Energy Savings in Methanol Synthesis : Use of Heat Integration Techniques and Simulation Tools.

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Abstract :   Starting with a classical process for producing methanol using the reforming and synthesis steps, a combined approach applying simulation models and a new synthesis strategy, named Effect Modelling and Optimisation (EMO), has been used to optimise the energy efficiency of the process. The method allows to identify different ways of improving the energy efficiency of the process. The modifications concern the synthesis reactor and the reforming reactor designs, the exploitation of the purge stream as fuel gas to satisfy the process requirement and its integration to a gas turbine system. The EMO approach allows to target the impact of a process modification at the global level of the energy cost of the process, including the combined production of heat and mechanical power in a gas turbine and the steam network. Starting with a classical methane conversion of 60% for the classical system, we identify solutions with up to 93% of the overall methane conversion when we transform the net mechanical power produced into methane savings at the country level. The interest of the approach is the possibility of computing the impact of the process modifications suggested by the analysis of the shape of the heat cascade on the overall energy balance of the plant without having to simulate in many details the steam and the heat exchanger network.

Keywords :   Energy efficiency, optimisation, steam network, process synthesis, methanol production

INTRODUCTION

Methanol is one of the most important chemicals as far as production is regarded. Its applications as motor fuel or base chemical for synthesis of octane booster such as MTBE has still increased the interest in improving the economy of its production.

The present methanol processes are mostly based on natural gas, and allow to produce 0.60 to 0.65 mole of methanol for each mole of methane used. The balance is used as energy supply to make the process feasible and operate compressors and distillation columns.

Methanol production is based on catalytic conversion of carbon oxides and hydrogen :

$$CO + 2\,H_2 = CH_3OH + 90.7 \text{ kJ/mole}$$

$$CO_2 + 3\,H_2 = CH_3OH + H_2O + 49.5 \text{ kJ/mol}$$
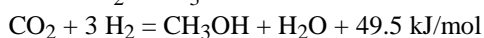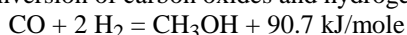
A high selectivity copper catalyst is used in modern units. Its activity requires temperatures above 210°C. Since the reactions are exothermic and limited by chemical equilibrium, the yield decreases with increasing temperature. In order to achieve high rate and significant conversion, the reactors are operated under pressure (4 MPa or more). However equilibrium limits the conversion, and unconverted reactants must be recovered and recycled to use the raw materials economically.

Methanol is separated by condensation and is further purified by distillation. The extent of side reactions producing e.g. ethanol and dimethylether is limited, but distillation is nevertheless needed when high purity methanol is required. Unreacted gas must be recompressed, and reheated before being recycled to the reactor inlet.

Synthesis gas can be produced by steam reforming, involving reactions :

$$CH_4 + H_2O = CO + 3\,H_2$$

$$CO + H_2O = CO_2 + H_2$$
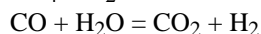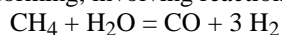
An alternative route is partial oxidation, that requires a source of pure oxygen :

$$CH_4 + O_2 = CO_2 + 2\,H_2$$
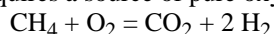
Stoichiometry for methanol synthesis requires that :

$$\frac{H_2 - CO_2}{CO + CO_2} = 2$$

Any departure from this proportion implies that the reactant in excess needs to be purged from the synthesis loop.
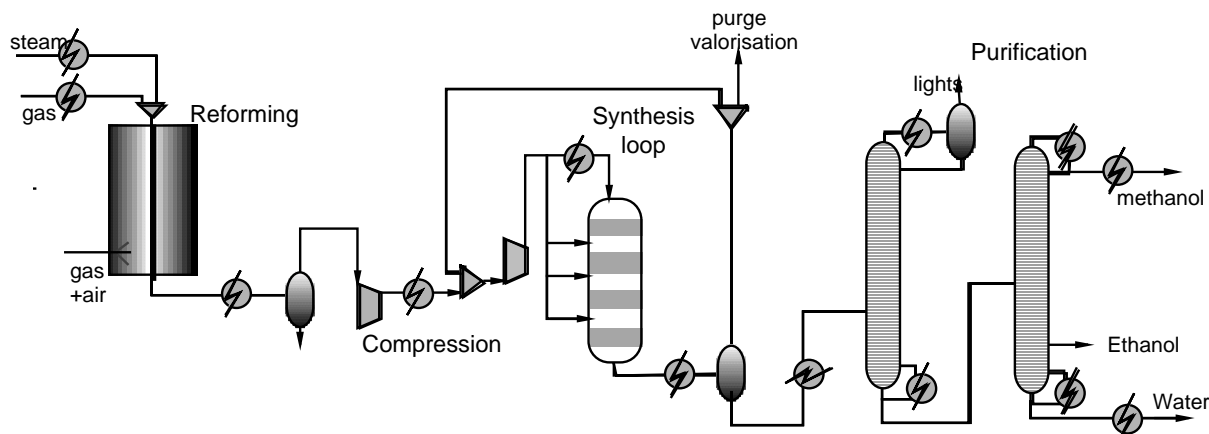
Figure 1 : reference flowsheet for I.C.I. low pressure methanol synthesis

Steam reforming produces a synthesis gas too rich in hydrogen (ratio close to 3). This can be corrected by operating a partial oxidation in parallel with a steam reformer, but this requires a source of oxygen and is seldom favoured, except in the largest units. If a source of carbon dioxide is available, it can help in adjusting the stoichiometric ratio.

The alternative is to purge the excess hydrogen, and to find a way to valorise it at best. The easiest way is to burn it in order to supply heat to the reformer and to raise steam.

A recent publication (Westerterp 1993) has examined alternative processes which require no recycle for the production of methanol. The RSIPR (reactor system with interstage product removal) allows to increase the methanol conversion to such an extent that recycle is no more necessary; this allows large savings in investment costs and energy consumption, but requires the design of high-temperature gas absorbers.

In this paper, we examine what energy savings could be gained by improving the energy integration and the purge valorisation of an existing reactor type. Technical and economic comparison will be based on the I.C.I. low pressure process, that has good market acceptance.

THE REFERENCE I.C.I. PROCESS

The I.C.I. low pressure process (Rogerson 1973) uses a series of adiabatic packed bed reactors. The inlet temperature to the beds is adjusted by injecting cold synthesis gas. No heat exchanger is needed between the beds, and this makes the reactor simpler than for competitive reactor designs, such as the Lurgi process (multitubular reactor, tubes cooled by boiling water) or the Kellog process (waste heat boilers to remove heat after each bed).

Figure 1 shows a simplified flowsheet of the reference process

SIMULATION MODEL

Physical properties for all mixtures in the synthesis gas preparation section and in the methanol synthesis loop have been estimated using Redlich-Kwong-Soave equation of state. For the purification section, UNIQUAC model has been used to predict liquid phase activity coefficients, and binary interaction parameters have been optimised to reproduce vapour-liquid equilibrium in mixtures made of water, methanol, ethanol and dimethylether. Solubility of CO_2, H_2, CO and N_2 in water and methanol has been adjusted by tuning Henry's constants for each pair. Lee-Kesler equation of state has been used to predict enthalpy departures.

The reforming tubes have been modelled using the "approach to equilibrium" approximation. The pressure in the tubes is set to 10 bar, and the outlet temperature is set to 850°C. The steam to carbon ratio is set to 2.68. The methanol synthesis occurs at 85 bar. The reactor has been modelled as a series of four adiabatic plug flow reactors. A pseudo homogeneous rate equation has been adopted to describe the kinetic model; it is based on data published by Skrzypek et al (1991). Frequency factors in the rate equation have been adjusted to better reproduce typical operating conditions of I.C.I. methanol synthesis reactors (Rogerson 1973).

The process has been scaled to produce 2000 metric tons methanol per day. Key figures for the synthesis loop and reactor system are :
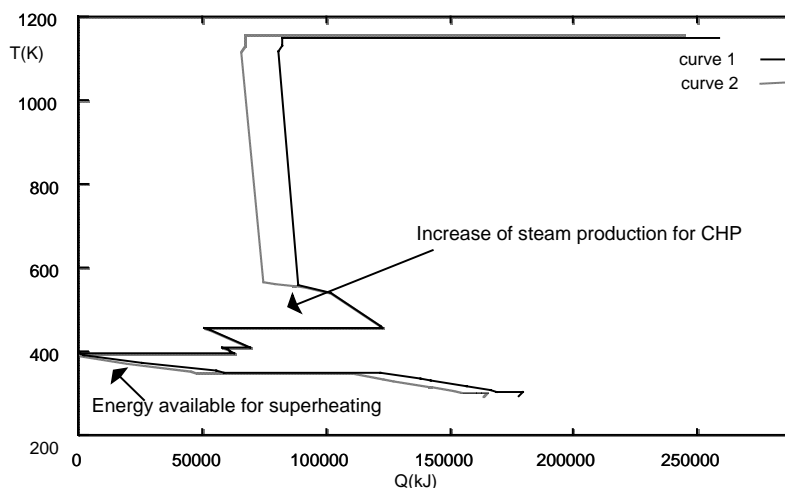

Figure 2 : GCC of the process.

- Syngas feed flowrate : 3.655 kmol/s
- Syngas loop flowrate : 16.14 kmol/s
- Purge ratio : 7%
- Catalyst productivity : 0.3 kg CH3OH/kg cata/hr
- Catalyst volume : 287 m^3 (55+70+78+84)
- Relative flow in beds : 0.60, 0.72, 0.86, 1.00
- Conversion : 40.8% for CO, 25% for CO_2
- Methanol mole fraction at reactor outlet : 4.36%
- (CH_4+N_2) fraction at reactor outlet : 11.2%
- Selectivity : 99.5%

Distillation columns have been modelled as series of equilibrium stages, corrected by constant Murphree efficiency. The first column removes the light impurities. Light key component is dimethylether. Second column removes the heavier components (ethanol and water). Distilled methanol purity is specified as 99.9 weight %.

The simulation model corresponding to the flowsheet in figure 1 allows to estimate the mass and energy balance of the process. However this simplified model does not consider the way energy is exchanged between the process and its environment : energy is only transferred using heaters or coolers. Energy integration will allow to match properly hot and cold streams to minimise the overall energy demand.

ANALYSIS OF ENERGY INTEGRATION

From the simulation results, composite curves can be drawn easily. From that information, we have used the EMO (Effect Modelling and Optimisation) strategy (Maréchal and Kalitventzeff, 1995) to target the Minimum Energy Requirements (MER) of the process and afterwards the Minimum Cost of Energy Requirements (MCER). The EMO approach is a new modelling and synthesis strategy based on the identification of the elementary thermal, mechanical and other effects involved in each unit of the process. It allows to model the energy distribution in the overall system.

The energy model of the process is made with different building blocks (*"effects"*). The thermal effects define the hot and cold streams to be considered in the ideal HEN (Heat Exchanger Network) of the process, i.e. the heat cascade. The steam network includes the different headers linking hot and cold streams (steam production and consumption) and the mechanical power productions (steam expansion). The mechanical power effects (mechanical power production and consumption) define the electrical import and export constraints. This method allows to identify areas for energy savings and for process improvements.

The Grand Composite Curve of the process is given on figure 2 (curve 1). It shows a high temperature requirement that corresponds to the demand of the reforming furnace. We should note that

this requirement fixes the fuel flowrate. It results in an excess of energy in the flue gas. Part of this energy can be valorized by CHP in the steam network.

Pressure levels of the steam network have been set to 85 bar, 12 bar, 3 bar and 0.065 bar. A condensation level was considered to maximise the energy recovery of the energy excess in the flue gas by generating mechanical power. The mechanical power produced by the turbine is used to satisfy the compressors needs, the balance being exported to the grid.

For the methanol process under study, a first area for energy savings is the synthesis loop. The original synthesis reactor design (the ICI one) is given on Figure 3, configuration A. The main idea of the EMO approach applied to the synthesis reactor is to decouple thermal and material effects between the different beds. Without changing the operating conditions of the reactor, the injections between the beds have been represented by one cold stream to cool down and one hot stream to heat up followed by an isothermal mixer (Figure 3, configuration B). By this representation the heat loads of the hot and cold streams are identical, but their energy quality, i.e. their temperatures, are considered when the new MER and GCC are computed (Figure 2, curve 2). The MER is reduced by 5.8%; this is explained by considering that the reactor inlet temperature is below the pinch point while the mixing temperature is above. Part of the heat above the pinch point is thus used below the pinch point. This creates an energy penalty : *"the more in - the more out"*. Furthermore, when we consider the mechanical power that could be produced in the system by CHP, the increase of the pocket in the GCC corresponds to an increase of the mechanical power production to be produced by steam expansion.

The configuration C of figure 3 gives the best reactor design obtained by this analysis. The reactor configuration is a compromise between ICI design (cold quench) and Kellog design (intercooling with waste heat boilers). Feed is preheated using the heat available below the pinch point and afterwards preheated by the heat of reaction, part being used for the injections. The remaining heat is used to produce MP steam to be expanded in the steam network.

In order to decrease the complexity of the reactor, we suggest the configuration D of Figure 3, where the steam production has been removed from the reactor design. With this configuration we do not loose energy but we produce less mechanical power because the size of the pocket of the GCC is smaller. The difference (3730 kW) is to be balanced with the higher investment cost if the more complex design is adopted. We insist on the fact that the preheating temperature depends on the process pinch point, it is thus specific to the plant location. In our example the pinch point is defined by the boiler of the second purification column.
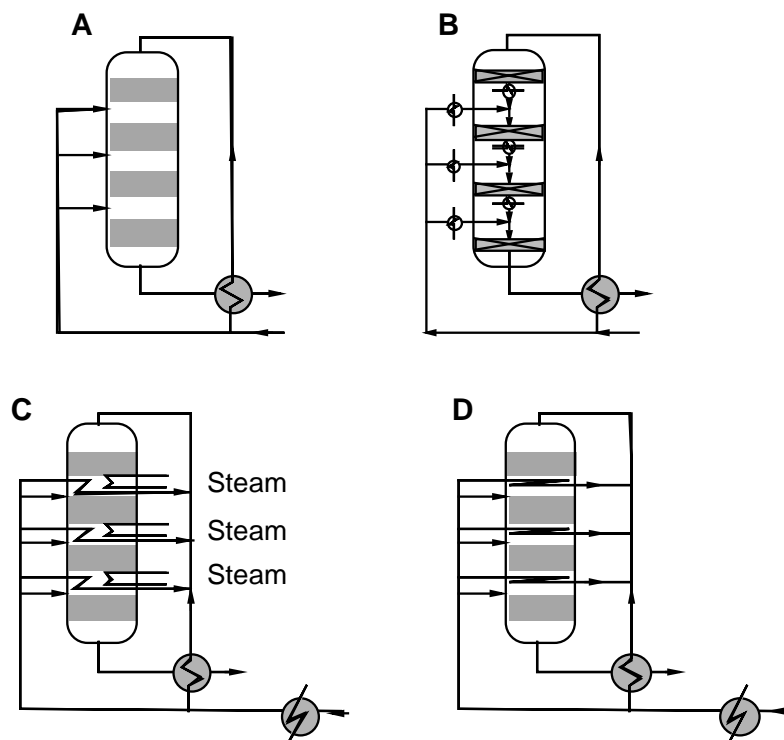
Figure 3 : Reactor design : A : standard configuration
B : effect modelling representation
C : adapted design with steam production
D : adapted design without steam production

In the compressor section (Figure 1), the introduction of an intermediate cooler before the recycle injection allows to reduce the energy requirement. This is suggested by the EMO approach: the stream leaving the compressor has to cooled down above the pinch point where it plays the role of the hot utility then it is mixed with the recycle below the pinch point to reach the inlet temperature of the next stage of the compressor. This allows to reduce the mechanical power consumption of the compressor and the overall MER of another 2.4%.

Another area of energy efficiency improvement is the exploitation of the purge stream. We propose to use its pressure (85 bar) by expansion through a four stages turbine. The maximisation of the mechanical power produced is based on the GCC analysis (Figure 2), which suggests introducing interstage reheaters. The heat for reheating is taken below the pinch point that defines therefore the maximum reheating temperature. When the overall purge stream is expanded to atmospheric pressure, the mechanical power recovered by this solution corresponds to 32.6% of the total work required in the compression section.

Since the purge stream contains H2 and CH4, we have chosen to use it as a fuel to satisfy the MER of the process. This is only one of the possible ways that has been adopted for demonstration purpose. The fuel gas flowrate has been determined according to the high temperature energy requirements of the reforming section. This leads to an excess of energy in the flue gas that will be valorized via combined heat and power production in the steam network. In this situation, the process is able to export electricity to the grid. The pressure levels in the steam network were defined using the approach described in Maréchal and Kalitventzeff (1996b). The mechanical power produced has been optimised, it allows to target the Minimum Cost of Energy Requirements as described in Maréchal and Kalitventzeff (1996a). The optimisation of the mechanical power production efficiency leads to the conclusion that the purge stream and the air for the combustion have to be preheated before entering in the furnace. This allows to recover the heat available below the pinch point as well as the excess of energy available in the flue gas. When CHP is used, the pinch point to take into account is not the process pinch point anymore, but the temperature of the first steam draw-off of the expansion turbine. This is explained by the fact that air preheating and combustion act as a heat pump (Maréchal and Kalitventzeff (1996c), the energy of steam is used to preheat air that produces more high pressure steam, what leads to an increase of mechanical power production. Considering expansion of the purge stream and preheating, the net mechanical power production is increased from 11122 kW to 26840 kW.

A second alternative utility system using a gas turbine has also been studied. This scheme is also suggested by the analysis of the GCC of the process. It corresponds to an efficient usage of the pressure of the purge stream. The operating pressure of the gas turbine is 10 bar, corresponding to a typical industrial gas turbine. The optimal integration of the gas turbine and the optimal integration of the steam network is computed using the EMO approach. The effects considered are the one linked with the fuel combustion and the one linked with the excess air used in the gas turbine to cool down the flue gas to the inlet temperature of the expansion turbine. The first effect corresponds to a hot stream to be cooled down, the second corresponds to a cold stream to be heated. The two effects are illustrated on figure 4.

Figure 4: EMO model of the gas turbine

Figure 5 : Valorization of purge gas energy
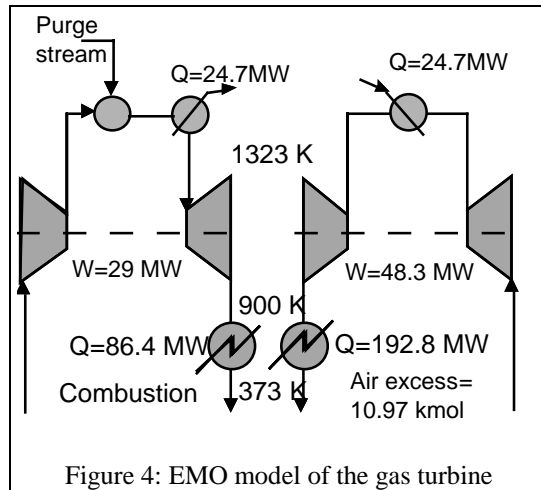
For the energy integration, we determined the optimal air flowrate required in the gas turbine, allowing possible heat exchanges with other streams of the process. In the computed optimal situation, the heat of combustion in the gas turbine is used to satisfy the needs of the reforming reactor and of the gas turbine air preheating. The air flowrate is maximised by recovering the heat of the gas turbine exhaust gas for air preheating. The final configuration is given on figure 5. When the overall purge is used in the gas turbine, the net electricity export of the process goes up to 47259 kW.

Table 1 gives the comparison of the alternative process configurations suggested by our approach. They have been computed for a daily production of 2000 metric ton of methanol. The efficiency is defined as the ratio of methanol production (kmol/h) to the methane consumption (kmol/h). If we only account for methane used as a reactant, the methane conversion to methanol is 75.2%. In order to account for the use of methane as process fuel and for net electricity generation, the efficiency definition is extended as :

$$\eta = \frac{P}{M1 + M2 - M3} \qquad (1)$$
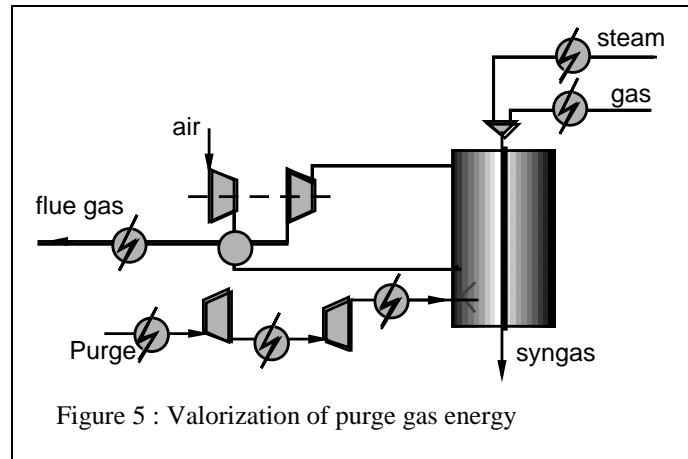
where P is the methanol production (kmol/h)

M_1 is the flowrate of CH4 used as a reactant (kmol/h);

M_2 is the flowrate of methane equivalent to the caloric value of all fuels used in the process (kmol/h);

M_3 is the equivalent flowrate of methane corresponding to electricity exported to the grid (kmol/h)

To convert the electricity exported to the grid in terms of equivalent overall methane savings, we used a conversion factor set to 14.2 kmol of CH_4/MWh. This value is derived from the average efficiency figures published by Belgian utilities (natural gas consumption per kWh in gas fired power plants).

In the reference case we consider that the energy requirements are satisfied by burning extra methane; the efficiency obtained is then 61%, considering the best integration scheme for the heat exchanger network, but neither a gas turbine nor reactor integration. This corresponds to the typical efficiency values of the current methanol processes (Westerterp 1993).

The first alternative (first line in table 1) considers that all the purge stream is used as a fuel, and extra energy is converted to electricity. The corresponding efficiency, based on equation (1), raises to 78.7%. Efficiency figures for all other alternatives are shown in table 1. When converting the benefits of the maximisation of the electricity production into an equivalent methane saving, the efficiency of the methanol process can be increased from 61% to 93.1%.

This compares well with figures published for alternative designs, where efficiency as high as 80-85% are expected (Westerterp 1993, DECHEMA 1995). However in the case we consider, higher efficiency is achieved using a classical process route.

PROPOSED PROCESS MODIFICATION

After the targeting phase, the final process

Table 1: comparison of different solutions for 2000 T/day methanol

Alternative	Net Electricity export (kW)	Efficiency η (%)
Purge combustion	11122	78.7
Purge + preheating to process pinch point	15840	80.3
Purge + preheating to LP steam level	17500	80.9
Purge + preheating+ expansion	26824	84.3
Gas turbine + expansion + reactor D	43529	91.2
Gas turbine + expansion + reactor C	47259	93.1

structure has to be defined. When the effect modelling strategy is used, not only the HEN (Heat Exchanger Network) structure must defined but also the design of the reactors, the gas turbine and the steam network. For the reforming reactor that operates at 10 bar for both sides, we suggest to split the reactor in several parallel reactors designed like the burners of a gas turbine but with the reforming tubes inside. For the synthesis reactor, configurations C and D of Figure 3 have been proposed. A careful evaluation of the reactor internal design should be performed in order to define a compact and feasible design of this reactor. The HEN and steam network system are rather complex since these have been designed to maximise the energy recovery in terms of mechanical power. The HEN includes 22 heat exchangers and a special design of the steam network and the recovery boiler is necessary.

The optimisation of the steam and heat exchanger network is out of the scope of this paper. We only wanted to illustrate the power and usefulness of the method to generate alternative flowsheets at the design stage, in order to find good candidate proposals to be later optimized.

CONCLUSIONS

The Effect Modelling and Optimisation (EMO) approach is a new modelling strategy based on the identification of the elementary effects involved in each unit of the process. Based on the results of a base case process simulation using classical approach (in our case sequential modular approach), the application of the EMO strategy allows to give some insights or orientations to be followed to optimise the energy usage in the process. The approach highlights the importance of the process pinch point and the shape of the GCC that drive process design optimisation. The application to the methanol process illustrates the energy savings that might be obtained when combined heat and power approach is used. The targeting procedure using the EMO strategy allowed to optimise the use of the purge stream as a fuel gas. This is obviously only one of the possible solutions to be compared on an economical basis with other alternatives. By concentrating the design effort during the targeting phase without having to compute the complex interactions in the heat exchangers and utility networks, the EMO targeting strategy is a very powerful tool for configurations screening. It allows to evaluate the impact of the process modifications, even in the design of the internal layout of a reactor, at a global level. It helps engineers to identify ways of process improvements and to find the best solutions according to the specific constraints and goals of the plant location.

Application of the design methodology allows to identify process modification able to increase the efficiency of a well known process design, and to achieve efficiency figures which compare with the most recent alternative designs.

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