

SYNTHETIC NATURAL GAS (SNG) FROM PETCOKE: MODEL DEVELOPMENT AND SIMULATION

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In this work the issue of producing SNG from petcoke was addressed by developing a new process. First, a model for petcoke gasification, taking into account kinetics and mass transfer was developed; the simulation model was applied to a conceptual dual bed gasification scheme (Sudiro *et al.*, 2008).

Then, a number of alternatives to produce synthetic natural gas (SNG) from syngas were investigated, facing the main issue of this type of process: the temperature control in the methanator. The complete process was simulated with Aspen Plus™, and its performances have been evaluated, with respect to product yield, CO₂ emissions and overall energy efficiency.

1. INTRODUCTION

Nowadays there are significant opportunities for the extended use of petcoke as a mean to replace imported petroleum and petroleum products for transportation fuels and chemicals by using petcoke-to-liquids (CTL) technology, and for the production of synthetic natural gas (SNG) from petcoke. The use of coal and/or petcoke for these purposes can assure additional independence from oil imports and provide new incentives for coal production. In particular, the delayed coker plant, which produces petcoke, is a very important plant in the oil refinery when heavy crudes are processed, which are particularly abundant in the world.

Coal is a largely available fossil fuel with a ratio between reserves and production of approximately 165 years (<http://www.eia.doe.gov/neic/infosheets/coalreserves.html>). Natural gas is a fossil fuel cleaner than coal and its exploitation has been increasing for years; however, its price has been increasing as well, especially in the latest times, so its production from coal or biomass is an interesting topic to investigate (Ullmann's, 1989). The main interest is from China and USA, Countries which have coal reserves larger than their oil and natural gas ones.

The only commercial scale coal-to-SNG plant in operation is located in the United States, many others are planned and some of them are expected to be operational by 2010-2014 (http://www.energy.psu.edu/osd/reports/DPetruci_2009.pdf). About projects, in China, the China National Offshore Oil Corporation (CNOOC) has signed agreements with the local governments of Shanxi province and the Inner Mongolia Autonomous Region to build three SNG plants with total capacity of 12 billion cubic meters per year; the company aims to build pipelines from northwest China to economically developed areas in the east (<http://www.chinamining.org>).

In spite of the strong market interest, the commercial deployment of technologies for the production of SNG is constrained by certain economic and technical barriers.

Aim of this work is the development and simulation of a process to produce SNG from petcoke via gasification. The process consists in at least three section: petcoke gasification, syngas purification system and methanation reactor. In this work we focus our attention on two sections of the plant: the syngas generation, obtained with a dual bed petcoke gasification system, and the methanation reactor. For the first section a detailed model including kinetics and mass transfer was investigated and for the methanation section three different possible configurations of the plant have been developed, exploiting the concept of product recycling.

2. PROCESS MODELING

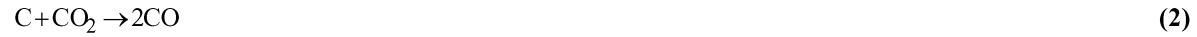
The system to be modeled consists of three main parts: a gasification section, the syngas purification system and the methanation plant. The model of the process considered was developed using Aspen Plus™ as the process simulator. Material and energy balances were accounted for and solved for every process unit, taking into account the chemical kinetics in the reactors.

Suspended petcoke was assumed as char. The following species were included in the model: O₂, N₂, H₂, H₂O, CO, CO₂, CH₄, char (as graphite C), S (solid), H₂S and NH₃. User specified non-conventional solids have been defined to represent petcoke and ash. Petcoke composition is from Nagpal *et al.*, 2005. The Peng-Robinson equation of state with Boston-Mathias alpha function was applied as a thermodynamic model.

2.1 Gasification model

The combustion and gasification steps were modelled as CSTR reactors.

Four heterogeneous and three homogeneous reactions have been considered (data were taken from Nagpal *et al.*, 2005 and Weimer *et al.*, 1981):



Because fluidized-beds operate at temperatures lower than 1000°C the syngas produced is richer in methane with respect to that produced in entrained-flow reactors. Therefore, an additional reaction has been included in the model: methanation of CO, whose kinetic was derived from Dobrego *et al.*, 2008.



For the heterogeneous reactions the rate expressions consider both chemical kinetics and mass transfer phenomena between gas phase and char particles, under the hypothesis that reactions occur on the surface of the particles only, thus neglecting the contribution within the pores; according to Johansson, 2006 the relationships is:

$$r_j = \frac{Ac \cdot c_{i,bulk}}{\left(\frac{1}{h_{M,i}} + \frac{1}{k_j} \right)} \quad (9)$$

where r_j is the reaction rate ($\text{kmol/m}^3 \text{ s}$), $c_{i,bulk}$ is the average reacting gas concentration in the bulk (kmol/m^3), k_j is the kinetic constant (the Arrhenius law expression) and $h_{M,i}$ is the mass transfer coefficient for gas component i between solid and gas phase (m/s): $h_{M,i}$ depends on Reynolds and Schmidt numbers, particle diameter and diffusivity. Ac is the specific char surface area per unit reactor volume (m^{-1}). The char particles are all assumed as spherical.

Three homogenous reactions are accounted for (i.e. eq. 5, 6 and 7). The rate of the water-gas shift reaction, r_5 , is:

$$r_{WGS} = k_{WGS} \cdot \left(c_{CO} \cdot c_{H_2O} - \frac{c_{CO_2} \cdot c_{H_2}}{K_{WGS}} \right) \quad (10)$$

where K_{WGS} is the WGS equilibrium constant, which is calculated in according to (Bustamante *et al.*, 1968) (with T expressed in K):

$$\ln K_{WGS} = -4.33 + \frac{45778}{T} \quad (11)$$

Reaction rates for reactions r_6 and r_7 are derived from Weimer, 1981 and Kim *et al.*, 2000, respectively:

$$r_6 = k_6 \cdot c_{CO} \cdot c_{O_2} \quad (12)$$

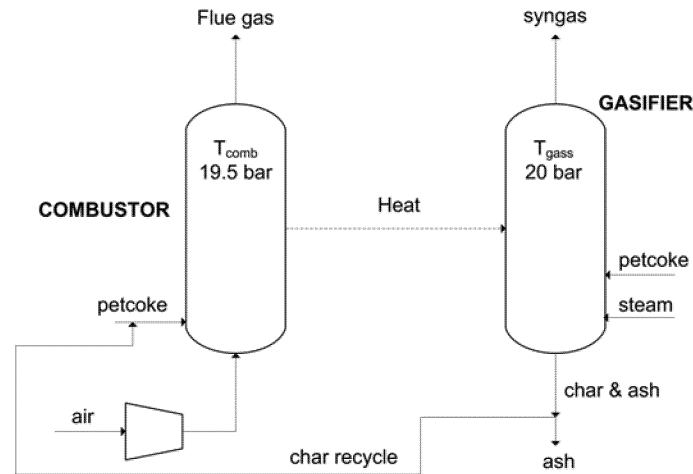
$$r_7 = k_7 \cdot c_{H_2}^2 \cdot \frac{c_{O_2}}{c_{CO}} \quad (13)$$

The chemical kinetics and mass transfer relations have been implemented in a Fortran routine, which is recalled by the source program of the process simulator.

The model has been first checked with literature data (Shelton *et al.*, 1998 and Ni *et al.*, 1995) for conventional gasification using coal, steam and oxygen as feedstocks. The validation of the model has already been explained in detail elsewhere (Sudiro, 2009).

Then, the scheme with two reactors was simulated: one for combustion and one for gasification, using the concept of dual bed gasification (Sudiro *et al.* 2008); Figure 1 shows the block flow diagram of this process.

Figure 1: Scheme of the dual bed gasification process.



2.1 Methanation model

A preliminary kinetic analysis of the methanation reactions has been carried out using the process simulator Aspen Plus™, with the kinetics taken into account through a user model. It will be shown that methanation reactions get very close to equilibrium conditions and in a reasonably low residence time, with high exothermic effects. So, the problem is the increase of temperature inside the reactor, rather than how much and how fast CO is converted into CH₄ and H₂O.

The system involves 5 compounds: CO, CO₂, CH₄, H₂ and H₂O with 2 independent reactions. Accordingly, CO and CO₂ methanation reaction are considered, eq. 14 and 15 respectively:



The kinetic of CO methanation were derived from Sughrue, 1982 while that of CO₂ methanation from Weatherbee, 1982.

First of all, a simulation has been carried out at a constant temperature of 600K (which is within the range of validity of experimental data) and with the same feed to check if the methanation reactions are close to equilibrium. From the results we have concluded that simulation at equilibrium or using kinetics lead to similar values.

Three process schemes have been developed to overcome the issue of methanator temperature control. All simulations have been carried out at equilibrium exploiting the concept of recycling as a method for temperature control in methanation reactor. Also, to control the temperature the H₂/CO molar ratio is set below the stoichiometric value (2 instead of 3).

Informations about catalyst was relevant for process simulation conditions. Typical reaction temperatures for Ni-methanation catalysts are in the range 240-500°C, or with special stabilized Ni catalyst maximum temperature can be 700°C. Recommended pressures are higher than 20 bar (Odermatt, 2008). In the following simulations on methanation it has been accepted 260°C as inlet temperature and 500°C as maximum temperature at the exit of the reactor.

2.1.1. Configuration processes for methanation

Figure 2 shows one configuration. In this scheme syngas from cooling and purification section is sent to methanation section. The purification section is an AGR unit, in this case a Rectisol® plant (Rectisol® process is used for acid gas removal, Preston, 1981, in order to remove the carbon dioxide). This stream of syngas is splitted into three streams. The first is sent to the first methanator together with part of the outlet stream from this reactor which is recycled by using a compressor. The part not recycled is sent to the second methanator with fresh syngas and then, in a similar way, the outlet from this second reactor is sent to the third methanator with a part of fresh syngas. Finally the exit from the third methanation reactor is sent to a cooling section and then to a unit to remove carbon dioxide, then the gas is dried and the SNG product is recovered.

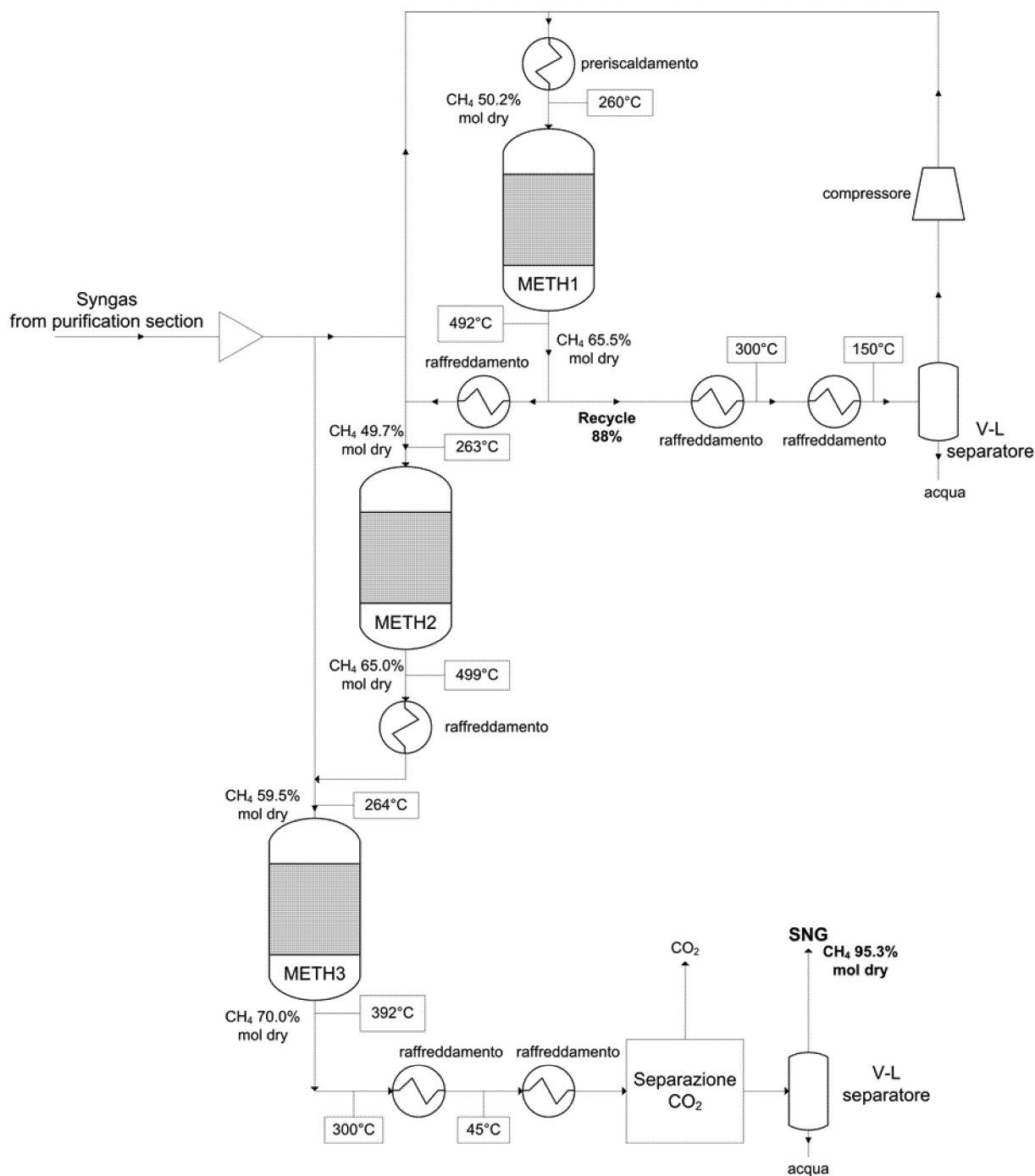
Two are the main disadvantages of this system. First, many AGR systems are needed: one unit at the output of gasifications section in order to remove CO₂ but especially H₂S, which is a poison for the methanation catalyst, a second one at the output of shift reactor and a final unit to separate the product, i.e. SNG, from carbon dioxide. The second disadvantage, which is the same for other next configurations, is the use of a compressor, which represents a complication in the plant, and a relevant additional energy consumption.

The scheme for configuration B is similar to the previous one with a difference. The water condensed and recovered from the product (SNG) is sent, after being pumped, partly to a second methanator, for another part to a third methanator, while the rest is purged out of the system. In this way the inert content in the streams sent to the reactors is higher and allow to control the temperature inside them.

Disadvantages of this second configuration are similar to the first one: many AGR systems are needed, and the presence of the compressor. But the main problem is about the water injection system, because liquid water

cannot be directly injected into the reactor owing to catalyst deactivation. An indirect injection system should be used, together with other feeds that allow water to vaporize before the stream is sent to the reactor.

Figure 2: Scheme of the methanation plant (configuration A).



The third configuration proposed (configuration C) is also similar to the second one with a difference. The second recycle is not the water condensed and recovered from SNG but part of the SNG produced is sent to the compressor together with the outlet of the first reactor. In this way the two streams are mixed and then

divided and sent partly to the first methanator, partly to the second and third methanators, and a final part exits the system as product. In this way the inert content (i.e. the products) in the inlet stream to the reactors is higher, and will allow to control the temperature inside. Disadvantages of configuration C are the same as for the first one. Additionally, in this scheme the power needed to run the compressor is higher than previous two (approximately three times higher) because a large gas flow rate is recycled.

The proposed schemes take advantages of the fact that working with a H_2/CO molar ratio lower than the stoichiometric one, is a safe method to control the reactor temperature. The inert recycle is the key factor, but many reactors in series are needed to obtain acceptable conversion of CO and CO_2 . The best solution would be to have a process that works without the use of the compressor, thereby reducing both the plant complexity and the operative costs.

3. SIMULATION RESULTS

3.1 Gasification section

Feedstock to the dual bed gasifier is petcoke (composition from Nagpal *et al.*, 2005 and reported in Table 1).

Table 1: composition of petcoke (Nagpal *et al.*, 2005).

Proximate analysis	% mass ar (as received)	Ultimate analysis	% mass dry
Fixed carbon	80.6	C	89.23
Volatile matter	9.6	H	3.59
Water	9.3	O	0.10
Ash	0.5	N	1.35
		S	5.22
		Ash	0.50

Results of simulation of the dual bed taking into account kinetics and mass transfer are shown in Table 2, where the compositions of the syngas produced is reported, and in Table 3, where the comparison of the performances between dual bed gasifier simulated is shown, taking into account both kinetics and dual bed calculated at equilibrium.

Table 2: composition of the syngas produced by the dual bed gasifier (calculated with kinetics).

	% mol (dry)
H_2	54.8
CO	27.4
CO_2	12.6
CH_4	3.9
H_2O	-
N_2	0.3
H_2S	1.0
NH_3	0.1

In summary, 223.0 t/h of steam and 100.0 t/h of petcoke are fed to the gasifier and roughly 4.7 t/h of unreacted char are recycled to the combustor; also, the combustor is fed with 46.3 t/h of coal, together with 755.3 t/h of air.

Table 3: performances comparison between dual bed with kinetics and dual bed at equilibrium.

	Dual stage gasification (KINETICS)	Dual stage gasification (EQUILIBRIUM)
H ₂ /CO molar ratio	2.0	2.0
CGE % (*)	83.4	87.4
Char conversion (gasifier) %	94.1	100.0
kg CO ₂ /kg H ₂ +CO	1.9	1.7
kmol H ₂ +CO/kmol C _{total}	1.2	1.2
Inerts/C _{total} (weight basis)	52.1	50.5
Duty required by gasifier (MW)	293.7	271.5

(*) CGE= cold gas efficiency, defined as the ratio between the energy content in the product and the energy content in the feed, based on lower heating value.

With respect to the equilibrium simulation, when taking into account the kinetics not all of the char is converted into syngas, so it must be recycled to the combustion to consume it all. Since a large amount of carbon has anyway to be sent to the combustion section, the degree of petcoke conversion in the gasifier section might be reduced to optimize the scheme. The comparison was arbitrarily targeted to producing a syngas with an equivalent energy content, based on the lower heating value.

Dual bed simulation using the kinetic model showed a general decrease in performance compared to the dual bed simulation with the equilibrium assumption. The heat needed for gasification at equilibrium condition is lower by about 8.2% if compared to the case with the kinetics. Also, due to the increased thermal power required by the gasifier with kinetics, an higher mass ratio between sand and char is needed.

For the same reason, the cold gas efficiency is lower (83.4%) than that obtained at equilibrium conditions (87.4%). Nevertheless, the value of cold gas efficiency remains high and similar to that of a conventional gasification with oxygen; this is due to the effect of the lower operating temperature.

3.2 Methanation section

Results for the simulation of methanation section are summarized in Table 4, with reference to scheme A.

Table 4: results for the configuration A proposed and simulated for the methanation section.

	Configuration A
CGE (from syngas to SNG)	81.2%
CGE (from coal to SNG)	67.7%
kg CO ₂ /kg SNG	2.2
kg CO ₂ /MJ SNG	0.044
Mass yield % (kg SNG/kg petcoke)	39.7

This process has very good values of performance parameters. The product yield is similar to that of a conventional Coal-to-Liquid (CTL) process (Sudiro, 2007) but the carbon dioxide emissions are about one half (2.2 versus 4.66 of a CTL process), and the overall energy efficiency is higher (67.7 versus 57.4% for CTL). Overall energy efficiency is also higher than in the case of a Gas-to-Liquid (GTL) process, which is 62.9% (Sudiro, 2007).

4. CONCLUSIONS

We have addressed the possibility of producing SNG from petcoke, which can easily enter the existing pipeline networks and be used both for transport sector, industrial and domestic use.

An alternative to conventional coal/petcoke gasification has been evaluated in order to avoid the use of pure oxygen and to reduce the overall CO₂ emissions. The process flow-sheets considered are based on dual bed reactors scheme: a gasifier and a combustor, which are thermally coupled by the circulation of an inert solid. Syngas produced can be the feedstock for both synthetic fuels (liquid or gaseous) production and for power generation. The cold gas efficiency of the dual bed system (83.4%) is high and comparable with those typical of conventional gasification with oxygen, with the advantage of avoiding the use of pure oxygen.

For the methanation section different plant alternatives have been proposed and evaluated. In all the schemes the problem of temperature control has been solved with a proper suitable use of recycle streams.

The global process of producing SNG from petcoke has been simulated and performances of the plant were calculated. With reference to configuration A the value of product yield is 39.7%, CO₂ emissions amount to 2.2 kg per kg of SNG produced and the overall energy efficiency is 67.7%, similar to that of a conventional Gas-to-Liquid (GTL) process (Sudiro, 2007).

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