OPTIMIZATION OF SYNTHESIS GAS (AUTOTHERMAL) REACTOR IN METHANOL PRODUCTION PROCESS USING NATURAL GAS AS FEED STOCK

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ABSTRACT: Optimization modeling and simulation of the autothermal reactor in the methanol production process was effectively done using the quasi –Newton scheme of optimization in Aspen Hysys 2006.5. The primary variables selected for this modeling were heat flow value of the following: Steam1;steam2; coolant1; coolant2; coolant3. After running the process optimization simulation, total cost was minimized from $1365.26 to $1266.754 while the net revenue, which is the profit was maximized from $60978 to $61077.3, tallying with our optimization goal which is; maximizing reactor profit while minimizing the reactor cost.

KEYWORDS: Autothermal, Optimization, Reactor, Modeling, Aspen Hysys, Methanol.

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INTRODUCTION

In the 1960's and 1970's Natural gas used to be continually flared in Texas and Saudi Arabia, but in more recent years, Russia and Nigeria flare the highest amount of Natural gas. Flaring Natural gas has pumped out about 110 million metric tonnes of carbon dioxide to the atmosphere each year, about 0.5% of the World's Carbon dioxide emissions(1). The act of gas flaring has reduced due to the potential energy use/commercialization of the associated gas (AG) and has led more oil extracting companies to devise means to trap and channel the gas for energy. Gas flaring has also reduced due to more awareness of the significant health and environmental effects it produces as well as because the high volume of carbon dioxide emitted during flaring is a major driver of Climate Change(2).

In Nigeria, burning off the associated gas (AG) has been illegal since 1984 and the Nigerian government has set up several deadlines to end the practice, but Gas flaring continues till this day. Some reductions have actually been seen in recent times in the volume of Gas Flares and documented by the Government but analysts say this reduction has been has a consequence of militancy in the oil producing Niger Delta region of Nigeria, which halved oil production and subsequently the flaring(4).

Natural gas consist of 95% methane, and instead of being flared, can serve as a very good source of raw material in the production of methanol. Discovered in the mid 1800's, methanol (also known as wood alcohol or methyl alcohol) is the simplest form of alcohol which is a light, colorless and flammable liquid with a distinctive odor which is similar to that of ethanol. Methanol burns with a colorless flame and is a liquid at normal temperature which is why it is used as an anti-freeze, solvent, fuel as well as a denaturant. Since its discovery, Methanol has been put to use in a lot of applications.

During the 1970's, in the event of the world oil crisis, methanol received a lot of attention as a motor fuel in the United States but the demand soon came down when the prices for it went up a couple of years later. Today the most expansive use of Methanol is in the chemical industry where it is being used to make other chemicals such as plastics, paints and explosives. Apart from this, it is also being used in other parts of the world to yield a form of biodiesel(5). Methanol is also used as an anti-freeze in pipelines and windshield washer fluids in vehicles in the winter. The upcoming application for methanol is in the manufacturing of fuel cells with many small versions of the fuel cell already available today(6,7). Methanol is also the choice of fuel for many hikers, because of its ability to burn well from an unpressurized container.

Methanol Production Technology

All commercial methanol technologies feature three process sections and a utility section as listed below:

1. Synthesis gas preparation (reforming)
2. Methanol synthesis
3. Methanol distillation and purification
4. Utilities

In the design of a methanol plant the three process sections may be considered independently, and the technology may be selected and optimized separately for each section. The normal criteria for the selection of technology are capital cost and plant efficiency. The synthesis gas preparation and compression typically accounts for about 60% of the investment, the methanol synthesis accounts for 10%, methanol distillation and purification accounts for another 10% and utilities account for the remaining 20% (8,9). Almost all energy and cost is consumed in the synthesis gas preparation process section. Therefore, the selection of reforming technology is of paramount importance, regardless of the site.

Methanol synthesis gas is characterized by the stoichiometric ratio $(H_2 - CO_2) / (CO + CO_2)$, often referred to as the module M. A module of 2 defines a stoichiometric synthesis gas for formation of methanol. Other important properties of the synthesis gas are the CO to CO_2 ratio and the concentration of inerts. A high CO to CO_2 ratio will increase the reaction rate and the achievable per pass conversion(10).

METHODOLOGY

Autothermal reforming combines the thermal effects of the oxidation and SR reactions by feeding the fuel, water and air together into the reactor. The thermal energy generated from oxidation is absorbed by SR (steam reforming) and hence the overall temperature is lower. This is favorable for the water-gas shift reaction which consumes carbon monoxide and produces more hydrogen. Hence, the autothermal reactor is more compact and practical for use in the methanol production process(11}.

It was desired to construct a simulation of a methane autothermal reforming system to identify potential design issues and obtain a preliminary estimate of the expected system efficiency. Significant operating conditions could then be identified, and their effect on the overall system performance or efficiency could be evaluated. Therefore, the objective of this study is to model and simulate a methane autothermal system for methanol production process using Aspen HYSYS 2006.5 and can be used to guide the design of an autothermal reformer.

This chapter describes the process and steady-state simulation of the methane autothermal system for methanol production process. Simulated ATR operating parameters

- **CHEMICAL REACTION SCHEME OF ATR**

The fuel gas processor is simplified to a reformer, three water gas shift reactors and a preferential oxidation reactor for the modeling purpose. The model includes detailed reactions associated with total oxidation reforming (TOR), partial oxidation reforming (POR) and steam reforming (SR). The detailed analysis of chemical reactions in these processes to determine the reaction scheme for ATR has been presented elsewhere.

ATR sometimes referred to as oxy-steam reforming, combines the effects of both the exothermic POR and the endothermic SR by feeding the fuel, oxidant, and water together into the reaction vessel normally containing a nickel catalyst bed. In the catalytic process (12), the catalyst can be tailored to control the reaction pathways, namely, the relative rates of POR and SR reactions, thereby resulting in a controlled product yield and a lower-temperature process. The reforming temperature and product composition are affected by the Air/CH_4 and H_2O/CH_4 molar ratios in the feed, CH_4 inlet flow rate, and CH_4 inlet temperature.

ATR for methane, the oxidation reactions involve the following: (13)

$CH_4 + 2O_2 = CO_2 + 2H_2O$ ΔH298 = -8.0e5 kJ/kgmole Conversion (%) = 70

(1)

$CH_4 + O_2 = CO_2 + 2H_2$ ΔH298 = -3.2e5 kJ/kgmole Conversion (%) = 10

(2)

$CH_4 + 1/2O_2 = CO + 2H_2$ ΔH298 = -3.6e4 kJ/kgmole Conversion (%) = 20

(3)

and methane may react with steam by SR and Water Gas Shift (WGS) reactions:

$CH_4 + H_2O = CO + 3H_2$ ΔH_{298} = +2.1e5 kJ/kgmole Conversion (%) = 35

(4)

$CH_4 + 2H_2O = CO_2 + 4H_2$ ΔH_{298} = +1.6e5 kJ/kgmole Conversion (%) = 65

(5)

$CO + H_2O \leftrightarrow CO_2 + H_2$ ΔH_{298} = -4.2e4 kJ/kgmole (6)

In order to reduce the CO concentration out of the LTS, the preferential oxidation reaction (PrOx) was performed.

$CO + 1/2O_2 = CO_2$ ΔH_{298} = -2.8e5 kJ/kgmole Conversion (%) = 50

(7)

$H_2 + 1/2O_2 = H_2O$ $\Delta H_{298} = -2.4e5$ kJ/kgmole Conversion (%) = 50

(8)

Thus, the model takes into account eight reactions (1)-(8) and seven gas species, i.e., methane (CH_4), oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), water (H_2O), hydrogen (H_2), and nitrogen (N_2).

- **SIMULATION DEVELOPMENT:**

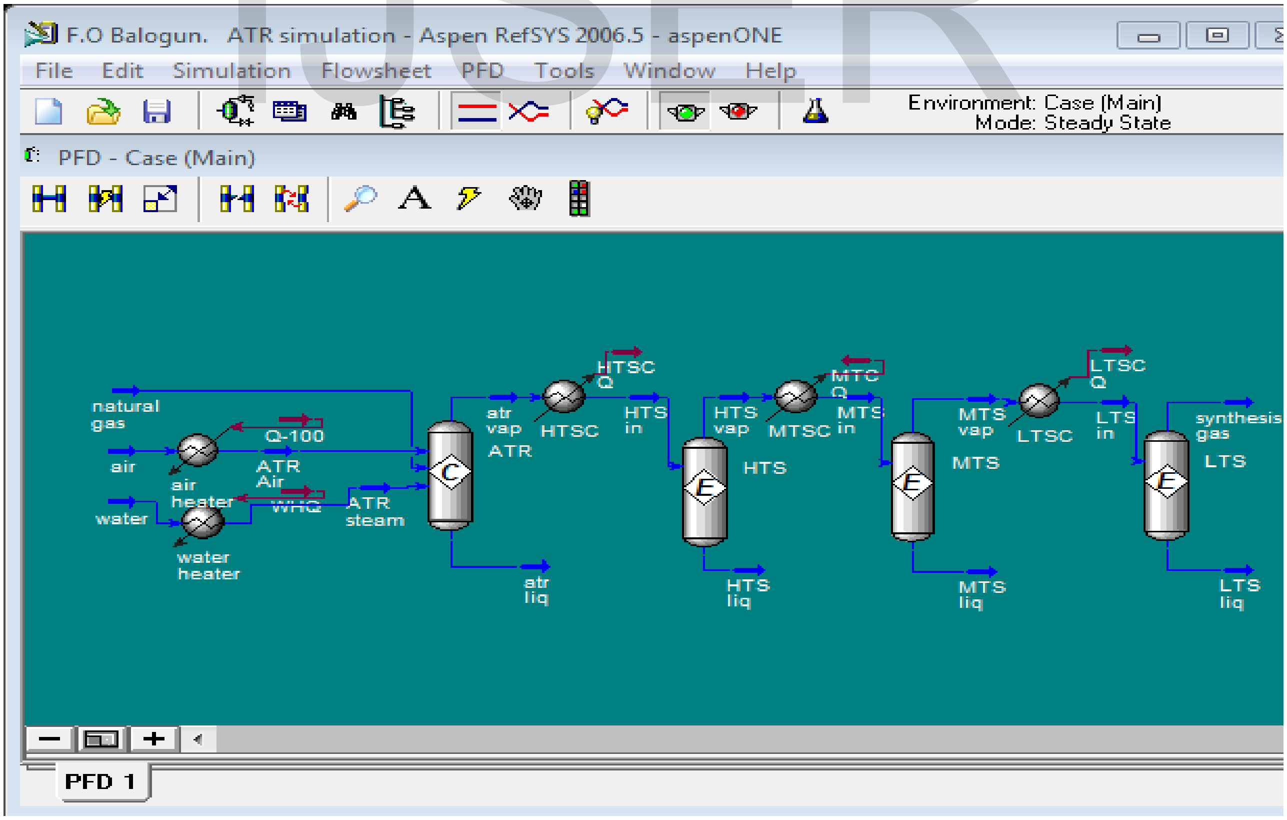


Fig 1: Aspen HYSYS 2006.5 simulation program

Aspen HYSYS 2006.5 simulation program has been utilized for simulation studies. Mass and energy balances have been established for all cases. The Peng-Robinson equations of state were used to calculate the stream physical and transport properties. The autothermal reforming of methane developed using HYSYS 2006.5 is shown in Figure below

SIMULATION OF THE AUTOTHERMAL REFORMER:

To operate the autothermal reformer, the methane and air are first fed to the reformer for combustion to heat up the catalyst of the reformer. When the catalyst temperature reaches about 300^{o}C, at which the autothermal reaction can be self-activated (known as light off), the predetermined mixture of methane, air, and water is fed to the reformer (14). The aim is to convert as much as the methane into hydrogen gas at acceptable yields in an efficient manner while decreasing CO formation. A considerably low steam carbon S/C ratio (0.6) and air to fuel (A/F) ratio which is changed between 2.5 and 3.5. In brief, this model takes into account five principal reactions (Eqs. (1)-(5)) and six gas species including methane (CH_4), oxygen (O_2), carbon dioxide (CO_2), water (H_2O), carbon monoxide (CO), and hydrogen (H_2) in chemical kinetics. Nitrogen (N_2) present in inlet air is considered as a diluent, which affects only the gas property (15). Since the stoichiometry of all the reactions and the conversion of the base component are known, the reformer was set up as a conversion reactor. By using conversion reactor, HYSYS will calculate the composition of the outlet stream.

SIMULATION OF WATER GAS SHIFT REACTOR:

The CO content can be reduced to about 0.5% by reacting it with water at lower temperatures to produce additional hydrogen according to the WGS reaction (Eq. 6). Commercial methanol plants generally perform the WGS in two stages: (i) High-temperature shift at 300-450^{o}C using a Fe-chrome oxide catalyst, and (ii) low-temperature shift at 160-270^{o}C using copper–zinc oxide [16]. Heat exchangers are required between shift reactors to provide cooling, and the conversion in an adiabatic reactor is limited because the reaction is exothermic and the temperature increases as the reaction proceeds (17). In this study, WGS reactors are modeled using equilibrium reactor. By using equilibrium reactor, HYSYS will determine the composition of the outlet stream given the stoichiometry of all reactions occurring and the value of equilibrium constant (or the temperature dependent parameters that govern the equilibrium constant) for each reaction.

RESULTS AND DISCUSSION OF RESULTS

From Eqs. (1-6) the overall reaction is obtained as below

$$5CH_4 + 3.5O_2 + 3H_2O = 3CO_2 + 2CO + 2H_2O \qquad \text{Eqn (9)}$$

With a basis of 100 kgmole/hr of n-methane feed molar flow rate, the calculated feed water using stoichiometry ratio is 60kgmol/h while the air flow rate is determined by:

$$\text{Air molar flow rate in kgmole/hr} = \frac{\text{moles of oxygen needed}}{\text{mole fraction of oxygen in Air}} \times 100\text{kgmol/hr}$$

Thus, air molar flow needed was 330 kgmole/hr.

➢ Base case simulation validation

Figure 2 illustrates the conversion of methane in the ATR reactor in Aspen HYSYS simulator environment. Raw materials, n-methane, water (steam) and air were channeled to the ATR reactor by heating them to 100°C. The composition of methane and water were pure while the air was composed of 0.21 mole fraction of oxygen and 0.79 mole fraction of nitrogen

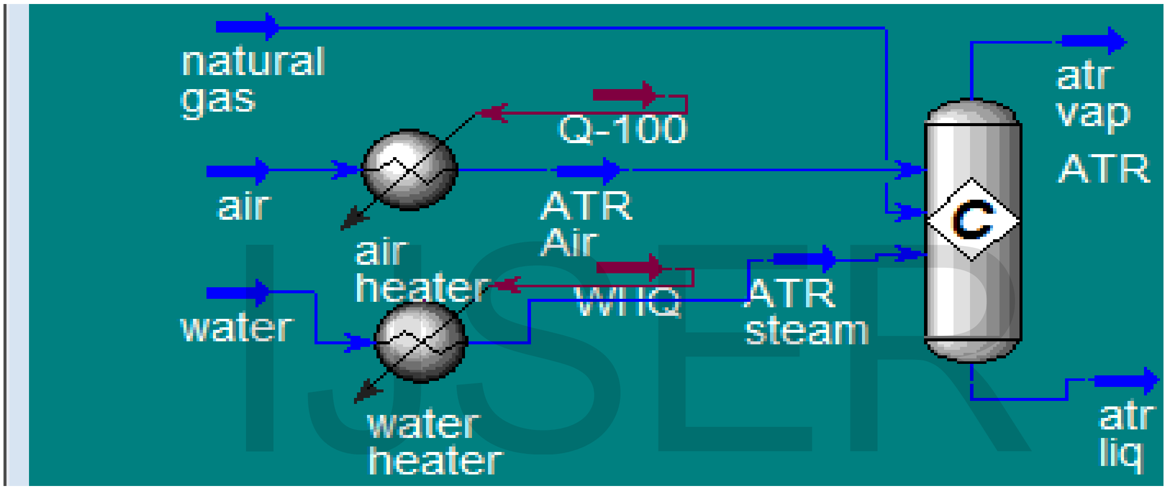


Figure 2. Base case simulation model

Table 1 shows the differences between output mole fractions of simulated case and calculated case. Whereby, the calculated case was obtained from the overall stoichiometric reactions as shown in reaction 9. At inputs flow rates of 330kgmole/h for air and 60kgmole/h steam, the errors of ATR output components mole fractions were minimum.

These results indicate that the base case simulation developed using Aspen HYSYS 2006.5 was valid and can be considered as a real plant for further analysis (18).

Table 1: Validation of base case simulation.

Components	Input flow rate	Output mole fraction

	(kgmole/hr)	Calculated	Simulated	Error
Methane	100	0.000	0.000	0
H_2O	60	0.065	0.055	0.010
CO	0	0.065	0.058	0.007
CO_2	0	0.097	0.103	0.006
H_2	0	0.355	0.363	0.008
O_2	70	0.000	0.000	0
N_2	260	0.419	0.420	0.001

Table 2 below shows the mole fractions of all components in the effluent of all the reactors involved in the simulation.

	CH_4	O_2	H_20	CO	CO_2	H_2	N_2
ATR	0.000	0.000	0.056	0.058	0.103	0.363	0.420
HTS	0.000	0.000	0.054	0.056	0.105	0.365	0.420
MTS	0.000	0.000	0.037	0.039	0.122	0.382	0.420
LTS	0.000	0.000	0.007	0.009	0.152	0.412	0.420

In the following, the results obtained for an autothermal reforming of methane system which is shown in Figure 2 are presented. With the developed system models which are implemented in the HYSYS 2006.5 process simulator, effluents from all reactors are simulated.

Table 1 shows the molar fractions of all components in the effluent of all reactors in the fuel gas processor system. In this model, the air to fuel ratio is set to 3.3 and the steam to fuel ratio is set to 0.6. In these conditions, 100% methane is converted to produce 36.3% hydrogen, 10.3% CO_2 and 5.8% CO. Also, under these conditions, oxygen is 100% consumed. As we know, WGS reaction will convert CO into CO_2 and hydrogen with the existence of steam. Therefore, the percentage of CO is decreasing from 5.8% to 0.1%, while the percentage of CO_2 and hydrogen is increasing from 10.3% to 15.2% and from 36.3% to 41.2%, respectively. In the same time, the percentage of steam is decreasing from 5.6% to 0.7%.

TEMPERATURE PROFILE OF FUEL PROCESSOR SYSTEM

The temperature profile of the fuel processor is illustrated in Figure 3. With 3.3 of A/F and 0.6 of W/F ratios, the outlet temperature of ATR reactor is about 834.2^{o}C which is higher than light-off temperature (300^{o}C) where the autothermal reaction can be self-activated (18,19).

The effluent is then cooled to 400^{o}C, 300^{o}C, 100^{o}C by passing it through hot temperature shift cooler (HTSC), mid temperature shift cooler (MTSC), low temperature shift cooler (LTSC) respectively and must be lower than outlet temperature of autothermal reformer (ATR), (HTS), MTS and LTS to prevent reversible reaction happened in Eq. (6). In the HTS, the inlet temperature is 400^{o}C, whereas the outlet temperature is about 402^{o}C. The slightly increased in the outlet temperature is due to the exothermic nature of WGS reaction. The same profile is shown by MTS and LTS.

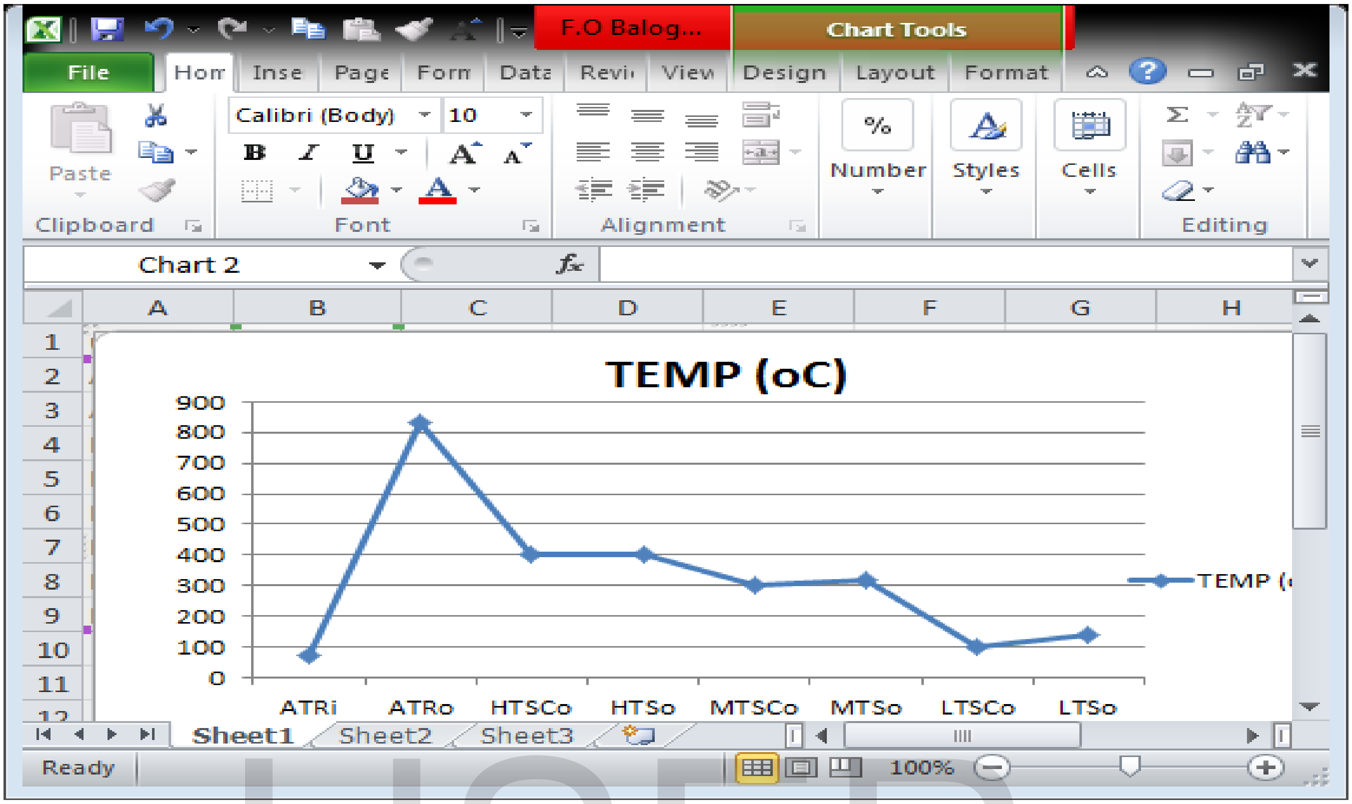


FIG. 3. The temperature profile of the fuel processor

PROCESS OPTIMIZATION:

Objective function is the function to be maximized or minimized and in this case, maximizing the synthesis gas yield and maximizing the reactor profit while minimizing the reactor cost by minimizing energy consumption are the optimization goals for this work. This is effectively done using Aspen Hysys 2006.5 optimizer (20,21).

In configuring the Aspen Hysys 2006.5 optimizer, the primary variables, which are variables whose values are manipulated in order to minimize or maximize the objective functions, are selected and entered into the optimizer. Below are the primary variables selected for this modeling; (22)

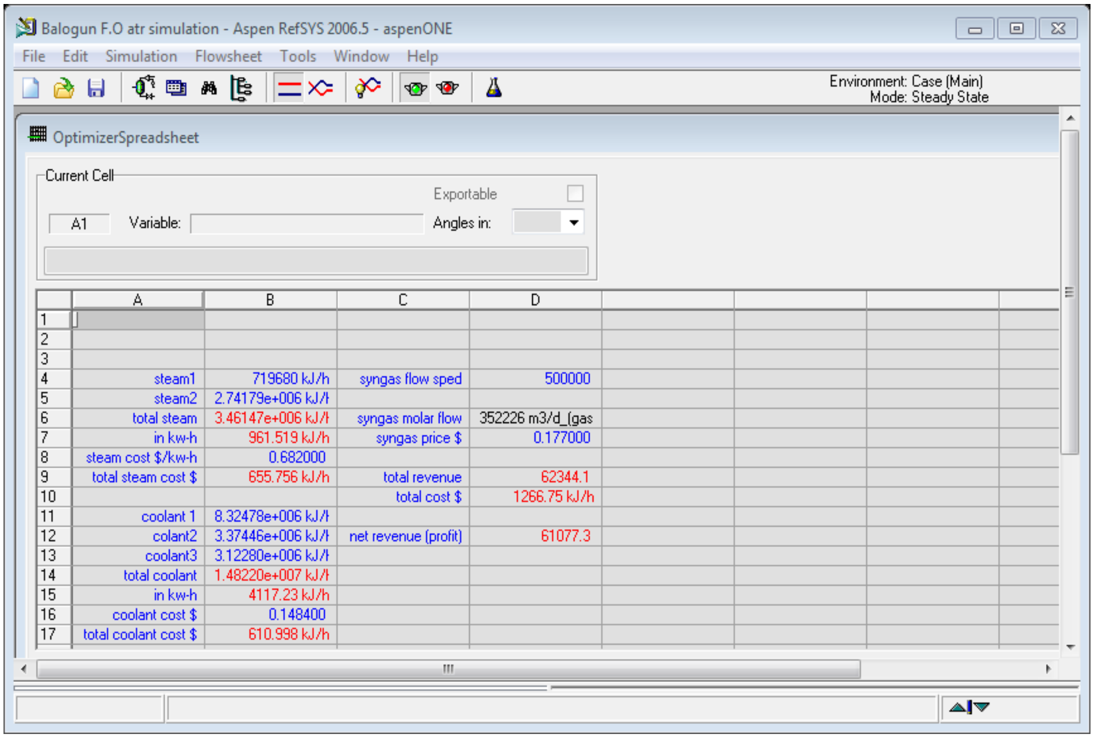
- Heat flow for stream1

- Heat flow for stream2
- Heat flow for coolant1
- Heat flow for coolant2
- Heat flow for coolant3

The process optimization was obtained using Aspen Hysys optimizer spreadsheet. The figure 4 below shows the process value before the process optimization

		Syngas flow spec	500,000
Total steam (steam 1 &2)	3.5406e+006	Syngas molar flow	35226m3/d-(gas)
In kw-h	983.5	Syngas price $	0.17700/m3-gas
Steam cost $/kw-h	0.682		
Total steam cost $	670.747	Total revenue $	62344.1
Total coolant (coolant 1 & 2)	1.68457e+007	Total cost $	1365.26
In kw-h	4680	Net revenue (profit)$	60978.8
Coolant cost $	0.148400		
Total coolant cost $	694.512		

The figure 4 below shows the process value before the process optimization



Environment: Case (Main)
Mode: Steady State

A1 Variable:

	A	B	C	D
1				
2				
3				
4	steam1	719680 kJ/h	syngas flow sped	500000
5	steam2	2.74179e+006 kJ/h		
6	total steam	3.46147e+006 kJ/h	syngas molar flow	352226 m3/d_(gas
7	in kw-h	961.519 kJ/h	syngas price $	0.177000
8	steam cost $/kw-h	0.682000		
9	total steam cost $	655.756 kJ/h	total revenue	62344.1
10			total cost $	1266.75 kJ/h
11	coolant 1	8.32478e+006 kJ/h		
12	colant2	3.37446e+006 kJ/h	net revenue (profit)	61077.3
13	coolant3	3.12280e+006 kJ/h		
14	total coolant	1.48220e+007 kJ/h		
15	in kw-h	4117.23 kJ/h		
16	coolant cost $	0.148400		
17	total coolant cost $	610.998 kJ/h		

FIG.4. **The result of the optimized process using the quasi-Newton method of optimization in Aspen hysys.**

From the figure above, we can deduce the following:

	Before optimization	After optimization
Total steam cost $	670.747	655.756
Total coolant cost $	694.512	610.998
Total cost $	1365.26	1266.754
Total revenue $	62344.1	62344.1
Net revenue (profit) $	60978.8	61077.3

CONCLUSION

This work has justified the optimization of an autothermal reactor in the production of methanol using natural gas as feed stock. The key gains of the work are: maximizing the reactor profit while minimizing the reactor cost and minimizing energy consumption. The total cost (coolant + steam) is minimized from \$1365.26 to \$1266.75, and also net revenue, which is the profit, is maximized from \$60978.8 to \$61077.3. The optimization modeling was done using the quasi-Newton optimization scheme in Aspen Hysys 2006.5. In future works, it is recommended to study and integrate the following aspects:

a. A real time dynamic simulation to investigate the dynamic behavior of the methanol autothermal reactor

b. Control structure design for better operability.

c. Energy integration basis: Achievement of a high efficiency fuel processor system requires very good energy integration. A good modeling of heat exchangers can further increase the efficiency of the methanol processor system as steam is required for the autothermal reformer.

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