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NLP optimization of a methanol plant by using H_2 co-product in fuel cells

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Abstract

Fuel cells, process heat integration and open gas turbine electricity cogeneration can be optimized simultaneously using nonlinear programming (NLP) algorithm. The NLP model contains equations of structural and parametric optimization and is used to optimize complex and energy intensive continuous processes. The procedure does not guarantee the global cost optimum, but it does lead to good, perhaps near-optimum designs. The optimization approach is illustrated by a complex low-pressure Lurgi methanol process, giving an additional profit of 2,65 MUSD/a. The plant, which is producing methanol, has a surplus of hydrogen (H_2) flow rate in purge gas. H_2 shall be separated from the purge gas by an existing pressure swing adsorption (PSA) column. Pure H_2 can be used as fuel in fuel cells.

Keywords: fuel cells, H_2 separation, simultaneous optimisation, NLP, Model, methanol.

1. Introduction

There have been several research studies published in literature on using fuel cells. Several types of fuel cells have been developed or are under development. Shin'ya has published a review of the system configuration and operation plan of a fuel cell energy network using a solid polymer membrane-type fuel cell and hot-water piping network [1]. Hamada and co-authors [2] described the performance evaluation of a polymer electrolyte fuel cell of the electric power and hot water system. Santarelli and Torchio [3] discussed the results obtained after an experimental session devoted to characterization of the behavior of a single proton exchange membrane fuel cell by varying values of six operation variables: cell temperature, anode flow temperature at saturation and dry conditions, cathode flow temperature at saturation and dry conditions, and reactant pressure.

2. Fuel cell

Fuel cell is a new energy-saving technology generating electrical power. Fuel cells convert chemical energy into electricity directly, without combustion. The advantages of fuel cells are that they produce no emission, there are no transmission and distribution losses, they make up a very compact system and refuelling of the system is very easy. In contrast, fuel cells are very costly and there are no facilities for hydrogen storage in them. They function on the principle of electric charge exchange between a positively charged anode plate and a negatively charged cathode (Fig. 1). When hydrogen is used as the basic fuel, reverse hydrolysis occurs yielding only water and heat as by-products while converting chemical energy into electricity. Pollutant emissions are practically zero.

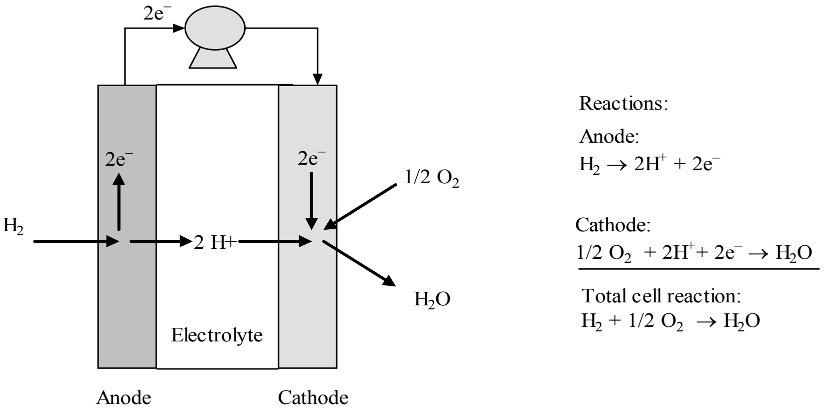

Fig. 1: Operating principle of fuel cell.

Fuel cells are classified according to the kind of electrolyte employed: phosphoric acid, polymeric, molten carbonate, or solid oxide. Despite differences in materials and operating conditions, all these fuel cells are based on the electrochemical reaction of hydrogen and oxygen for biomass power applications. These types of fuel cells operate at elevated temperatures, which present opportunities for heat recovery and integration into combined cycles. Although hydrogen is the ultimate energy carrier in the electrochemical reactions of this fuel cell, it has been designed to operate on a variety of hydrogen-rich fuels, including methane, diesel fuel, ethanol and producer gas. Within the fuel cell there is a reformer that converts these fuels into mixtures of hydrogen, carbon monoxide, carbon dioxide and water along with varying amounts of unreformed fuel.

The mass flow rate of 0,02 g/s of pure H_2 can produce 1kW of electricity and two times more heat with a cost of 2500 USD/kW using the solid polymer membrane-type fuel cells [1].

3. H_2 separation

A plant, which is producing methanol (see case study), has a surplus of hydrogen (H_2) flow rate in purge gas. H_2 shall be separated from the purge gas by an existing pressure swing adsorption (PSA) column. The purge gas is purified by the PSA column to deliver hydrogen at the 90 % to 99,99 % purity level by removing N_2, CO, CO_2, CH_4 and H_2O. The pressure swing adsorption uses an adsorber packed with a molecular sieve adsorbent having 50 % efficiency. The PSA column is operated at pressure of the 26 bar and temperature of 35 ^{o}C with the maximal capacity of H_2 at 488 kg/h. The flow rate of hydrogen can be varied from 0 kg/h to 488 kg/h. After start-up the PSA column will produce pure H_2 in 2–4 h. The purification system is completely automatic. The H_2 purification in the existing PSA column and inlet injection cost in the recycle (with inlet parameters 51 bar and 60 ^{o}C) is 0,1 EUR/kg [4]. Pure H_2 can be used as fuel in fuel cells.

4. Case study

The proposed use of fuel cells was tested for a complex, low-pressure Lurgi methanol process [5]. The simplified flow sheet of the methanol process is presented in Figure 2. In the first subsystem, natural gas is desulphurized (D101) and heated up 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. 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 reactor inlet stream is heated by a process stream (HEPR) or by high-pressure steam (HEST) or using a combination of both. 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 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, and REA-2 outlet gas as a working fluid.

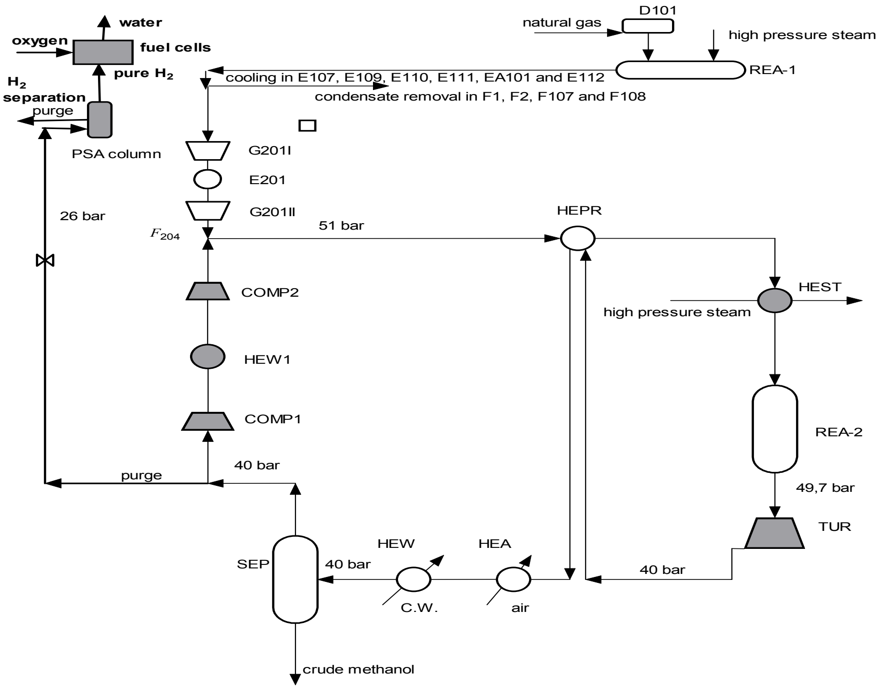

Figure 2: Simplified flow sheet of the methanol plant with fuel cells.

The second reactor is operated at the pressure of 51 bar and the unconverted gas is recycled. The outlet crude methanol stream of REA-2 is cooled with its inlet stream in the heat exchanger HEPR, in the air cooler HEA, and in the water cooler HEW. The methanol is flashed in SEP. In the third subsystem (not shown in Fig. 2), 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 producer can use the existing, inactive pressure swing adsorption (PSA) column for H_2 separation. Pure H_2 can be used as fuel in fuel cells.

The methanol process parameters are optimized using a nonlinear programming (NLP) model [4]. A mathematical model is applied, including integration of heat flows, generation of electricity, increased production, realistic catalyst model and fuel cells, and combined electricity and heat production. Simultaneous optimization could increase additional annual profit.

The parameters in the retrofitted model of the process units [4, 5] were simultaneously optimized using the GAMS/MINOS [6]. 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 a good results for non-trivial, complex processes. The NLP model contains variables of all the process parameters: molar heat capacities, material flow rates, heat flow rates and temperatures, which are limited by real constraints. 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. 3) with electricity generation using gas turbine pressure drop from 49,7 bar to 37 bar, and outlet temperature, $T_{\mathrm{tur,\ out}}$ = 110 °C was selected as a starting flow sheet.

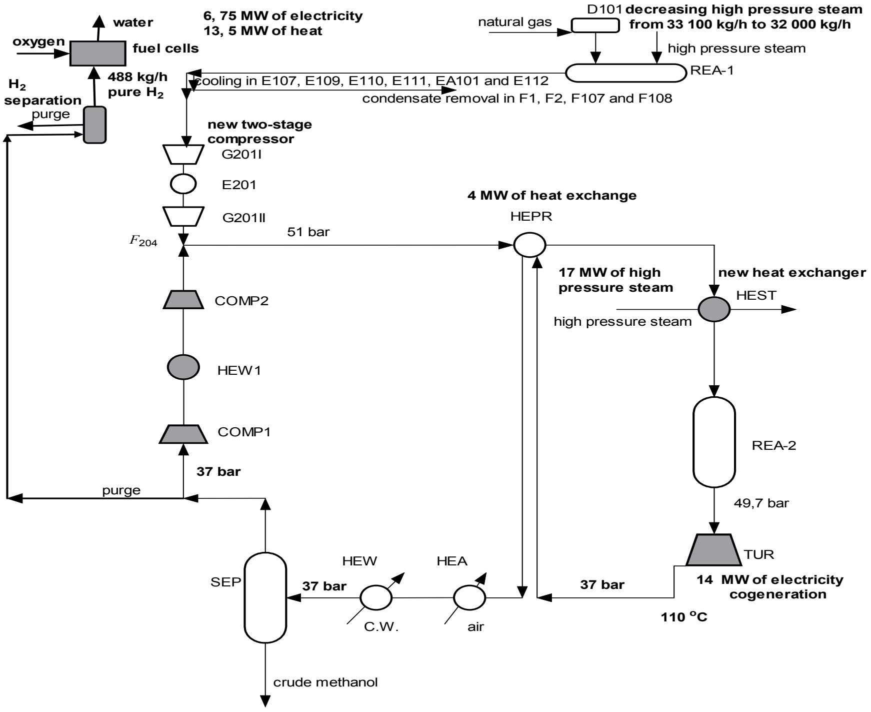

Figure 3: Simplified flow sheet of the retrofitted methanol plant.

The existing PSA column can be used for the purification of maximum 488 kg/h H_2 supplied as fuel to fuel cells, which can produce 6,75 MW of electricity and 13,5 MW of heat. The total additional annual methanol production is estimated to be 5 mol/s. The structure enables 14 MW of electricity power to be generated in the gas turbine. The steam exchanger (HEST) needs 17 MW of heat flow rate. The integrated process stream exchanges 4 MW of heat flow rate in HEPR. The powers of the first and the second compressor stage are 1,7 MW and 2,5 MW, respectively. The HEW1 is supposed to exchange 1,8 MW, the coolers HEW and HEA 4,5 MW and 6,7 MW of heat flow rate, respectively. The purge gas outlet flow rate fraction is decreased from 5,9 % to 5,4 %. The existing coolers of the synthesis gas (E107, E109, E110, E111, EA101, E112 and E201) need not be enlarged. The additional annual depreciation of the gas turbine, new heat exchangers (HEST, HEW1, having 942 m^2 and 324 m^2 of area, respectively) and the new two-stage compressor, is estimated to be 2,1 MEUR/a. The cost of the high-pressure steam used in HEST will be 1,8 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 in the gas turbine will be 6,0 MEUR/a, and that of the methanol 0,5 MEUR/a. The steam flow rate can be reduced by 9 192 t/a, giving additional annual savings of 0,06 MEUR/a.

The depreciation cost of fuel cells is 3,0 MEUR/a; then can produce 2,94 MEUR/a of electricity and 0,8 MEUR/a of heat. The H_2 purification cost from purge gas in the existing PSA column is estimated to be 0,4 MEUR/a. The additional profit of the process optimization including cogeneration (in gas turbine and fuel cells), additional methanol and heat production is estimated to be 2,65 MEUR/a, with a payback time $t_{\mathrm{PB}} \approx 2{,}3$ a.

5. Conclusions

This paper presents an efficient use of the NLP model formulation for simultaneous cogeneration of electricity using gas turbine, fuel cells and process heat integration. We have carried out simultaneous heat, power and product optimization with an additional potential profit of 2,65 MEUR/a.

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