Processes of Multi-production Products and Utilities

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Abstract: Process production of the different products should be more economical. The fact is we target that more products are being produced from raw materials. The basic primary goal is multi-production product processes, and the secondary goal is to save raw materials. During an oil crisis, the price of natural gas is too high, therefore the amount of natural gas could be reduced by 30 % by using cheaper raw materials or waste material.

This paper aims at replacing natural gas by 30 % during the methanol process using CO_2, which is separated from flue gas by using a pressure swing adsorption (PSA) column. The existing methanol production process can be enlarged by simultaneous structuring, such as selecting the optimal mass flow of both products (methanol and hydrogen), and the heat flow rate of steam production, using an NLP (nonlinear programming) model.

Optimal methanol and hydrogen conversion can take place during this operation, by applying optimal parametric data within a reformer unit (temperature = $840^{o}C$ and pressure = 8 bar), using 71% natural gas and 29% pure CO_2 separated from flue gas.

Key words: Methanol production; Hydrogen production; Flue gas, CO_2 separation; Mathematical model; Nonlinear programming

Nomenclatures
Abbreviations:
NLP   nonlinear programming
Variables:
q mass flow, kg/h
p pressure, bar
T temperature, K
Q heat flow rate, W

1. INTRODUCTION

Natural gas is a very important raw material for many substances. Natural gas consists primarily of methane, typically with 0-20% higher hydrocarbons[1, 2]. It is found in association with other hydrocarbon fuels, in coal-beds, is an important fuel source, and a major feedstock for fertilizers. Natural gas is a major feedstock for the

production of ammonia, via the Haber process, for use in fertilizer production and methanol production. Natural gas can be used to produce hydrogen, with one common method being the hydrogen reformer. Hydrogen has many applications: it is a primary feedstock for the chemical industry, an important commodity for oil refineries, and a fuel source in hydrogen vehicles[3].

Methanol is produced from natural gas, too. Methanol is an industrially important chemical, used mainly as a feedstock in the production of bulk chemicals such as formaldehyde and acetic acid. It has also been used, for example, in the manufacture of methyl tertiary-butyl ether, methyl methacrylate, and as a solvent[4]. The first commercial process for the production of methanol by the destructive distillation of wood was already operational in the 19th century. The first industrial plant producing methanol from synthesis gas was built by BASF in 1923. This process used zinc oxide/chromium oxide catalysts operating at 300 °C and 200 atm. This process, also known as high-pressure methanol, was carried out by synthesis. Later a low-pressure process ($p < 100$ atm) was developed. Today, this process is well-established in several companies, including ICI, Lurgi, and Mitsubishi (commercial technology solutions)[4].

This paper presents the replacing of natural gas by 30 % using pure CO_2, and separating hydrogen as the second product, by using NLP model.

2. PROCESS OF MULTI-PRODUCTION PRODUCTS AND STEAM

We intend to re-order the existing process so as to produce several products – primary and secondary (Fig. 1). Secondary products can be produced by separation using different absorption and adsorption methods (such as pressure swing adsorption – PSA column). Secondary products can be included within generation of different utilities, too. The ratio between primary and secondary products can be determined using different optimization methods (such as nonlinear programming – NLP model). The NLP model includes process equations, which present the process operation units, structural equations, objective function, and a real limit.
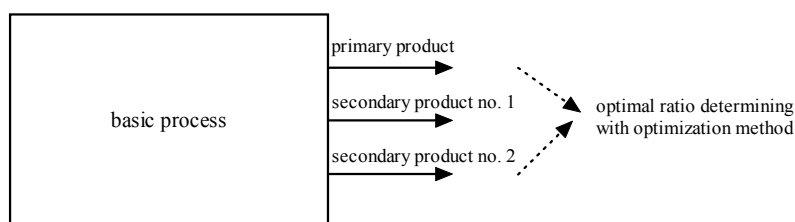

Fig. 1: Multi-production Process

3. CASE STUDY

This multi-production of an existing methanol process was tested by using an NLP model.
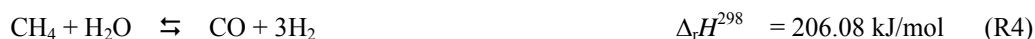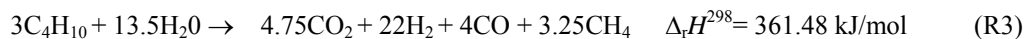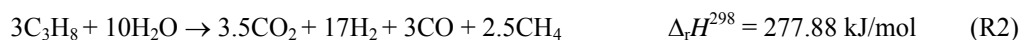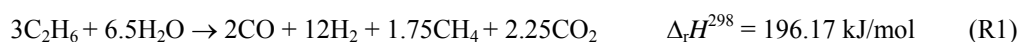
3.1 Methanol Production

This case study is based on a Lurgi methanol process[4] (Fig. 2). The methanol process is composed of three subsystems:

a. production of synthesis gas

b. production of crude methanol and

c. purification of methanol (F301, D301–D304).

The possibility of better conversion was studied regarding synthesis gas whilst retrofitting the Lurgi process for low-pressure crude methanol production (without purification) from natural gas.

Raw material (natural gas) is first desulphurized (D101) and then heated up in a steam reformer (REA-1), where synthesis gas is produced from raw material (natural gas) and steam, at 825 °C 15 bar:

$$3C_2H_6 + 6.5H_2O \rightarrow 2CO + 12H_2 + 1.75CH_4 + 2.25CO_2 \qquad \Delta_r H^{298} = 196.17 \text{ kJ/mol} \qquad (R1)$$

$$3C_3H_8 + 10H_2O \rightarrow 3.5CO_2 + 17H_2 + 3CO + 2.5CH_4 \qquad \Delta_r H^{298} = 277.88 \text{ kJ/mol} \qquad (R2)$$

$$3C_4H_{10} + 13.5H_2O \rightarrow 4.75CO_2 + 22H_2 + 4CO + 3.25CH_4 \qquad \Delta_r H^{298} = 361.48 \text{ kJ/mol} \qquad (R3)$$

$$CH_4 + H_2O \leftrightarrows CO + 3H_2 \qquad \Delta_r H^{298} = 206.08 \text{ kJ/mol} \qquad (R4)$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad\qquad \Delta_r H^{298} = -41.17 \text{ kJ/mol} \qquad (R5)$$

The hot stream of the synthesis gas is cooled in an E107 boiler, in E109, E110, E111 heat exchangers in an EA101 air cooler, and in an E112 water cooler. The condensate is expanded in flashes: F1, F2, F107 and F108. The synthesis gas is compressed in G201I and G201II two-stage compressors.
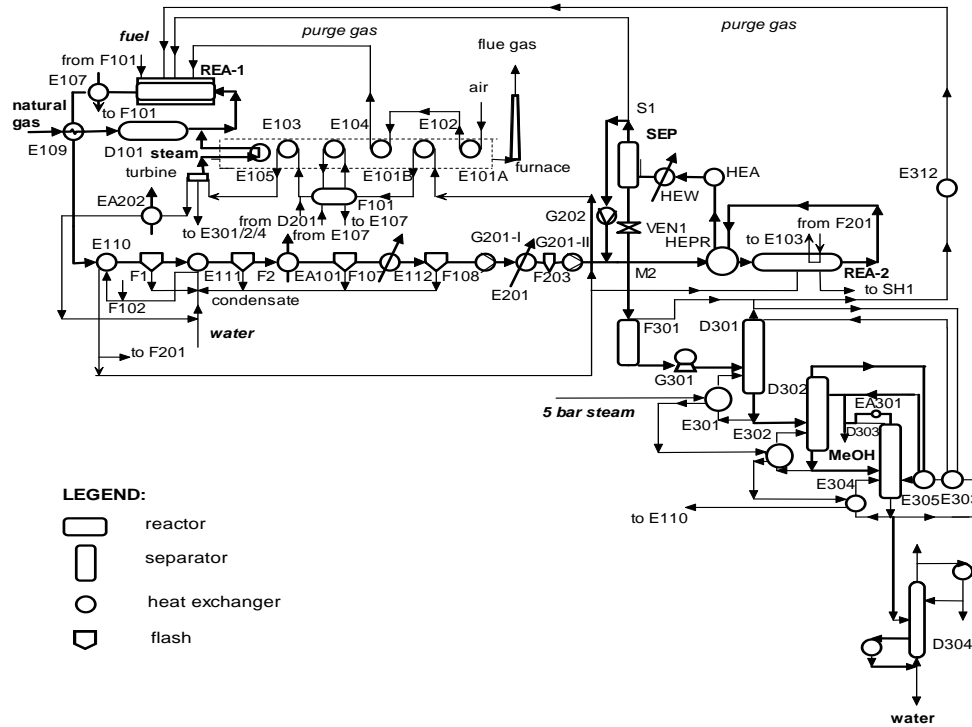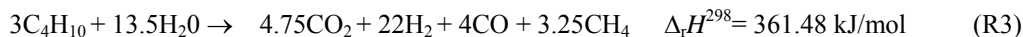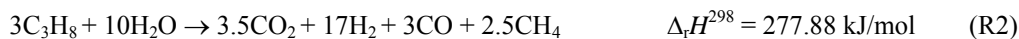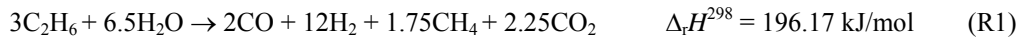

Fig. 2: Process Flow Diagram of a Low-pressure Lurgi Methanol Plant
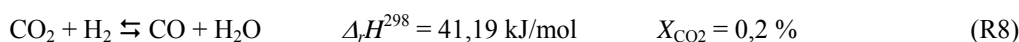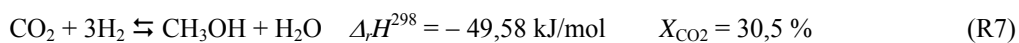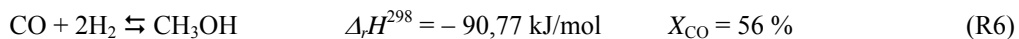
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In the second subsystem, methanol is produced by the catalytic hydrogenation of carbon monoxide and/or carbon dioxide in a REA-2 reactor using three main reactions (r = R6, R7, R8):

$$CO + 2H_2 \rightleftarrows CH_3OH \qquad \Delta_r H^{298} = -90{,}77 \text{ kJ/mol} \qquad X_{CO} = 56 \% \qquad (R6)$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \qquad \Delta_r H^{298} = -49{,}58 \text{ kJ/mol} \qquad X_{CO2} = 30{,}5 \% \qquad (R7)$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad \Delta_r H^{298} = 41{,}19 \text{ kJ/mol} \qquad X_{CO2} = 0{,}2 \% \qquad (R8)$$

The REA-2 high-pressure reactor is operated within the existing parameters and non-converted gas is recycled. The inlet stream of the reactor is heated by a process stream (HEPR).   Furthermore, the stream 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 purification includes the distillation columns (D301–D304).

Methanol production using natural gas as the raw material was simulated using an Aspen Plus simulator (with real chemical thermodynamic and selected processing units, which are very comparable to the existing material and energy flow rates)[5]. The thermodynamic properties of gases can be calculated using different methods and models. These models can estimate fugacity coefficients, enthalpies, densities, entropies, and free energies. The Grayson-Streed model of corresponding states correlation is used for synthesis gas. Fugacity coefficients, entropies and free energies can be estimated using this model. The Grayson-Streed model is a generalized method for predicting vapour-liquid equilibria in gaseous hydrocarbon and hydrogen mixtures. The thermodynamic model of component properties is very important for approaching a good simulation. The thermodynamic properties of synthesis gas were estimated by using the Grayson-Streed model with an Aspen Plus simulator, and the results are in relatively good agreement with the experimental data for an existing methanol production plant[6].

3.1.1 Retrofitted multi-production methanol process

The existing methanol process can be modified for the primary as methanol production and the secondary as hydrogen production. Before the G201-II compressor is ideal condition for the separation of 21 % available hydrogen ($q_{av,H2}$) by using an existing pressure swing adsorption (PSA), under 35 °C and 28 bar. After hydrogen separation, it is then ideal for adding a possible mass flow rate of pure CO_2 ($q_{ad,CO2}$), which could be separated from the flue gas by using a new PSA column (Fig. 3). The optimum ratio of available hydrogen separation and additional inlet of CO_2, which could replace natural gas by 30 %, may be found using an NLP model.
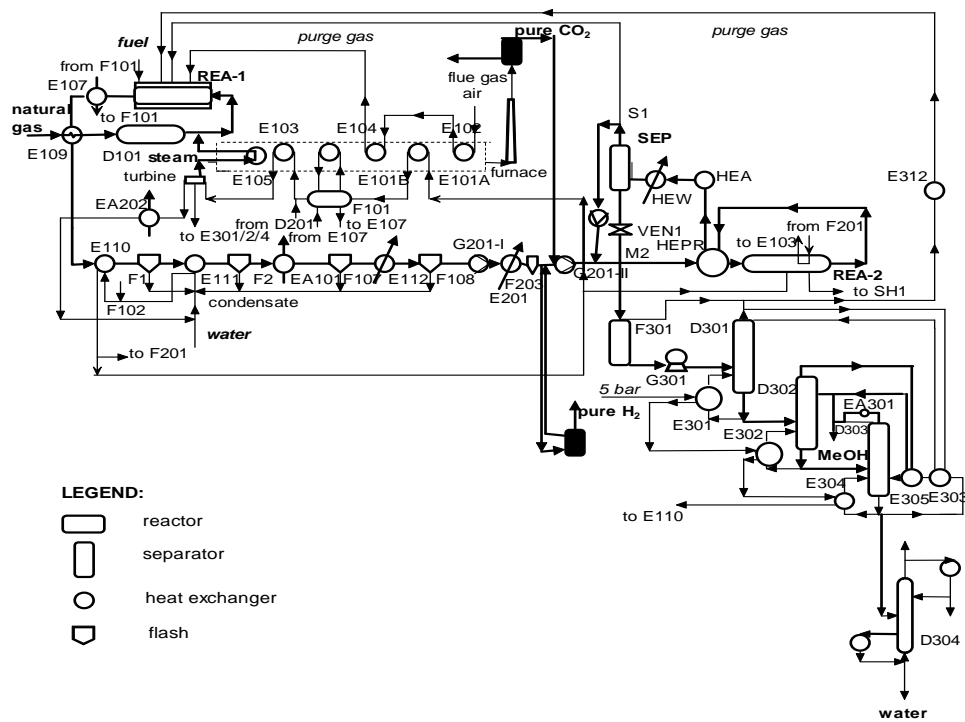

Fig. 3: Retrofitted Process Flow Diagram for Multi-production Methanol Process

Pressure Swing Adsorption (PSA) is a commonly used technology for purifying gases[7]. PSA technology was introduced commercially in the 1960's and today PSA is used extensively in the production and purification of CO_2, oxygen, nitrogen and hydrogen for industrial uses. PSA processes can be used for separating gases in a mixture because different gases tend to be strongly attracted to different solid surfaces, more or less. It operates at near ambient temperatures. PSA is the technology used to separate certain species from a gas under pressure, according to these species' molecular characteristics and affinities for an adsorbent material. Special adsorptive materials (e.g., zeolites) are used as a molecular sieve, preferentially adsorbing the undesired gases at high

pressure. PSA can separate carbon dioxide (CO_2) from flue gas. Application of the pressure swing adsorption (PSA) method was examined at 26 bar and 35 $^{\circ}$C using zeolite 13 X as adsorbent for CO_2 separation from the flue gas. PSA can separate the carbon dioxide (CO_2) from the flue gas. The existing PSA can separate the hydrogen (H_2) from synthesis gas under 28 bar and 35 $^{\circ}$C. The cleaning efficiency of the PSA column is above 50 % and reached a purity gas product of 99 % in both the cases of hydrogen and carbon dioxide separations.

3.1.2 Mathematical model for multi-production methanol process

In retrofitted methanol process can be enlarged for multi-production by using the natural gas, which can be replaced with CO_2 by 30 %. The methanol process parameters are optimized using a nonlinear programming (NLP) model[8]. The parameters in the retrofitted model of the reformer and the reactors were simultaneously optimized using the GAMS/MINOS[9]. This NLP can be solved using a reduced large-scale gradient method (e. g. MINOS). This model is non-convex, does not guarantee a global optimization solution but quickly gives 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 rates as all the streams and structures can also be varied by using it. The NLP model contains equations for structural and parametric optimization. The NLP model is formulated using a simplified process superstructure without binary, in order to determine the ratio of multi-production between methanol and hydrogen production from natural gas with 100 % capacity or lower. The lower limit is 70 % in order to obtain enough hydrogen to produce methanol under existing condition.

Methanol production using from 100 % to 70 % natural gas, and from 0 % to 30 % pure carbon dioxide was simulated using an Aspen Plus simulator.

The composition of synthesis gas has a strong effect on the composition of crude methanol mass flow. Most of the parameters' effects on material balance were studied, by using an Aspen Plus simulator to determine the material balance of the synthesis gas, the crude methanol mass flow (q_{MeOH}) depending on the mass flow of natural gas (q_{ng}) and the mass flow of added carbon dioxide ($q_{ad,CO2}$). The composition of synthesis gas has a strong effect on the composition of crude methanol mass flow (q_{MeOH}) and available hydrogen ($q_{av,H2}$).

The effects of mass flow of natural gas (q_{ng}), temperature (T), and pressure (p) on synthesis gas conversions were determined by using an Aspen Plus simulator and were modelled using equations (1— 23), and included in the NLP model.

Equation 1 presents the dependence on the composition of carbon dioxide in the synthesis gas, as a function of natural gas (q_{ng}) in the reformer:

$$q_{CO2,ng} = 0.228q_{ng} + 6708 \tag{1}$$

Equation 2 presents the dependence on the composition of carbon dioxide in the synthesis gas, as a function of temperature (T) in the reformer:

$$q_{CO2,T} = -9.267T + 7645 \tag{2}$$

Equation 3 presents the dependence on the composition of carbon dioxide in the synthesis gas, as a function of pressure (p) in the reformer:

$$q_{CO2,p} = -21.946 + 331 \tag{3}$$

The total mass flow rate of carbon dioxide (q_{CO2}) for methanol production, including added CO_2 ($q_{ad,CO2}$), is:

$$q_{CO2} = q_{CO2,ng} + q_{CO2,T} + q_{CO2,p} + q_{ad,CO2} \tag{4}$$

Equation 5 presents the dependence on the composition of carbon monoxide in the synthesis gas, as a function of natural gas (q_{ng}) in the reformer:

$$q_{CO,ng} = 1.05q_{ng} - 1543.3 \tag{5}$$

Equation 6 presents the dependence on the composition of carbon monoxide in the synthesis gas, as a function of temperature (T) in the reformer:

$$q_{CO,T} = 20T - 16500 \tag{6}$$

Equation 7 presents the dependence on the composition of carbon monoxide in the synthesis gas, as a function of pressure (p) in the reformer:

$$q_{CO,p} = -75.16p + 1130.8 \tag{7}$$

The total mass flow rate of carbon monoxide (q_{CO}) for methanol production is:

$$q_{CO} = q_{CO,ng} + q_{CO,T} + q_{CO,p} \tag{8}$$

Equation 9 presents the dependence on the composition of hydrogen in the synthesis gas, as a function of natural gas (q_{ng}) in the reformer:

$$q_{H2,ng} = 0.267q_{ng} + 892.3 \tag{9}$$

Equation 10 presents the dependence on the composition of hydrogen in the synthesis gas, as a function of temperature (T) in the reformer:

$$q_{H2,T} = 2.6T - 2145 \tag{10}$$

Equation 11 presents the dependence on the composition of hydrogen in the synthesis gas, as a function of pressure (p) in the reformer:

$$q_{H2,p} = -20.338p + 305.16 \tag{11}$$

The total mass flow rate of hydrogen (q_{H2}) is:

$$q_{H2} = q_{H2,ng} + q_{H2,T} + q_{H2,p} \tag{12}$$

The total mass flow rate of hydrogen is the sum of the needed hydrogen for the methanol's reaction ($q_{H2,R}$), and available hydrogen for purchase ($q_{H2,PUR}$) are:

$$q_{H2} = q_{H2,R} + q_{H2,PUR} \tag{13}$$

The mass flow rate of the hydrogen ($q_{H2,R}$) needed for the reaction of methanol production (conversion of reactions R6 and R7), including the ratio of the non-converted recycled gas (2.28) in reactor (REA-2) are:

$$q_{H2,R} = 2.28(q_{CO}0.56/28 + q_{CO2}0.30/44)2 \tag{14}$$

Equation 15 presents the dependence on the composition of crude methanol in the methanol reactor (REA-2), as a function of natural gas (q_{ng}):

$$q_{MeOH,ng} = 1.364q_{ng} + 2996.7 \tag{15}$$

Equation 16 presents the dependence on the composition of crude methanol in the methanol reactor (REA-2), as a function of temperature (T):

$$q_{MeOH,T} = 17.33T - 14300 \tag{16}$$

Equation 17 presents the dependence on the composition of crude methanol in the methanol reactor (REA-2), as a function of pressure (p):

$$q_{MeOH,p} = -102.7p + 1543 \tag{17}$$

Equation 18 presents the dependence on the composition of crude methanol in the methanol reactor (REA-2), as a function of added CO_2 ($q_{ad,CO2}$):

$$q_{MeOH,adCO2} = 0.736 q_{ad,CO2} - 1.5 \tag{18}$$

The total mass flow rate of crude methanol (q_{MeOH}) is:

$$q_{MeOH} = q_{MeOH,ng} + q_{MeOH,T} + q_{MeOH,p} + q_{MeOH,adCO2} \tag{19}$$

Equation 20 presents the dependence on the production of steam flow rate during the methanol process, as a function of natural gas (q_{ng}):

$$Q_{steam,ng} = 0.504 q_{ng} + 8020 \tag{20}$$

Equation 21 presents the dependence on the production of steam flow rate, as a function of temperature (T):

$$Q_{steam,T} = 0.424 T + 490 \tag{21}$$

The total steam flow rate (Q_{steam}) is:

$$Q_{steam} = Q_{steam,ng} + Q_{steam,T} \tag{22}$$

The lower temperature and pressure limits are 825 ^{o}C and 8 bar. The upper temperature and pressure limits are 840 ^{o}C and 15 bar regarding of real limits.

Tab. 1: Cost items for the Example Process.

Price of methanol, C_{MeOH}/(EUR/kg):   0.15
Price of hydrogen, C_{H2}/(EUR/kg):   1.
Price of HPsteam, C_{steam}/(EUR/kWa):   106
Cost of natural gas, C_{ng}/(EUR/kg): 0.33
Cost of   separating, C_{sep}/(EUR/kg): 0.05
Cost of additional heating, C_{heat}/(EUR/K a): 3 000
Operating hours, O_{time}/(h/a): 8000

The objective function (eq. 23) of the NLP model maximized the additional annual profit of the retrofit and included income and depreciation (Table 1). Incomes include the saving of natural gas ($q_{ng,ex} - q_{ng}$), the additional methanol ($q_{MeOH} - q_{MeOH,ex}$), hydrogen ($q_{av,H2}$), and steam ($Q_{steam} - Q_{steam,ex}$) productions, depending on the natural gas (q_{ng}), pressure (p), and temperature (T) functions. Temperature and pressure could have an affect on additional methanol and hydrogen productions. The existing methanol mass flow ($q_{MeOH,ex}$) from 100 % existing natural gas ($q_{ng,ex} = 10500 kg/h$) is 16 150 kg/h under existing unchanged process conditions. The existing steam heat flow from 100 % natural gas ($Q_{steam,ex}$) is 13 300 kW under existing unchanged process conditions. Depreciation includes the cost of additional heating in the reformer if the temperature is higher than the existing temperature ($T_{ex} = 825$ ^{o}C), and the separating of carbon dioxide from flue gas ($q_{ad,CO2}$) using the PSA column. Operating time (O_{time}) is 8000 h/a.

Maximal additional annual profit (V_{max}) for retrofit:

$$V_{max} = (q_{ng,ex} - q_{ng}) C_{ng} O_{time} + (q_{MeOH} - q_{MeOH,ex}) C_{MeOH} O_{time} + q_{H2} C_{H2} O_{time}$$
$$+ (Q_{steam} - Q_{steam,ex}) C_{steam} - q_{ad,CO2} C_{sep} O_{time} - (T - 825) C_{heat} \tag{23}$$

3.1.3 Optimal results of the multi-production methanol process

Retrofitting an existing plant focuses on the general mathematical NLP method including many result assumptions by the Aspen Plus simulator.

A retrofitted methanol production process would produce:

a. methanol with a higher mass flow of 250 kg/h (q_{MeOH}=16400 kg/h), compared with the existing production,

b. hydrogen of 640 kg/h, this is the total available hydrogen, which cannot be used for methanol reaction

by using 71% natural gas (q_{ng}=7500 kg/h), and 29 % pure CO_2 ($q_{ad,CO2}$=3000 kg/h) separated from flue gas, selecting optimal parametric data within a reformer unit (temperature = 840 ^{o}C and pressure = 8 bar).

The optimal condition within the reformer can increase the conversion of synthesis gas, especially hydrogen mass flow available and the needed mass flow for crude methanol production. The selected mass flow of natural gas (71%) is close to the minimum 70%, because of the high price of gas, and it is cheaper to add pure CO_2 separated from the flue gas. Steam production (Q_{steam}=12650 kW) was reduced by 5%. The profit was 7.2 MEUR/a depending on the optimized conditions, taking into account the 40% contingency costs.

Individual graphical curves showing the effects of (Fig. 4):

a. natural gas (1; using eq. 15),

b. natural gas and added CO_2 (2; using eqs. 15 and 18),

c. natural gas, added CO_2 and the optimum conditions (3; using eqs. 15, 16, 17 and 18).

If the reconstruction of the basic restriction is placed close to the existing production and where it intersects the selected curve, which takes into account the various constraints (1, 2 or 3), an optimal reconstruction can be obtained of the ratio of natural gas and the added CO_2.
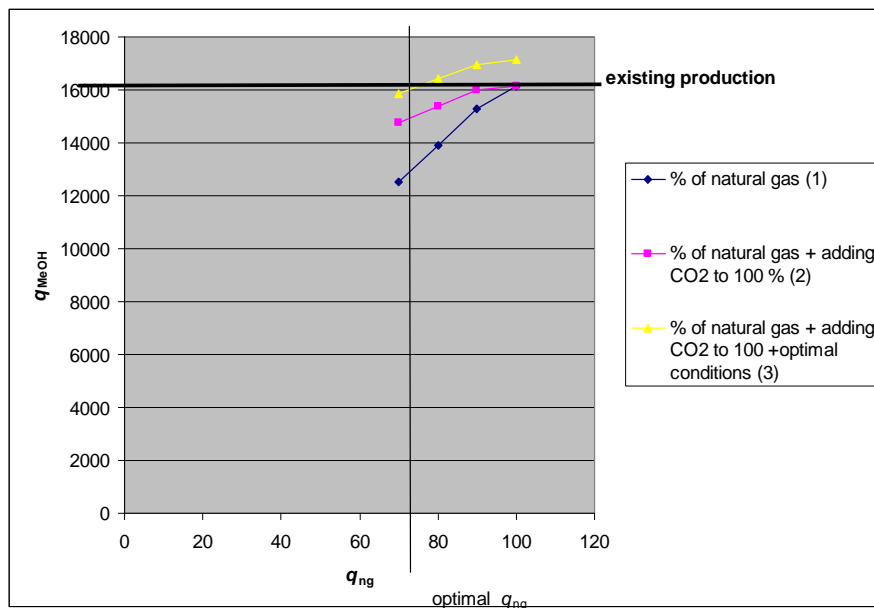

Fig. 4: Graphical Presentation of Any Reconstructions

4. CONCLUSIONS

This paper aimed at selecting different raw materials using – the rationing of natural gas and adding pure CO_2 by using an NLP (nonlinear programming) model, whilst considering the usage of a more favourable ratio of raw materials for a multi-production methanol process, which could produce hydrogen as the secondary product.

The NLP model contains equations which enable optimal methanol, hydrogen, and steam productions by using simultaneous parametric optimization and the rationing of raw materials. Optimal synthesis gas conversion could take place by an operation using the optimal parametric data within a reformer unit and within a methanol reactor using a ratio of raw materials. Mathematical problems could include equations which represent synthesis gas composition, adding pure CO_2, which is separated using a PSA column, and crude methanol, available hydrogen,

and steam productions. The primary objective of retrofit is usage ratio of raw materials with a minimum of additional costs, and thus maximizing the production of methanol, hydrogen, and steam. The optimal ratio of raw material was 71 % of natural gas and 29 % of pure carbon monoxide. The optimal production of methanol and hydrogen from 71 % natural gas and 29 % pure CO_2 was 1.5 % higher (16 400 kg/h) under optimal parameters (temperature=840 ^{o}C and pressure=8 bar) than under existing parameters within the reformer. Adding pure carbon monoxide can be more favorable under the same optimal conditions, because the price of natural gas is too high, and thus reduce emissions. The profit was 7.2 MEUR/a depending on the optimized conditions, taking into account the 40% contingency costs.

REFERENCES

[1]   Luis, F. H. Ayala, Alp D., & Al-Timimy, M. (2009). Intelligent design and selection of natural gas two-phase separators. *Journal of Natural Gas Science and Engineering, 1* (3), 84–94.

[2]   Barros Zárante P. H, & Ricardo Sodré J. (2009). Evaluating carbon emissions reduction by use of natural gas as engine fuel. *Journal of Natural Gas Science and Engineering, 1* (6), 216–220.

[3]   Carbo, P., & Migliardini, F. (2009). Natural gas and biofuel as feedstock for hydrogen production on Ni catalysts. *Journal of Natural Gas Chemistry 18* (1), 9–19.

[4]   McKetta, J. J., & Cunningham, W.A. (1985). Encyclopaedia of chemical processing and design (v.29, pp. 418–474). New York: Marcel Dekker.

[5]   Aspen Technology (2002). ASPEN PLUS User Manual Release 11.1, Aspen Technology Inc., Cambridge, MA 02139, USA.

[6]   Kovač Kralj A., Glavič, P., & Kravanja, Z. (2000). Retrofit of complex and energy intensive processes   II: stepwise simultaneous superstructural approach. *Comput. chem. Engng 24* (1), 125–138.

[7]   Kovač Kralj A., & Glavič P. (2007). H_2 separation and use in fuel cells and CO_2 separation and reuse as a reactant in the existing methanol process. *Energy fuels 21* (5), 2892–2899.

[8]   Biegler L. T., Grossmann I. E., & Westerberg A. W. (1997). *Systematic methods of chemical process design, Prentice Hall* (pp.1–408). New Jersey: Upper Saddle River.

[9]   Brooke A., Kendrick D., & Meeraus A. (1992). *GAMS: a user's guide*. Palo Alto: Scientific Press.