

# Process Design of a Novel Low Temperature Methanol Synthesis Process Using an Air-blown Autothermal Reformer

Christian Ahoba-Sam, Lars Erik Øi, Klaus-Joachim Jens

Department of and Process, Energy and Environmental Technology, University College of Southeast Norway,  
Norway  
lars.oi@usn.no

## Abstract

Methanol (MeOH) synthesis at low temperature (100 °C) presents an opportunity for full syngas conversion per pass. This presents a cheaper alternative for MeOH synthesis using an air-blown autothermal reformer (ATR) rather than the conventional high temperature (>250 °C) MeOH synthesis approach which requires an expensive cryogenic O<sub>2</sub>-blown ATR. The aim of this work was to use the process simulation program Aspen HYSYS to simulate and optimize the reactor conditions for a complete MeOH process design using an air-blown ATR. Our results revealed that, while syngas produced from 'normal' air-blown ATR (syngas composition 0.20CO:0.40H<sub>2</sub>:0.39N<sub>2</sub>) required 100 bar to obtain full conversion per pass, syngas produced from enriched air-blown ATR (syngas composition 0.31CO:0.62H<sub>2</sub>:0.07 N<sub>2</sub>) required 60 bar total syngas pressure to achieve the same. Even though the energy generated in both processes was enough to cover the heating demand in the total process with surplus, the enriched air-blown system provides a better energy recovery if the surplus energy is not used for extra power generation. The total process energy demand due to compression was estimated to be 2270 and 983 MJ/ton MeOH product for the normal air-blown and enriched air-blown systems respectively. A process design was proposed based on the optimized conditions for the enriched air-blown process.

*Keywords: Air-blown reformer, syngas, methanol, low temperature, simulation, Aspen HYSYS*

## 1 Introduction

Methanol (MeOH) is a multi-purpose molecule widely used as a base chemical, and for storage of energy and CO<sub>2</sub> (Olah, 2005). MeOH can be used as a fuel blend or directly converted to valuable hydrocarbons such as gasoline over acidic microporous materials (Olsbye et al., 2012), thereby providing an alternative source of petrochemical feedstock used today.

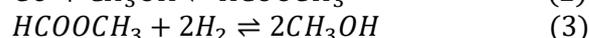
The current technology for MeOH synthesis is based on conversion of syngas and operates around 250-300 °C and 50-100 bar (Hansen & Højlund Nielsen, 2008). While this technology is highly optimized, the relatively high operating temperature limits conversion to barely 20 % per pass due to thermodynamics of the

exothermic MeOH synthesis reaction (Equation (1)). As a result, the current process requires several recycling steps to optimize production (Lange, 2001).

Furthermore, the low conversion per pass of this process requires the use of a rather 'pure' syngas other than a N<sub>2</sub>-diluted syngas for the MeOH synthesis. Such pure syngas production alone accounts for more than half of the total operation and capital cost in current methanol processes (Marchionna et al., 1998). This is due to the use of expensive cryogenic O<sub>2</sub> for partial oxidation of hydrocarbons. The lowest cost of syngas production is by the use of either an ordinary air or an O<sub>2</sub> enriched air rather than a cryogenic O<sub>2</sub>-blown autothermal reformer (ATR) (Hansen & Højlund Nielsen, 2008). The highly exothermic syngas conversion to MeOH requires a relatively low temperature to achieve a full conversion per pass. Hence, such a low temperature process will allow for the use of N<sub>2</sub>-diluted syngas for MeOH production, with reduced capital and operation cost as there will be no need for recycling.



Alternatively, a low temperature MeOH synthesis (LTMS) process which proceeds rapidly in a liquid medium at about 100 °C presents the possibility for full syngas conversion per pass (Christiansen, 1919). The LTMS process is known to occur in two steps (Equations (2) and (3)), via a methyl formate intermediate (Ohyama & Kishida, 1998). Typically alkali alkoxide is known to catalyse the carbonylation step (Equation 1) and Cu based materials catalyse the hydrogenolysis step (Equation 2). Cu nanoparticles due to largely exposed surface area accelerate the hydrogenolysis step in the LTMS process (Ahoba-Sam, Boodhoo, et al., 2018). For example, in diglyme solvent, Cu nanoparticles in combination with sodium methoxide led to up to 92 % conversion per batch with 20 bar syngas composed of 0.33CO:0.67H<sub>2</sub>, at 100 °C (Ahoba-Sam, Olsbye, et al., 2018).



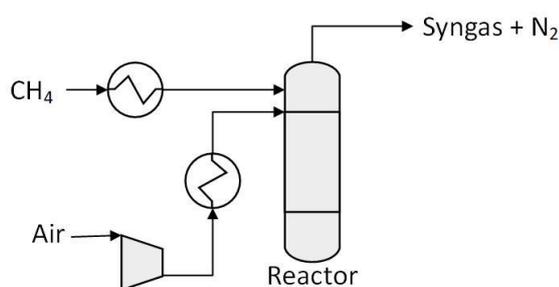
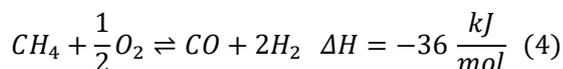
In this paper, our focus was to design a complete process for the LTMS reaction using Aspen HYSYS simulation

program. Considering that the LTMS process can tolerate N<sub>2</sub> diluent, the use of ordinary air and other O<sub>2</sub> enriched air can be simulated for the syngas production, and subsequently be used to design a complete MeOH plant. Even though the concept has been described as a ‘dream reaction’ (Hansen & Højlund Nielsen, 2008), the current work demonstrates that the suggested concept is feasible. The specific aim of this work was to simulate and optimize the reactor conditions in order to propose a complete design of the LTMS process using an air-blown ATR. Different parameters such as chemical compositions, temperature and pressure in the reactors were varied to optimize the process parameters.

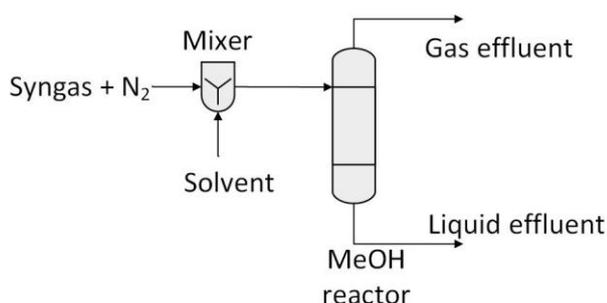
## 2 Process Description

### 2.1 Principles of the Syngas Production

The syngas production process involved partial oxidation of methane (CH<sub>4</sub>) using air, illustrated in Equation (4). The Figure 1 shows a syngas production process using air as the source of O<sub>2</sub>. The process consists of a reactor (ATR), compressor and heat exchangers. Compressed air was used to make-up for the stoichiometry between CH<sub>4</sub> to O<sub>2</sub>. The CH<sub>4</sub> feed used was assumed to be pure, without any sulphur or heavier hydrocarbon present, while the air feed consisted of only O<sub>2</sub> and N<sub>2</sub> to simplify the simulation. The compressed air together with the CH<sub>4</sub> feed were pre-heated and fed directly into the reactor.



**Figure 1.** Principle for the syngas production process



**Figure 2.** Principle for the low temperature MeOH synthesis process

### 2.2 Principles of the MeOH Synthesis Process

Figure 2 shows the MeOH synthesis process using N<sub>2</sub> containing syngas as feed. The LTMS process involved a MeOH reactor and a mixing unit. Since this step is highly exothermic (see Equation (1)) and requires lower operating temperature, the process is often carried out in liquid medium to absorb excess heat to minimize adiabatic rise in temperature beside other solvent’s polarity role for the catalysis (Ahoba-Sam et. al., 2017). The syngas feed is mixed with a liquid solvent and fed into the MeOH reactor. For simplicity of the model, we have taken MeOH as a solvent and due to the 100 % thermodynamic syngas conversion, we have neglected the effect of MeOH solvent in the equilibrium calculations.

## 3 Models

All the simulations were performed using the Aspen HYSYS (version 8.6) program. Gibbs reactors were employed for both the syngas production and LTMS processes. A Gibbs reactor calculates the composition with the theoretical free energy minimum, which is the theoretical equilibrium composition. The Peng-Robinson equation of state (Peng & Robinson, 1976) fluid package was used in all the simulations. The equilibrium for the partial oxidation of CH<sub>4</sub> was calculated for the process in the ATR reactor, while CH<sub>4</sub> was assumed to be inert in the MeOH reactor. After the individual reactors were optimized, an overall system was designed.

Separating units were added in the overall system to represent, (i) a pressure swing adsorber (PSA) and (ii) H<sub>2</sub>O/CO<sub>2</sub> absorber. The PSA was included to help regulate the O<sub>2</sub>/N<sub>2</sub> composition that is fed into the ATR. The H<sub>2</sub>O/CO<sub>2</sub> absorber was used to separate the H<sub>2</sub>O and CO<sub>2</sub> from the syngas effluent before the MeOH reactor. After establishing reasonable pressure and temperature conditions in the individual reactors, the total compression, and heating requirements were simulated, to find out whether additional heating was necessary for the total process.

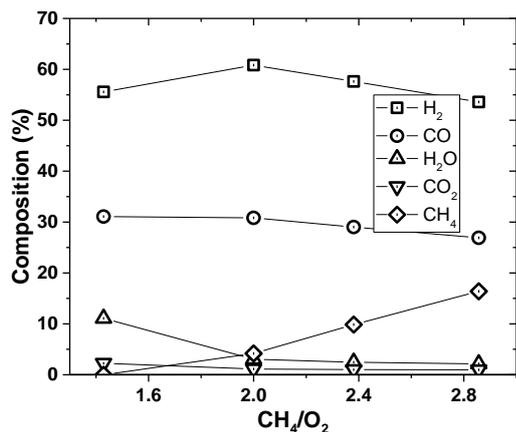
## 4 Process Simulations

### 4.1 Simulation and Optimization of the ATR for Syngas Production

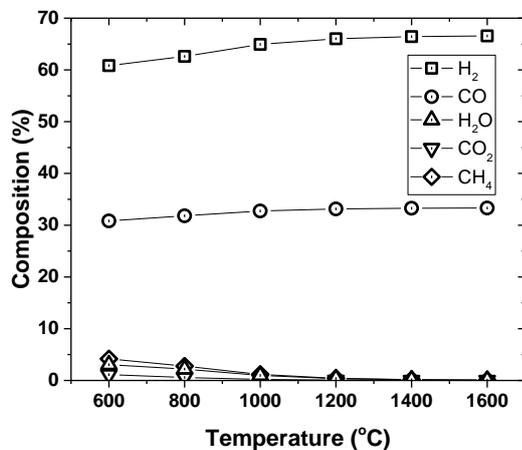
To optimize the feed composition, different mole fractions of the CH<sub>4</sub>: air (containing O<sub>2</sub> and N<sub>2</sub>) were fed into the ATR reactor. The O<sub>2</sub>/N<sub>2</sub> ratio was kept constant at air composition of 21/79. The Figure 3 shows the effect of the ratio of CH<sub>4</sub>/O<sub>2</sub> on the syngas produced at 600 °C. The highest amount of CO + H<sub>2</sub> coupled with the least H<sub>2</sub>O and CO<sub>2</sub> side product (3 and 1 % respectively) was observed at CH<sub>4</sub>/O<sub>2</sub>=2. While H<sub>2</sub>O and CO<sub>2</sub> side products increased below the CH<sub>4</sub>/O<sub>2</sub>=2

ratio due to increase in oxidation, lower CH<sub>4</sub> conversion was observed at higher CH<sub>4</sub>/O<sub>2</sub> ratio as the amount of O<sub>2</sub> became limiting. When the ratio of CH<sub>4</sub>/O<sub>2</sub> was kept constant and O<sub>2</sub>/N<sub>2</sub> ratios were varied (not shown), no variation was observed in the composition of the products. Overall CH<sub>4</sub>/O<sub>2</sub>=2 was chosen as a reasonable composition as this gave the highest amount of syngas (CO+H<sub>2</sub>) with H<sub>2</sub>/CO=2.

The temperature was varied to determine a reasonable temperature required for the feed inlet. Figure 4 shows the effect of temperature on the syngas produced between 600 to 1600 °C. This was done at 0.30CH<sub>4</sub>:0.15O<sub>2</sub>:0.55N<sub>2</sub> feed composition set to 20 bar. Generally, the overall CH<sub>4</sub> conversion increased while side products decreased with increasing temperature. After 1200 °C, subtle changes were observed in the main products such that both the amount of syngas and H<sub>2</sub>/CO=2 were similar. The amount of H<sub>2</sub>O and CO<sub>2</sub> side product at 1200 °C decreased from 0.36 and 0.06 % to 0.06 and 0.01 % respectively at 1600 °C. Nevertheless, considering the exothermic nature of the process and its significance on the reactor material, 1200 °C was the temperature of choice for the syngas production.

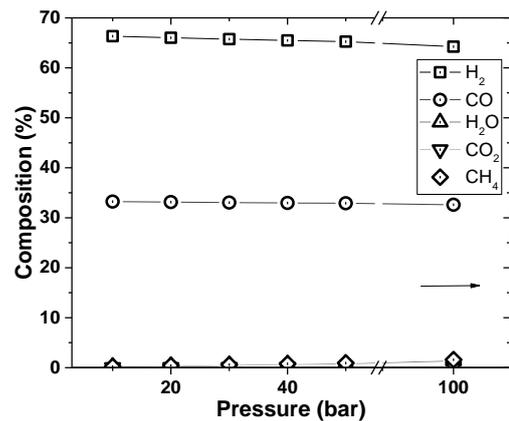


**Figure 3.** Effect of feed composition on the syngas production, at 600 °C and 10 bar.



**Figure 4.** Effect of temperature on the syngas production, 20 bar

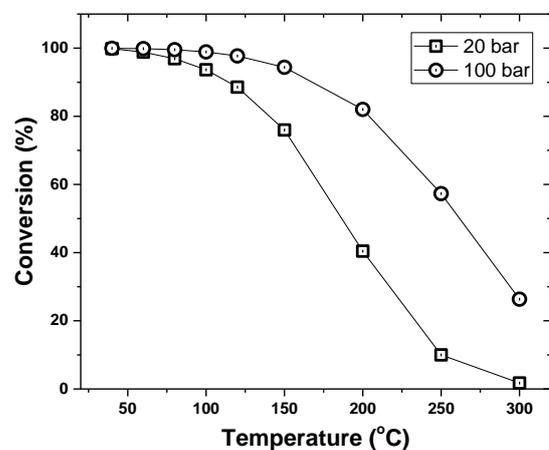
Furthermore, the total inlet pressure was varied to determine a reasonable pressure required for the optimal feed inlet. Figure 5 shows the effect of pressure on the syngas produced between 10 to 100 bar. This was done using similar syngas composition as was done for the temperature (0.30CH<sub>4</sub>:0.15O<sub>2</sub>:0.55N<sub>2</sub>) at 1200 °C. The overall CH<sub>4</sub> conversion increased while side products decreased with decreasing pressure. After 30 bar, no significant changes were observed as both the amount of syngas produced and H<sub>2</sub>/CO=2 remained the same. Therefore 20 bar was a reasonable pressure of choice for the syngas production.



**Figure 5.** Effect of pressure on the syngas production

## 4.2 Simulation and Optimization of the MeOH Synthesis Process

The operating conditions for MeOH production was simulated to optimize the LTMS process. Figure 6 shows the effect of temperature on conversion at 20 and 100 bar syngas pressure. This was calculated using syngas ratio of 0.21 H<sub>2</sub> : 0.41 CO : 0.39 N<sub>2</sub>. The syngas conversion rose exponentially from 300 °C to 120 °C and then increased slightly with decreasing temperature. The optimum temperature however depends on the operating pressure as the 20 and 100 bar syngas pressures showed similar trend but different conversions.



**Figure 6.** Effect of temperature on the LTMS process

Figure 7 shows the effect of pressure with and without N<sub>2</sub> at 100 °C. The conversion with N<sub>2</sub> was calculated using 0.21H<sub>2</sub>:0.41CO:0.39 N<sub>2</sub> syngas ratio while the conversion without N<sub>2</sub> was calculated based on 0.67H<sub>2</sub>:0.33CO composition. The syngas without N<sub>2</sub> showed more than 99 % conversion from 5 to 100 bar total syngas pressure. The syngas with N<sub>2</sub> however exponentially increased with pressure such that about 99 % conversion was achieved at 100 bars. This indicated the importance of N<sub>2</sub> diluent on the partial pressures of the syngas composition required for optimal conversion. Nevertheless, a reasonable pressure chosen for achieving optimal conversion in the presence of 39 % N<sub>2</sub> syngas diluent was 100 bar.

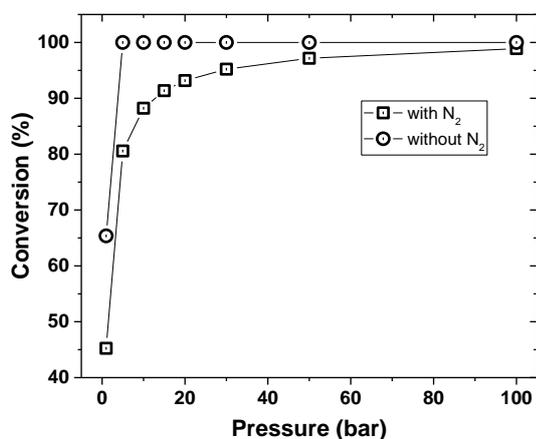


Figure 7. Effect of pressure on the LTMS process

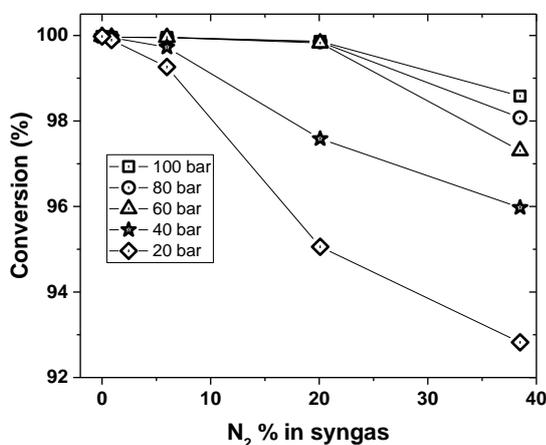


Figure 8. Effect of N<sub>2</sub> diluent concentration on LTMS process at different pressures

Furthermore, the importance of N<sub>2</sub> diluent was determined by varying its composition in the syngas. Figure 8 shows the effect of N<sub>2</sub> composition in the MeOH synthesis at 100 °C at different syngas total

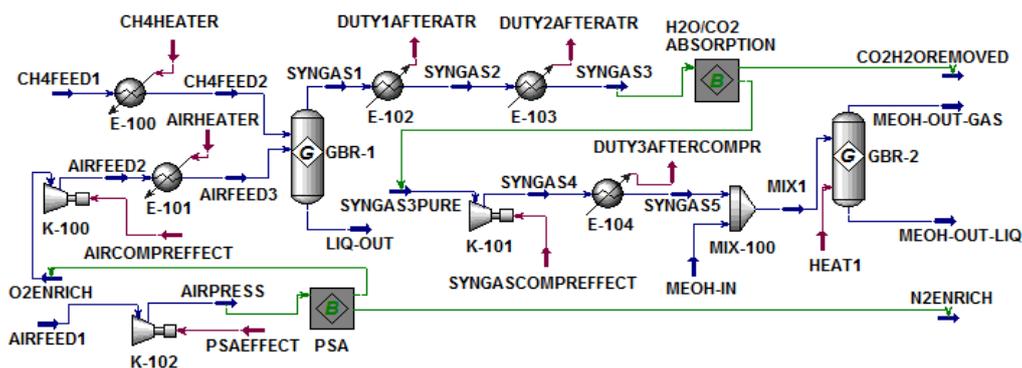
pressures. Syngas conversion increased with decreasing the amount of N<sub>2</sub> diluent in the syngas. Interestingly, a slight decrease of the amount of N<sub>2</sub> in the syngas from 39 % (from normal air composition) to 20 %, leads to full conversion even at 60 to 100 bar. Further N<sub>2</sub> reduction below 7 % in syngas will thermodynamically allow more than 99 % conversion at 100 °C and 20-100 bar. PSA for example can easily be used to enrich air up to 90 % O<sub>2</sub> content in air (Rao & Muller, 2007). Hence for the enriched air, 7 % N<sub>2</sub> in syngas, which can achieve full conversion per pass at 60 bar was chosen for the LTMS process.

### 4.3 Simulation of the Overall LTMS Process

The optimized operation conditions for the two reactors were put together as an overall LTMS process. Two scenarios were considered; one involving ‘normal’ air-blown ATR (0.21 O<sub>2</sub>:0.79 N<sub>2</sub>) and the other involving an O<sub>2</sub> enriched air-blown-blown (0.70 O<sub>2</sub>:0.30 N<sub>2</sub>) system. Figure 9 shows the Aspen HYSYS flow-sheet for the overall standard LTMS process for an enriched air-blown ATR. The set-up in the Figure 9 differs from the normal air-blown system by the inclusion of a PSA unit for enriching the air.

The details of the selected operating conditions used for the calculation is tabulated in Table 1. The partial oxidation was carried out at 1200 °C and effluent from the ATR cooled down to 30 °C in both systems. The 20 bar N<sub>2</sub> containing syngas produced was compressed to either 60 or 100 bar in the compressor where adiabatic efficiencies were specified to 75 %. Starting with 3990 kmol/h CH<sub>4</sub> flow, the normal air-blown system yielded 3842 kmol/h MeOH at 100 bar syngas pressure while that with the enriched air-blown yielded 3919 kmol/h MeOH at 60 bar.

The heat/energy flow for the two systems is shown in Table 2. The negative signs in the table represent heating demands, while the positive represented heat release. For the normal air-blown system, a surplus (after recovery) of 7.68x10<sup>8</sup> kJ/h heat was released as calculated from the heating and cooling. The total energy demand for the compressors was estimated to be 2.80x10<sup>8</sup> kJ/h or 2270 MJ/ton MeOH product for the air-blown system. For the enriched air-blown system, a surplus (after recovery) of 6.10x10<sup>8</sup> kJ/h heat was released when the heating and cooling streams were considered. The energy demand due to compression was estimated to be 1.23x10<sup>8</sup> kJ/h or 983 MJ/ton MeOH product required for the enriched air-blown system. Overall the heat demand is covered by the surplus heat in both air-blown ATR systems.



**Figure 9.** Aspen HYSYS flow-sheet for the overall standard LTMS process

**Table 1.** Specifications of Operation Conditions for the Overall LTMS Process as used in Figure 9

Parameter	Air-blown ATR system				Enriched air-blown ATR system			
	Molar flow (kmol/h)	Pressure (bar)	Temperature (°C)	Main composition	Molar flow (kmol/h)	Pressure (bar)	Temperature (°C)	Main Composition
CH <sub>4</sub> Feed	3990	20	20	1 CH <sub>4</sub>	3990	20	20	1 CH <sub>4</sub>
CH <sub>4</sub> Feed2	..	..	1200	..	..	..	1200	..
AirFeed	9500	1.01	20	0.21 O <sub>2</sub> : 0.79 N <sub>2</sub>	14250	1.01	20	0.21 O <sub>2</sub> :0.79 N <sub>2</sub>
AirPress	-	-	-	-	..	1.50	66.5	..
O <sub>2</sub> Enrich	-	-	-	-	2850	1.10	67	0.70 O <sub>2</sub> :0.30 N <sub>2</sub>
AirFeed2	9500	20	515	0.21 O <sub>2</sub> : 0.79 N <sub>2</sub>	..	20	595	..
AirFeed3	..	..	1200	..	..	..	1200	..
Syngas1	19375	..	1356	0.20 CO : 0.40 H <sub>2</sub> : 0.39 N <sub>2</sub>	12727	..	1439	0.31 CO:0.62 H <sub>2</sub> :0.07 N <sub>2</sub>
Syngas2	..	..	652	..	..	..	687	..
Syngas3	..	..	30	..	..	..	30	..
Syngas3pure	-	-	-	-	12678	20	33.5	..
Syngas4	19375	100	265	0.20CO:0.40H <sub>2</sub> :0.39N <sub>2</sub>	..	60	186	..
Syngas5	..	..	30	..	..	60	100	..
Mix1	..	..	..	..	..	..	..	..
MeOH out (Liquid+Gas)	11642	..	100	0.33CH <sub>3</sub> OH: 0.64N <sub>2</sub>	4839	..	..	0.81CH <sub>3</sub> OH: 0.18 N <sub>2</sub>

**Table 2.** Heat/Energy flow for the overall LTMS process in reference to Figure 9

Heating	Air-blown (10 <sup>6</sup> kJ/h)	Enriched-air (10 <sup>6</sup> kJ/h)
CH <sub>4</sub> HEATER (-)	306	306
AIRHEATER (-)	219	60.2
DUTY1AFTERATR (+)	451	315
DUTY2AFTERATR (+)	366	252
DUTY3AFTERCOMPR (+)	141	32.2
HEAT1 (+)	335	377
Compression		
PSAEFFECT	-	19.4
AIRCOMPREFEFFECT	144	47.6
SYNGASCOMPREFEFFECT	135	56.4

## 5 Discussion of the Process

The air-blown ATR process for LTMS technology differ from conventional MeOH synthesis technology by the inclusion of N<sub>2</sub> diluent. The use of normal air for syngas production presents a cheaper alternative rather than a cryogenic O<sub>2</sub> which is more capital intensive. Alternatively, cheaper O<sub>2</sub> enriched air can be produced either by PSA or membrane separation technologies.

PSA was preferred for the model since membrane separation is usually economical only at small scale (i.e. < 20 ton/day). When an enriched air is used, the cost of production using a PSA will be cheaper than the use of a cryogenic air separation (Rao & Muller, 2007) considering the 70 % O<sub>2</sub> (in air) purity estimated for the partial oxidation in this work.

The exothermic partial oxidation reaction for the syngas production generates excess energy. The reaction specified at 1200 °C indicates outlet temperatures between 1350-1440 °C. This can raise concerns about the choice of the reactor material. Nevertheless, a typical ATR reactor has a burner operating above 2000 °C (Dybkaer, 1995), and hence a 1440 °C stream outlet with a good heat transfer does not pose extra danger compared to the existing reactors. It is also important to note that the partial oxidation process is already a commercial process in ammonia plants (York et. al., 2003) and considering the high operating temperature, the conversions obtained are practically close to equilibrium.

Furthermore, the difference in energy input and output due to heating indicated surplus of 7.68x10<sup>8</sup> and 6.10x10<sup>8</sup> kJ/h released in the normal air-blown and the



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