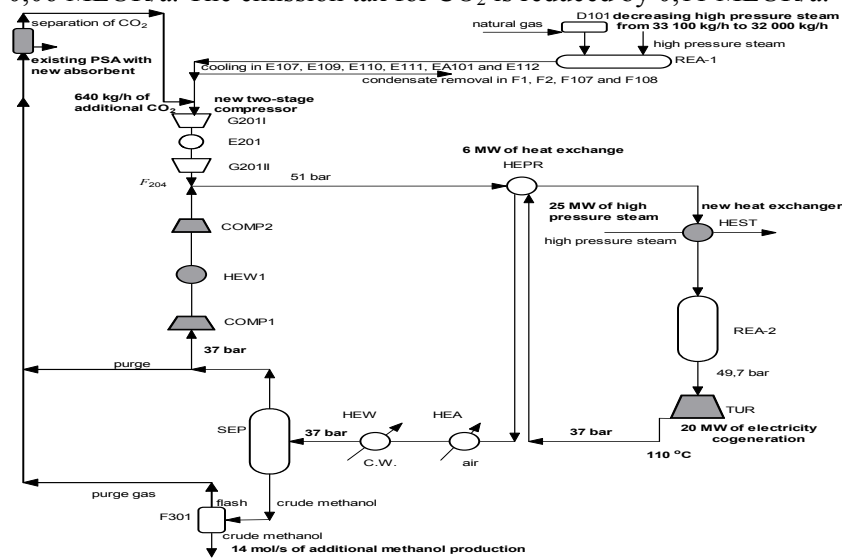

Figure 2: Simplified flow sheet of the retrofitted methanol plant.

4. Conclusions

This paper presents an efficient use of the NLP model formulations for simultaneous cogeneration of electricity using gas turbine and process heat integration, CO_2 reuse as reactant and existing catalyst model. The CO_2 emission can be reduced at source. We have carried out simultaneous heat, power, product and emissions optimization with a potential additional profit of 3,5 MEUR/a, and a payback time $t_{PB} \approx 1,7$ a. Improved process integration and cogeneration can decrease environmental emission by 5 600 t/a.

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