

# Methane combustion with no CO<sub>2</sub> production

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# Methane combustion with no CO<sub>2</sub> production

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Semester Project

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## Abstract

In this work, a process producing carbon black instead of carbon dioxide, by reacting methane with carbon dioxide and burning the product gases, is investigated. The process, patented by Szego and Biardi in 1994, has the advantage of combusting methane without releasing carbon dioxide but carbon black, which is easier to store than the  $\text{CO}_2$ .

The process was modeled by means of mole and energy balances, equilibrium stages and with the ideal gas assumption. This process model was investigated concerning process conditions and efficiencies.

The results show a comparable efficiency (over 43%) to today's gas cycles with  $\text{CO}_2$  capturing, operating the system at a temperature above 1000 K and pressures above 100 bar.

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## Notation

### Abbreviations

CCS	[-]	Carbon capture and storage
LHV	[-]	Lower heating value

### Greek Letters

$\Delta$		difference
$\gamma$	[ <i>bar</i> ]	activity coefficient

### Latin Letters

$G^o$	[ $\frac{J}{mol}$ ]	Gibbs free energy of formation
$\Delta G^o_{Rx}$	[ $\frac{J}{mol}$ ]	Gibbs free energy of reaction
$h$	[ $\frac{J}{mol}$ ]	enthalpy
$H$	[ <i>bar</i> ]	Henry's constant
$n$	[ <i>mol</i> ]	number of mols
$n_{tot}$	[ <i>mol</i> ]	total number of mols
$Q$	[ <i>J</i> ]	energy
$T$	[ <i>K</i> ]	temperature
$W$	[ <i>J</i> ]	work / electrical energy
$x$	[-]	liquid phase mol fraction
$y$	[-]	gas phase mol fraction

### Subscript and Superscript

$i$	species $i$
0	entering a stage
1	leaving a stage
2	leaving the process

# 1 Introduction

Due to its role in global warming, the emission of carbon dioxide ( $\text{CO}_2$ ) has to be avoided [8]. In order to do so, there are different approaches. In the case of power generation by natural gas combined cycles (NGCC), different methods are used to capture and store the carbon dioxide (CCS)[2]. One is to capture the  $\text{CO}_2$  from the flue gas by scrubbing with a regenerable amine solvent, known as post combustion capture. A second method uses pure oxygen instead of air for the combustion, resulting in a flue gas consisting mainly of  $\text{CO}_2$  and water ( $\text{H}_2\text{O}$ ). This method is called oxy combustion. A third method is called pre combustion capturing, where the fuel is reacted with air or oxygen, producing a fuel gas containing carbon monoxide ( $\text{CO}$ ) and hydrogen ( $\text{H}_2$ ). Through a shift reaction of this fuel gas, using steam, a mixture of  $\text{CO}_2$  and  $\text{H}_2$  is formed. The  $\text{CO}_2$  is separated and the hydrogen used as fuel for a gas turbine combined cycle.

As all of these methods have their own limitations and all pay with an energy penalty for the  $\text{CO}_2$  capturing. In order to overcome such limitations, alternative processes have been proposed. One of these processes was proposed in 1994 and shows a total different approach than the methods introduced before, but was never explored in depth. The process produces carbon black instead of carbon dioxide by combusting methane. Obtaining carbon black, a solid, means no energy costly capturing of  $\text{CO}_2$  and it is also interesting concerning the storage problematics of  $\text{CO}_2$ .

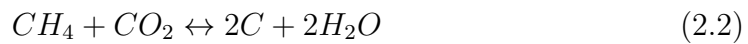
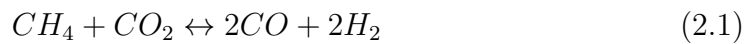
Within the scope of this work, this process was investigated concerning material and energy balances and efficiencies.



## 2 Model

### 2.1 Process

In 1994 Szego and Biard patented a scheme of a process for hydrocarbon combustion without carbon dioxide emission and a plant for its implementation [9]. A schematic drawing of the patented plant is shown in figure 2.1. In the first stage of this process, methane and recycled carbon dioxide, produced in the second stage of the process, are fed into a reactor. There the following reactions take place:

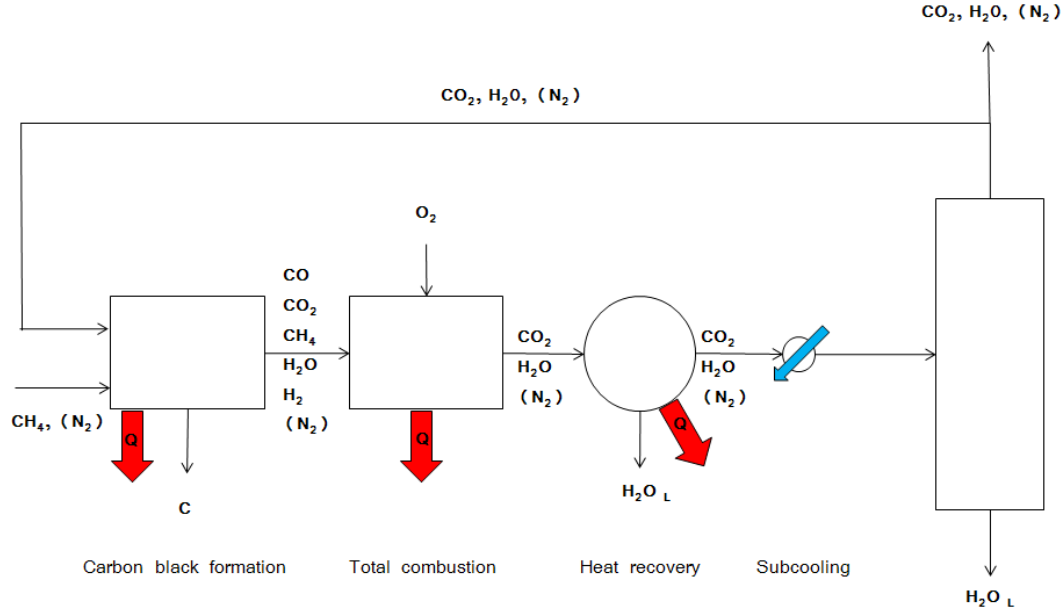


The carbon black produced in reaction (2.2) is separated and removed from the reactor. The gas mixture from the first stage is feed to a second stage for combustion with pure oxygen. The resulting carbon dioxide and water steam of the second stage are feed to the third stage for heat recuperation in a steam boiler. In a next stage the gas steam enters a condenser, where most of the water vapor condenses and is separated from the carbon dioxide in a collector vessel. The  $CO_2$  leaving this last stage is recycled to the first stage. In order to prevent an accumulation of inert gases like nitrogen, a purging line is attached to the recycle. Temperature and pressure conditions in the patented system are chosen within  $500^\circ$  to  $800^\circ C$  and 1 to 50 bar.

### 2.2 Principals

In order to investigate the patented process of Szego and Biardi, the process was modeled in MATLAB. Therefore the system was divided in stages. These are basically three stages, the carbon black forming stage one, the total combustion stage two and the heat recovering stage three. For the model of the whole process, the stages were connected and the cycled closed.

The model assumes for all stages steady state and equilibrium conditions. The ideal gas assumption was chosen for all gases, as the deviation from real gas behavior is sufficiently small, just a weak pressure dependence of the real gas.



**Figure 2.1:** Schematic drawing of a plant for methane combustion without carbon dioxide emission, patented by Szezo and Biardi.

For the occurring real gases in this process, enthalpy change for a pressure change of 100 bar is approximately 1%, except for water around 2%. The model is based on energy and material balances.

So the reaction equilibrium constant  $K$  of a reaction  $aA + bB \rightleftharpoons cC + dD$  is defined as [7]:

$$K = \frac{\gamma_C^c \gamma_D^d \frac{P_C^c P_D^d}{\gamma_A^a \gamma_B^b P_A^a P_B^b}}{\quad} \quad (2.4)$$

With  $\gamma_i$  the activity coefficient and  $P_i$  the partial pressure of species  $i$ . For ideal gases, the activity coefficient term is equals one with the units of  $[\text{bar}]^{c+d-a-b}$ . The pressure term can be rewritten according to Dalton's law  $y_i = P_i/P$ , so:

$$K = \frac{y_C^c y_D^d P^{c+d-a-b}}{y_A^a y_B^b} = \frac{n_C^c n_D^d P^{c+d-a-b}}{n_A^a n_B^b n_{tot}^{c+d-a-b}} \quad (2.5)$$

The  $y_i$  denotes the mole fraction and  $n_i$  the number of moles of species  $i$ .  $P$  stands for the total pressure as  $n_{tot}$  stands for the total numbers of moles. The equilibrium constant can also be calculated from the change in the Gibbs free

energy and is only depending on temperature:

$$K(T) = \frac{n_C^c n_D^d P^{c+d-a-b}}{n_A^a n_B^b n_{tot}^{c+d-a-b}} = \exp \frac{-\Delta G_{Rx}^o(T)}{RT} \quad (2.6)$$

The change in the Gibbs free energy  $\Delta G_{Rx}^o = cG_C^o + dG_D^o - aG_A^o - bG_B^o$  as well as the gas constant  $R$  and the temperature  $T$  appear in the additional term.

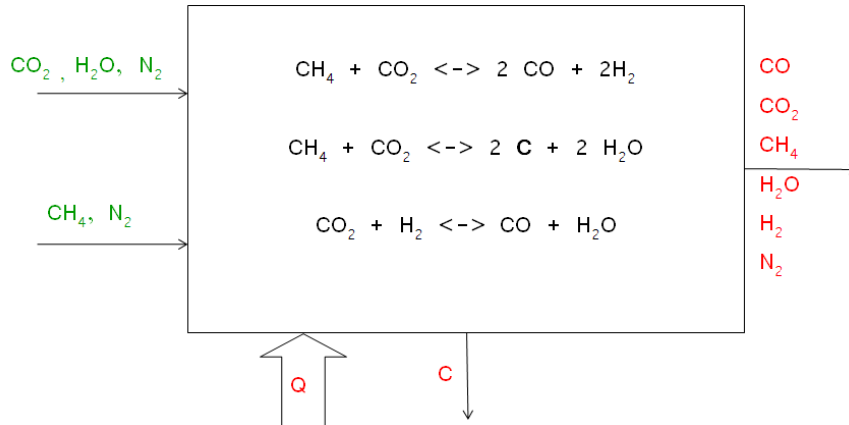
For the phase equilibrium, Henry's law can be applied [5]:

$$Py_i = P_i = Hx_i \quad (2.7)$$

With  $x_i$  the mole fraction of species  $i$  and  $H$  the Henry's constant.

### 2.3 Stage 1

In stage 1, the carbon black formation takes place in a reactor at temperature  $T$  and pressure  $P$ , schematically shown in figure 2.2. The reactor from stage 1 is fed with methane ( $\text{CH}_4$ ) and depending on the purity also nitrogen ( $\text{N}_2$ ) to account for real natural gas composition. From the recycle, a mixture of carbon dioxide ( $\text{CO}_2$ ), nitrogen ( $\text{N}_2$ ) and water vapor ( $\text{H}_2\text{O}$ ) is fed. From the three reaction (2.1)-(2.3), taking place in the reactor, it can be seen that at equilibrium a mixture of  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{C}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$  and  $\text{N}_2$  is formed. The quantities of the species



**Figure 2.2:** Schematic drawing of the carbon black forming stage 1. Feeds of green species are assumed known, red ones as unknown. Amount of energy produced also unknown. Three competing reactions take place.

fed to the reactor (green) are assumed to be known, as the feed of methane is a process parameter, as is the addition of nitrogen. The amount of recycled species will be determined by the steady state of the whole system. On the other hand there are 8 unknowns (red), the amount of the species leaving the reactor (7) and the energy required.

So in order to solve stage one, seven equations are needed to obtain the seven unknowns. Looking at the reactor as a black box, one can derive the material balances over the reactor for each element, C, O, H and N:

$$n_{CO_2}^0 + n_{CH_4}^0 = n_{CO}^1 + n_{CO_2}^1 + n_C^1 \quad (2.8)$$

$$4n_{CH_4}^0 + 2n_{H_2O}^0 = 2n_{H_2}^1 + 2n_{H_2O}^1 + 4n_{CH_4}^1 \quad (2.9)$$

$$2n_{CO_2}^0 + n_{H_2O}^0 = n_{CO}^1 + 2n_{CO_2}^1 + n_{H_2O}^1 \quad (2.10)$$

$$2n_{N_2}^0 = 2n_{N_2}^1 \quad (2.11)$$

The superscript 0 stands for a species entering a stage, 1 for leaving.

Further an energy balance over the reactor can be set up:

$$\begin{aligned} (n_{CH_4}^0 - n_{CH_4}^1)h_{CH_4} + (n_{CO_2}^0 - n_{CO_2}^1)h_{CO_2} + (n_{H_2O}^0 - n_{H_2O}^1)h_{H_2O} + \\ (n_{N_2}^0 - n_{N_2}^1)h_{N_2} = n_{CO}^1 h_{CO} + n_{H_2}^1 h_{H_2} + n_C^1 h_C + Q \end{aligned} \quad (2.12)$$

With  $h_i = h_i(T)$  the enthalpy of species  $i$  at temperature  $T$  and  $Q$  the energy used in stage 1. For carbon black, the enthalpy values of graphite were chosen. For the three missing equations, one has to look inside stage 1. In order to apply the equilibrium conditions for the three reactions taking place in stage 1, the correlation for the equilibrium constant  $K$  (2.6) is applied for the reactions (2.1)-(2.3):

$$K_I = \frac{(n_{CO}^1 n_{H_2}^1)^2 P^2}{n_{CH_4}^1 n_{CO_2}^1 n_{tot}^2} = \exp \frac{-\Delta G_I^o(T)}{RT} \quad (2.13)$$

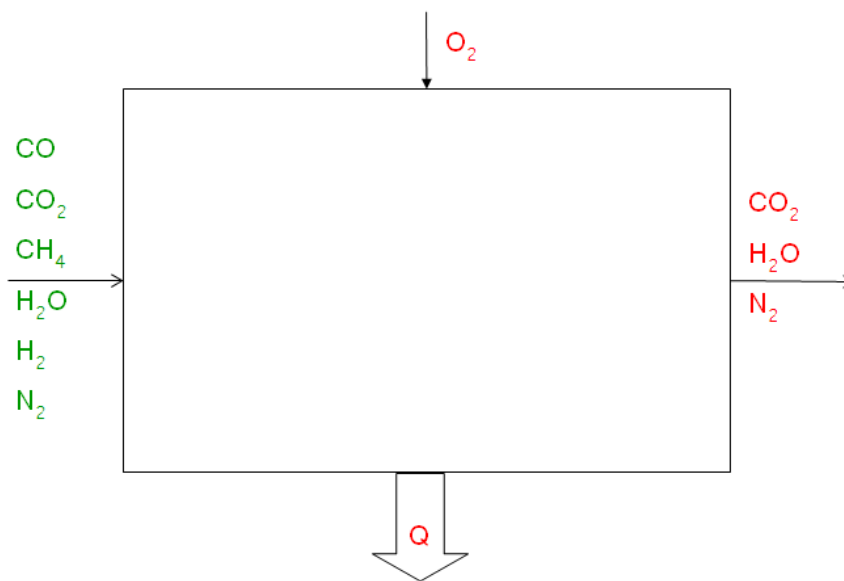
$$K_{II} = \frac{(n_{H_2O}^1)^2}{n_{CH_4}^1 n_{CO_2}^1} = \exp \frac{-\Delta G_{II}^o(T)}{RT} \quad (2.14)$$

$$K_{III} = \frac{n_{CO}^1 n_{H_2O}^1}{n_{CO_2}^1 n_{H_2}^1} = \exp \frac{-\Delta G_{III}^o(T)}{RT} \quad (2.15)$$

Where the Gibbs free energy of reaction  $\Delta G^o$  derives from the Gibbs free energy of formation  $G^o$  of the reaction elements, as shown in the previous section. With this three equilibrium relations, there are 7 unknowns and 7 equations, so the system is fully defined. In order to solve the problem, a numerical solver may be used. The material data like enthalpy  $h(T)$  and Gibbs free energy of formation  $G^o(T)$  are calculated from fitted polynomials, issued from [1] and [4] respectively.

## 2.4 Stage 2

The off gases from stage 1 are fed to the second stage. So the calculated values from stage 1 are used as inlet values for stage 2, as marked red in figure 2.3, showing the schematic of stage 2. As complete combustion is assumed to take



**Figure 2.3:** Schematic drawing of the total combustion in stage 2. Feeds of green species are assumed known, red ones as unknown. Energy output is also unknown. Feed of pure oxygen for the combustion.

place, oxygen ( $O_2$ ) is fed to the gas mixture coming from stage 1. The resulting products of a complete combustion are carbon dioxide and water vapor, as the nitrogen is assumed to be inert. Hence the amount of  $O_2$  that has to be fed to the stage and the amount of  $CO_2$  and  $H_2O$  leaving the stage are unknown, as well as the energy output. So there are four unknowns (marked red in figure 2.3).

Like in stage 1, material balances for all four elements present can be set up:

$$n_{CH_4}^0 + n_{CO_2}^0 + n_{CO}^0 = n_{CO_2}^1 \quad (2.16)$$

$$2n_{CH_4}^0 + n_{H_2O}^0 + n_{H_2}^0 = n_{H_2O}^1 \quad (2.17)$$

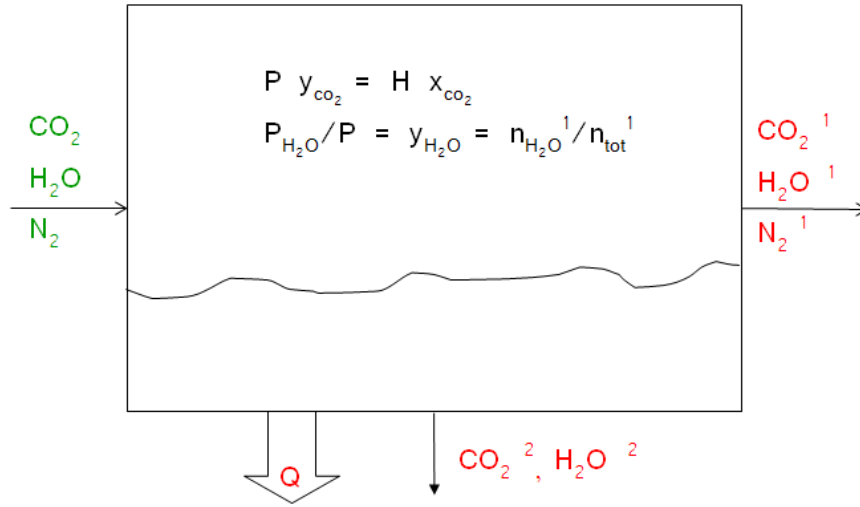
$$n_{CO}^0 + 2n_{CO_2}^0 + n_{H_2O}^0 + 2n_{O_2}^0 = 2n_{CO_2}^1 + n_{H_2O}^1 \quad (2.18)$$

$$2n_{N_2}^0 = 2n_{N_2}^1 \quad (2.19)$$

Additionally an energy balance can be done. For the energy balance the temperature of  $O_2$  is assumed to be  $25^\circ C$ , all others are at temperature  $T$ . With these four equations, all four unknowns can be determined.

## 2.5 Stage 3

The feed to stage 3 is the off gas stream from stage 2, which consists solely of carbon dioxide, water vapor and nitrogen. Stage 3 is a cooling and separation stage, as it can be seen in figure 2.4. The entering species are cooled down from



**Figure 2.4:** Schematic drawing of the cooling and separating stage 3. Feeds of green species are assumed known, red ones as unknown. Amount of energy produced also unknown. Superscript 2 indicates the species being separated and removed from the system.

temperature  $T$  to  $35^\circ C$ . Therefore the main part of the water vapor will condense and water in liquid form will be extracted. Due to the solubility of carbon dioxide

in water, also small amounts of carbon dioxide will be extracted with the liquid water. The nitrogen is assumed to be insoluble, as it is about 50 time less soluble in water than carbon dioxide [5].

As the water vapor is cooled down, the partial pressure of water vapor  $P_{H_2O}^{sat}$  is equals its saturation pressure for 35°C. Therefore one can apply Dalton's law, so:

$$\frac{P_{H_2O}^{sat}}{P} = y_{H_2O} = \frac{n_{H_2O}^1}{n_{tot}^1} \quad (2.20)$$

In order express the solubility of carbon dioxide in water, Henry's law (2.7) can be applied:

$$P_{CO_2} = P y_{CO_2} = P \frac{n_{CO_2}^1}{n_{tot}^1} = H x_{H_2O} = H \frac{n_{CO_2}^2}{n_{tot}^2} \quad (2.21)$$

Temperature depending polynomials for the saturation pressure of water  $P_{H_2O}^{sat}$ , as well as for the Henry's constant for carbon dioxide in water  $H$  are found in [5].

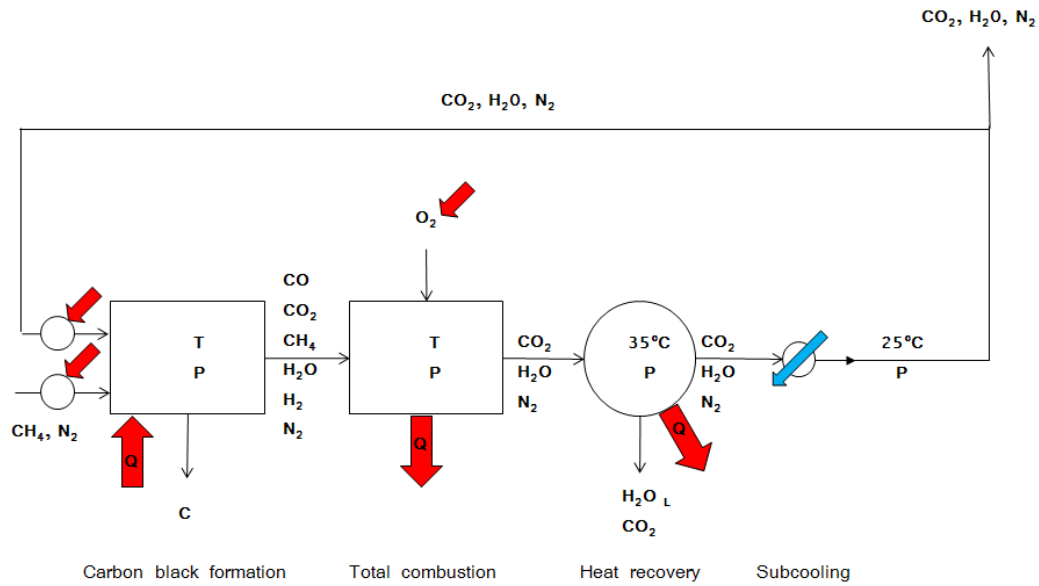
The equilibrium behavior is described with equations (2.20) and (2.21). As there are six unknowns, four equations are missing. With a material balance for each species, CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>, and the energy balance over stage 3, one is able to solve the system.

## 2.6 Overall process model

In order to model the overall process, the single stages have to be brought together. Therefore the output of the previous stage is feed in the next stage. In figure 2.5, the schematic of the implemented model is shown with all accounted energy in and outputs.

After stage 3, the gas stream is further cooled down to 25°C and then recirculated. Before the recirculated gases enter stage 1, a part of the cycle can be purged. Therefor one implements a recycle factor, so the amount of recycled species times the recycle factor enters stage 1. Additionally heating up of the recycled gas and the feed gas of stage 1 has to be accounted for, as well as the energy used to separate the amount of fed oxygen in stage 2. The energy taken out of the system when cooling from 35 to 25°C is not taken into the energy balance, as recovery at this temperatures would be very inefficient.

As the recycle stream is not known in the beginning, an initial assumption is



**Figure 2.5:** Schematic drawing of the overall process model as it is implemented.

implemented and the model run in a loop, until the recycle equals the recycle for the runtime step before, and therefore reached steady state.



### 3 Results and Discussion

The obtained results for the mole balances are in agreement with the results from a previous work [3], investigating the same process. Though the energy output is in the same order, but not as accurate as the mole streams. The results are compared in table 1. All quantities are normalized in respect to one mole of methane. Comparing the single stages, especially stage 1, the deviation in the

**Table 1:** Comparison between this and a previous work on the investigated process. Similar results with small deviation in energy output.

	IN		OUT	
	O <sub>2</sub>	Carbon black	H <sub>2</sub> O/CO <sub>2</sub>	Energy
T=600°C				
P=30 atm	[mol/molCH <sub>4</sub> ]	[mol/molCH <sub>4</sub> ]	[mol/molCH <sub>4</sub> ]	[J/molCH <sub>4</sub> ]
pure CH <sub>4</sub>				
Prev. work [3]	1.00	1.00	2.00/0.00	391'845
This work	1.03	0.97	2.00/0.03	472'532
1.5% N <sub>2</sub> Purge 2.4%				
Prev. work [3]	1.007	0.963	1.97/0.00	383'399
This work	1.040	0.960	2.00/0.018	476'298

input and output streams are very small, coming from differences in the model, especially the ideal gas assumption used for this work and lack of separation of water from 35 to 25°C. Also the previous work did not account for the CO<sub>2</sub> solved in the separated water. On the other hand, the energy terms for the different stages showed bigger deviations, resulting in the difference visible in table 1. The models for material data were compared and showed also a good agreement, this differences in energy derives from known and unknown differences of the modeling.

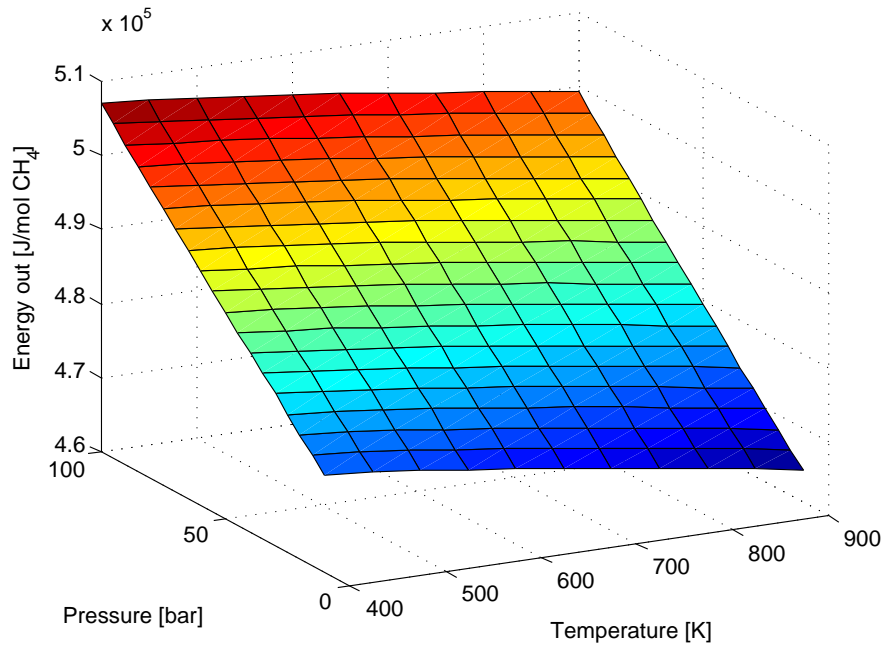
For a feed of pure methane only the parameters, temperature  $T$  and pressure  $P$ , can be varied in order to change the process. Therefore a parameter study concerning these parameter was carried out. Figure 3.1(a) displays the obtained

energy as function of temperature and pressure.

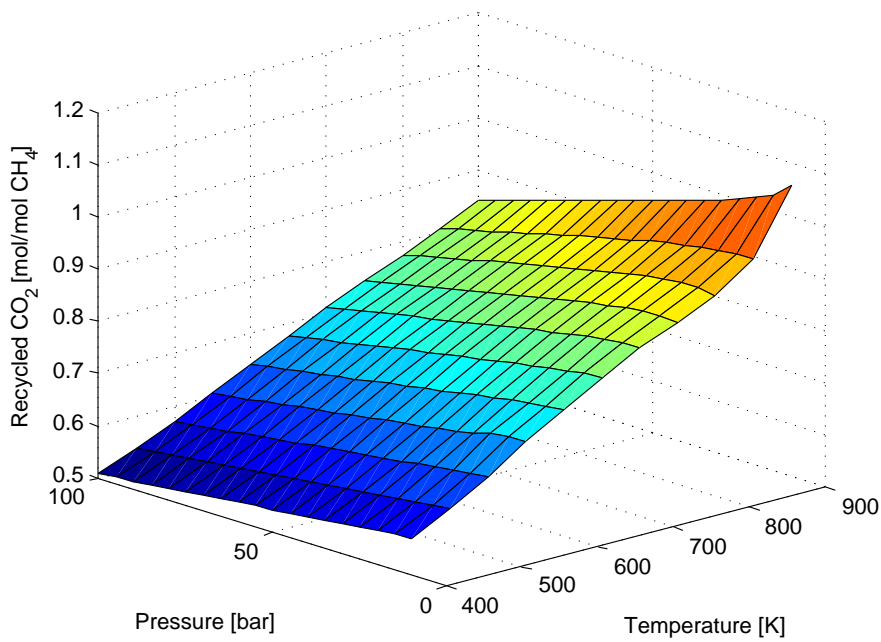
As visible, the higher the pressure and lower the temperature, the higher the energy output. As for a feed of pure methane the purge has not to be used, it can be seen from an overall balance of carbon, that the number of moles of carbon black is almost equal the moles of methane fed, almost because small amounts of carbon dioxide are taken out of the process with the liquid water. The amount of recycled carbon dioxide relative to the methane feed for different pressures and temperatures is shown in figure 3.1(b). The recycle stream shows the opposite behavior, the higher the pressure and lower the temperature, the lower the recycle ratio. This behavior would be of advantage for a real plant, as a high energy output means a small recycle stream and therefore lower operational and also investment costs due to a small recycle.

An other parameter studies is shown in the figures 3.2(a)-(d). Here methane and additionally 10% nitrogen per methane is fed, similar to certain natural gases. The energy output and recycle  $\text{CO}_2$  show the same behaviour as for the pure methane feed. For lower pressures the impure feed shows even a higher energy output, but for higher pressures, the pure is by far dominant. In order to avoid nitrogen accumulation, a purge line is used, removing 2.5% of the stream, comparable to separation efficiencies of other processes, leaving stage 3. The so purged  $\text{CO}_2$  is shown in figure 3.2(d) and behaves like the recycle carbon dioxide stream, as they are coupled. Due to the additional losses of carbon in form of carbon dioxide in the purge, the amount of produced carbon black is depending on the purge and solubility of  $\text{CO}_2$ .

As mentioned, if using methane that is containing nitrogen, a purge has to be implemented in order to avoid enrichment of nitrogen in the system. Especially in the first stage, the increasing partial pressure of nitrogen influences the reaction equilibrium of reaction (2.1). This results in a continuous increase of the carbon dioxide recycle, as shown in figure 3.3, the first downward peak comes from the initial condition of no recycle, so in the first step, no carbon dioxide is present in stage 1 and therefore no reaction takes place. So all methane is burned in the second stage and the so produced carbon dioxide is recycled. This first recycled  $\text{CO}_2$  can then participate in the reactions in stage 1, so its amount is decreased in the next steps, until the partial pressure of nitrogen becomes dominant and more and more  $\text{CO}_2$  is produced. So the system never reaches steady state, therefore

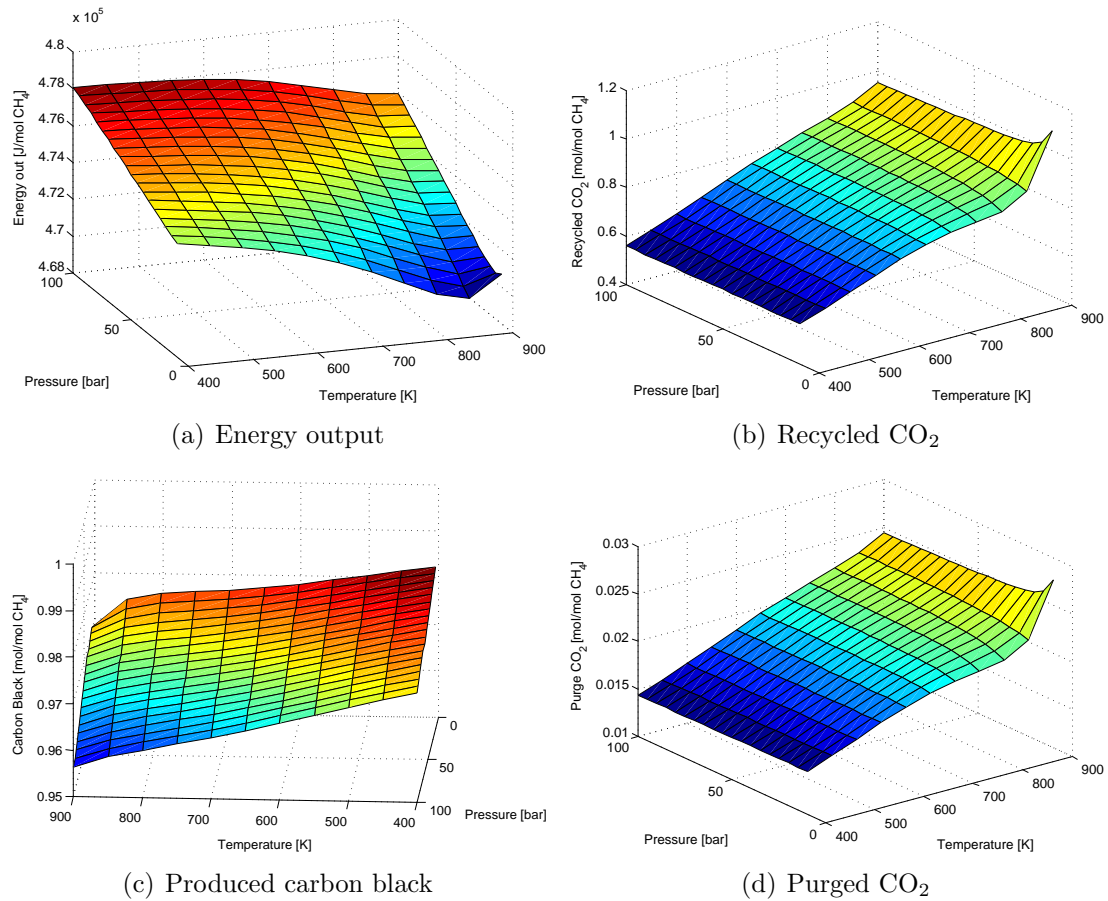


(a) Energy output of the process as function of temperature and pressure for a feed of pure methane. Highest energy outputs for low temperatures and high pressures.



(b) CO<sub>2</sub> recycle of the process as function of temperature and pressure for a feed of pure methane and no purge. Highest recycle ratio at high temperatures and low pressures.

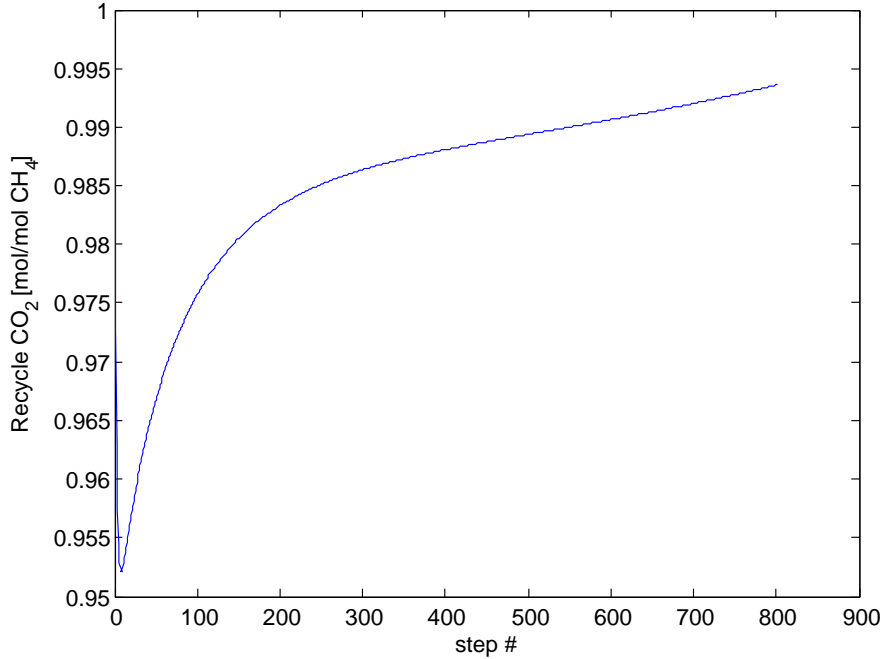
**Figure 3.1:** Energy output and CO<sub>2</sub> recycle for different pressures and temperatures for a feed of pure methane.



**Figure 3.2:** Energy output,  $\text{CO}_2$  recycled, carbon black produced and purged  $\text{CO}_2$  for different pressures and temperatures. Feed of methane and 10% nitrogen, purge of 2.5%.

a purge is needed to hold the nitrogen in the system on a constant level. The main disadvantage of this purge is that with the purge ether carbon dioxide is released into the atmosphere, or additional energy is needed to capture and store the  $\text{CO}_2$  from the purge.

As the calculated energy output is found in form of heat, one has to use a steam



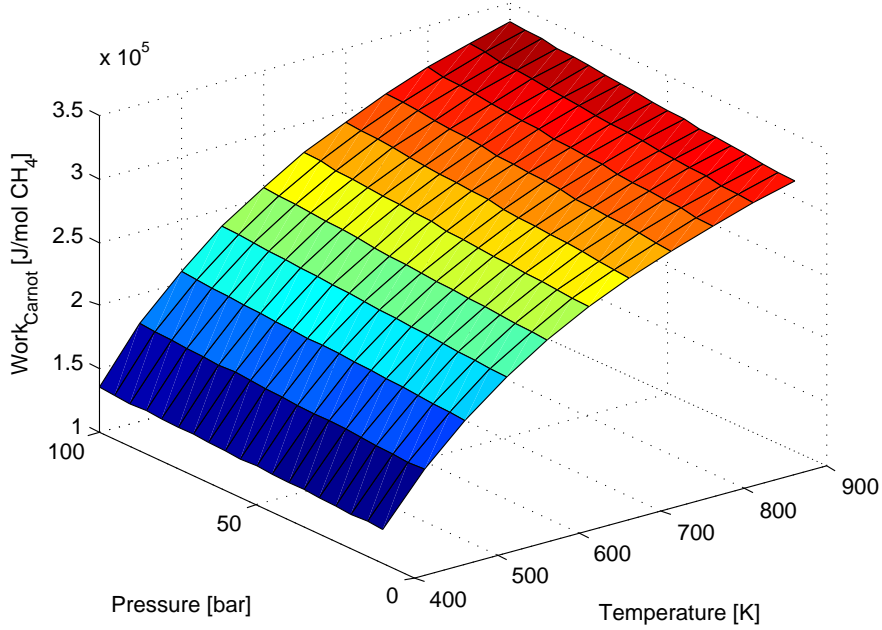
**Figure 3.3:** Start of the model with a feed of  $\text{CH}_4$  plus 1%  $\text{N}_2$  of  $\text{CH}_4$ . Initially recycle is set to zero, no purge. Enrichment of nitrogen influences the reaction equilibrium and prevents a steady state.

or gas or even combined cycle to convert this energy into more useful and comparable electrical energy. The efficiencies of all cycle processes strongly depend on the temperature difference between the cold  $T_C$  and the hot  $T$  (process) reservoir. The best efficiency such a cycle theoretically reach is the Carnot efficiency [6], defined as:

$$\eta_C = 1 - \frac{T_C}{T} \quad (3.1)$$

Assuming all output energy to be available at the process temperature  $T$ , the energy multiplied by the according Carnot efficiency gives a best case for an electrical energy output  $W$ . The assumption of all the energy being available at process temperature  $T$  is optimistic as this energy is not only from stage 2, where the assumption holds, but also from stage 3 where this is not the case. Also the

cold reservoir temperature  $T_C$  is optimistically assumed 20°C. Replotting figure 3.1(a) multiplied with the corresponding Carnot efficiencies, the electrical energy output of the process is displayed for different temperatures and pressures (Figure 3.4). The electrical energy output is highest for high temperatures and pressures



**Figure 3.4:** Electrical energy output of the process for different temperatures and pressures. For a feed of pure methane and no purge. Due to the Carnot efficiency, the highest output is found at high temperature and pressure.

due to the strong temperature dependence of the Carnot efficiency. Although the slope decreases for higher temperatures, the maximal temperature is not yet reached with the displayed 900 K. So for even higher temperatures and pressures, higher electrical energy outputs are possible.

For comparability reasons, the electrical energy output  $W$  can be expressed as efficiency on lower heating value (LHV) basis for methane:

$$\eta_{LHV} = \frac{W}{LHV} \quad (3.2)$$

The so obtained LHV efficiencies can be compared with efficiencies of state of the art power plants with CO<sub>2</sub> capturing [2]. Although CO<sub>2</sub> capturing has not yet been demonstrated in large commercial NGCC power plants In table 2, obtained efficiencies for this process are compared to such state of the art processes. These

**Table 2:** LHV efficiency for this process compared to net efficiencies on LHV basis of state of the art power plants with CO<sub>2</sub> capturing.

	This work	This work	This work	Flour[2] Post-comb.	MHI[2] Post-comb.	Oxi-comb.[2]
T [K]	900	1000	1100			
P [bar]	100	100	200			
$\eta_{LHV}$	0.419	0.438	0.492	0.474	0.496	0.447

power plants have net efficiencies up to 49.6%, LHV basis. In this net efficiency, the CO<sub>2</sub> capturing as well as auxiliary power consumptions are included. For high temperature and high pressure, the efficiency of this process model can reach or even surpass those efficiencies. Although, the LHV efficiency of this process model is very optimistic in terms of Carnot efficiency and ideal heat transfer. Also auxiliary power consumptions as for compressors, pumps and others are not taken into account as it is done by the compared power plant net efficiencies.

The biggest advantage of this process is the formation of carbon black instead of carbon dioxide, as it is a solid and therefore easy to store. Handling and storage of CO<sub>2</sub> on the other hand has not been implemented on a large scale yet. The storage has to be safe and close for a long time, as well as accepted by the population, terms the solid carbon black fulfills. As the storage of carbon black is unproblematically, auxiliary energy costs are saved compared to CCS processes. Another advantage is, that the potential energy from incompletely combusted carbon black is stored in it. At the moment, this energy can not be used without releasing CO<sub>2</sub>, but this might be possible in the future.

As seen in table 2, reaching comparable efficiencies to other processes is possible with process conditions of high temperature and pressure. The range of temperature and pressure is similar to high temperature and pressure reactions in the chemical industry. As most common stainless steels are only able to withstand temperatures up to 600°C, special temperature resistant steel would be needed for this process. Additionally the high pressure requires special constructive measures to withstand these demanding conditions.

Another challenge is the carbon black extraction from stage one. In order to guarantee long undisturbed operation, it has to be possible to extract the carbon

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black from a running plant. If the process requires a catalyst, the task is difficult to fulfill, as the carbon black may deposit on the catalyst and is therefore hard to extract. In addition, the catalyst performance might be reduced. If no catalyst is required, the first stage could be constructed as a cyclone to separate the carbon black. In order to decide if a catalyst is necessary or not, investigations on the reaction kinetics of the reactions taking place in stage one have to be performed.



## 4 Conclusions

The investigated process model reaches efficiencies, on lower heating value basis and for absolutely ideal conditions, comparable to the net efficiency (LHV basis) of state of the art power plants with capturing of carbon dioxide. In order to reach such efficiencies of 43% and more, the process has to be operated at temperatures over 1000 K and at pressures over 100 bar.

For the combustion of methane with nitrogen, similar to natural gas, a purge stream is needed in order to avoid nitrogen enrichment, which would prevent the process from reaching steady state. This purge means either release of carbon dioxide to the environment or an additional, energy costly, separation step. Also the energy output for high pressures is lowered by the nitrogen present in the system.

The technical realization of the modeled process would be very challenging, as these operational conditions, very high temperatures and pressures, lead to high demands concerning mechanical properties of the material used for the reactors and pipes, as well as for the design. Additionally, the first stage has to be heated up to such high temperature values, so one has to think of a special heating system. Another realization problem occurs in the removal of carbon black from stage one during operation. If it is necessary to use a catalyst for the first stage reactions, the carbon black is likely to deposit on the catalyst, what hinders the removal of carbon black and influences the catalysts performance.

The big advantage of this process is the resulting carbon black instead of carbon dioxide. Although the carbon black contains still potentially useful energy that is bound, at least for the presence, the storage of the solid carbon black is much easier and cheaper than for CO<sub>2</sub>.

Today the investigated process can not compete with state of the art power plants capturing carbon dioxide, as in order to reach comparable efficiencies, very challenging process conditions have to be chosen and the model predicts very optimistic values. So in order to compensate the additional losses, not implemented in the model, temperature and pressure have to be chosen even higher, which makes the realization of a plant unlikely.

Never the less, this process is an interesting alternative to the CCS technologies, especially because of the simple storage of carbon black. The process could get interesting if the storage problematics of CO<sub>2</sub> can not be solved, or such tech-

niques are not accepted by the population. Further a development for the big scale use (CO<sub>2</sub> neutral) of carbon black, or usage of the energy stored in the carbon black might make it competitive.

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