

Synthetic Natural Gas (SNG) from petcoke: model development and simulation

M. Sudiro¹, C. Zanella¹, L. Bressan², M. Fontana³, A. Bertucco¹

¹Dipartimento di Principi e Impianti di Ingegneria Chimica "I. Sorghato" (DIPIC),
Università di Padova, via Marzolo 9, 35131 Padova

²Foster Wheeler Italiana S.p.a., via Caboto 1, 20100 Corsico, Milano

³Independent Consultant

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

Then, a process to produce synthetic natural gas (SNG) from syngas was developed, facing the main issue of this process: the temperature control of the methanator.

Performances of the global process simulated with Aspen Plus™ have been evaluated, with respect to product yield, CO₂ emissions and overall energy efficiency.

1. Introduction

Nowadays there are significant opportunities for the expanded use of coal as a mean to replace imported petroleum and petroleum products for transportation fuels and chemicals by using coal-to-liquids (CTL) technology, and for the production of synthetic natural gas (SNG) from coal. The use of coal for these purposes can assure additional independence from oil imports and provide new incentives for coal production. Coal is a very available fossil fuel with a ratio between reserves and production approximately of 164 years [1]. Natural gas is a fossil fuel cleaner than coal and its exploitation has been substantially increasing; however, its price has been increasing as well, especially in the latest years, 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.

Unfortunately, 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 coal via coal gasification.

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 chemical kinetics in the reactors.

Coal particles were assumed as char. The following species were included in the model: O_2 , N_2 , H_2 , H_2O , CO , CO_2 , CH_4 , char (as graphite C), S (solid), H_2S and NH_3 . User specified non-conventional solids have been defined to represent coal and ash. Coal composition is from Nagpal et al. (2005). The Peng-Robinson equation of state with Boston-Mathias alpha function was applied as thermodynamic model.

2.1 Gasification model

The combustion and gasification steps were described as CSTR reactors; it was also assumed that, before entering gasification, pulverized coal undergoes a pyrolysis step according to which the composition of the gas entering the reactor is calculated using the simplified method described by Lee et al. (1998).

Four heterogeneous and four homogeneous reactions have been considered (data are taken from Nagpal et al., 2005, Johansson et al. 2006 and Kim et al., 2000). For the heterogeneous reactions the rate expressions consider both the chemical kinetics and the mass transfer phenomena between gas phase and char particles.

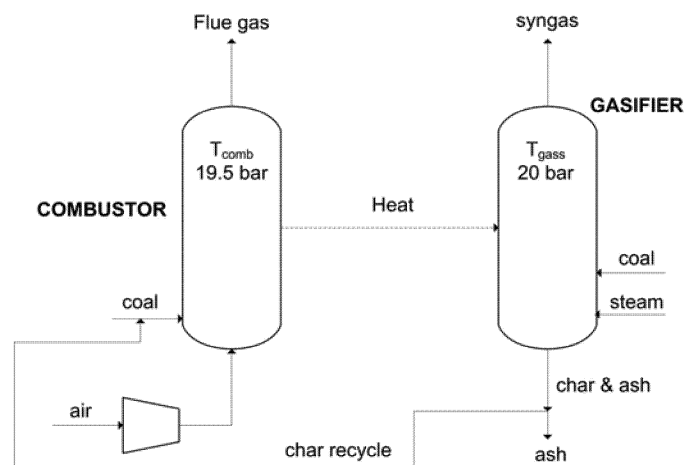
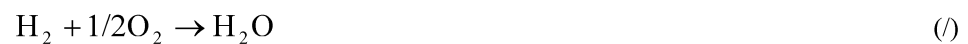
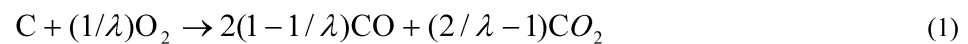


Figure 1 Scheme of the dual bed gasification process.

The model has been first checked with literature data (Higman, 2003) for conventional gasification using coal, steam and oxygen as feedstocks. Then, 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 the process.

The gasification section is followed by a syngas purification system, consisting in a Rectisol[®] unit for acid gas removal (Preston, 1981).

2.2 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 was shown that the methanation reactions get very close to equilibrium conditions and in a reasonably low residence time, with high exothermic effects. So, the problem is not how much and how fast CO is converted into CH₄ and H₂O but the increase of temperature inside the reactor.

The system involves 5 compounds: CO, CO₂, CH₄, H₂ and H₂O with 2 independent reactions. Accordingly, both CO and CO₂ methanation reactions are considered:



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. Results are shown in Table 1, from which it is possible to conclude that simulation at equilibrium or using kinetics lead to similar values. As shown in Table 1, the only difference between a CSTR and an equilibrium reactor is about the CO flow rate, which is higher in the case of kinetics (less CO is reacted). For all the other compounds the flow rate at the exit of the two reactors are very similar, and essentially the same amount of methane is produced.

Table 1 Comparison between results of the methanation at equilibrium and taking into account kinetics; reactor are at constant temperature of 600K.

	INPUT	OUTPUT Rgibbs	OUTPUT CSTR $\tau = 0.02$ s
kmol/h	16612	14576	14598
Tin (K)	533.1	533.1	533.1
Tout (K)	600	600	600
Molar flow rate (kmol/h)			
CO	33.23	0.70	21.83
H ₂	4184.57	145.76	168.19
H ₂ O	9639.94	11645.83	11642.44
CH ₄	166.12	1180.62	1173.06
CO ₂	2513.40	1530.43	1517.84
N ₂	46.51	46.51	46.51
Ar	28.24	28.24	28.24

Three process schemes have been developed to overcome the issue of methanator temperature control. All simulations have been carried out at equilibrium.

In scheme A (Figure 2) syngas from gasification section is partly sent, together with steam, to a water-gas shift reactor (isothermal at 210°C); the other part is by-passed. When the two streams (one from the shift reactor and the by-passed one) are mixed, the H₂/CO molar ratio is 3, corresponding to the stoichiometric. The two streams are both sent to a cooling section and to an acid gas removal unit (AGR) in order to remove the carbon dioxide and the water condensed, before entering the methanation section. Then the gas stream out of the AGR is split into three streams. A first one is fed to the first methanator together with part of the outlet stream from this reactor, which is recycled by a compressor. The part not recycled is sent to the second methanator with a part of 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, the gas is dried and the SNG produced can be recovered.

Scheme B is similar to A with a difference. The water condensed and recovered from the product (SNG) is sent partly to the second methanator, partly to the third methanator and partly to treatment. The temperatures in the second and in the third reactors are well controlled by the inert content in the feed streams.

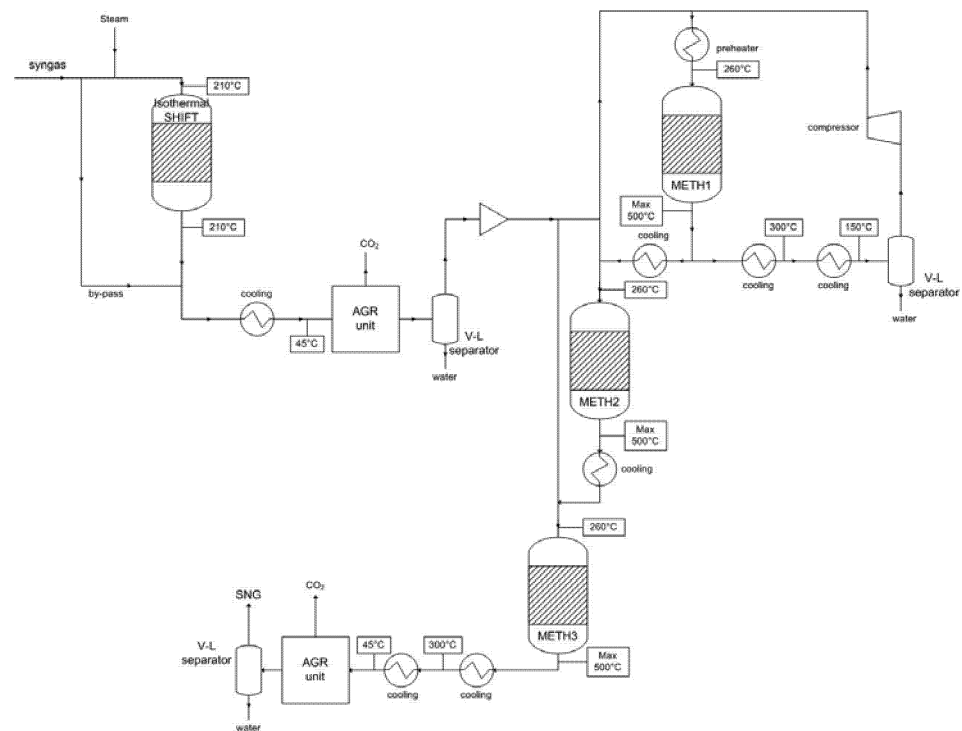


Figure 2 Scheme A developed for the methanation section plant.

Scheme C differs from scheme B because the second recycle is not the water condensed and recovered from the product (SNG) but part of the SNG produced. This is fed to the compressor together with the outlet from the first reactor. In this way the two streams are mixed, divided and sent partly to the first methanator, partly to the second methanator, partly to the third methanator, and partly to storage as final product. Doing this, the inert content (i.e. the products) in the inlet stream to the reactors is higher and allows to control the temperature inside the reactors.

3. Simulation results

3.1 Gasification section

Feedstock to the dual bed gasifier is petcoke (composition from Nagpal et al., 2005). 120 t/h of steam and 87 t/h of coal are fed to the gasifier and 15 t/h of unreacted char are recycled to the combustor; also, the combustor is fed with 13 t/h of coal, together with 300 t/h of air. The ratio between mass flow rate of inerts, circulating between the two reactors, and coal is about 35.3, considering sand as heat carrier. Results of simulation of the dual bed taking into account kinetics and mass transfer are shown in Table 2.

Table 2 Composition of the syngas produced by dual bed gasifier.

	MOLAR FRACTION
N ₂	0.002
H ₂ O	0.216
H ₂	0.473
CO	0.236
CO ₂	0.067
CH ₄	27 ppm
H ₂ S	0.002
NH ₃	0.004

3.2 Methanation section

Results for the simulation of methanation section are summarized in Table 3, referred to scheme A.

Table 3 Results of the methanation plant simulation (scheme A)

PARAMETER	VALUE
Cold gas efficiency (from syngas to SNG)	78.3%
Cold gas efficiency (from coal to SNG)	42.4%
Emissions (kg CO ₂ /kg SNG)	0.9
Mass yield (kg SNG/kg coal)	64.3%
H ₂ content in the SNG produced	5.1% molar

In the three schemes simulated the temperature is well controlled, in accordance with typical reaction temperatures accepted for Ni-methanation catalysts (BASF), which are in the range 240-500°C. The H₂/CO molar ratio is set to the stoichiometric value (3), which

is adjusted with the water-gas shift reaction. So by using a recycle, the aim of the work has been achieved. It could also be possible to control this temperature by adjusting the H₂/CO ratio in the syngas fed to the methanator.

4. Conclusions

We have addressed the possibility of producing SNG from coal, which can enter the existing pipelines and be used both for transportation, industrial and domestic use.

An alternative to conventional coal 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. For the methanation section the problem of temperature control has been resolved with a suitable use of recycle streams. The global process of producing SNG from coal has been simulated and the performance of the plant was calculated.

References

- Higman C. and Van Der Burgt, M., 2003, Gasification, Gulf Professional Publishing (Elsevier), Burlington - USA.
- Johansson, R., Thunman, H. and Leckner, B., 2006, A model for simulation of fixed bed combustion. Thesis for the degree of licentiate of engineering. Department of Energy and Environment, Chalmers University of Technology, Göteborg, Sweden.
- Kim, Y.J., Lee, J.M. and Kim, S.D., 2000, Modeling of coal gasification in an internally circulating fluidized bed reactor with draught tube, *Fuel*, 79, 69-77.
- Lee J.M., Kim Y.J., Lee W.J. and Kim S.D., 1998, Coal-gasification kinetics derived from pyrolysis in a fluidized-bed reactor, *Energy*, 23, 475-488.
- Nagpal S., Sarkar T.K. and Sen P.K., 2005, Simulation of petcoke gasification in slagging moving bed reactors, *Fuel Processing Technology*, 86, 617-640.
- Preston, R.A., 1981, A computer model of the Rectisol process using the Aspen Simulator, submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering, MIT, Dep. of Chemical Engineering.
- Sudiro M., Bertucco A., Ruggeri F., Fontana M., 2008, Improving process performance in coal gasification for power and synfuel production, *Energy & Fuels*, 22, 3894-3901.
- Sughrue, E. L. and C. H. Bartholomew, 1982, Kinetics of carbon monoxide methanation on nickel monolithic catalysts, *Applied Catalysis*, 2, 239-256.
- Ullmann's Encyclopedia of Industrial Chemistry, fifth completely revised edition, 1989, VHC Verlagsgesellschaft mbH, D-6940 Weinheim, Federal Republic of Germany.
- Weatherbee, G. D. and C. H. Bartholomew, 1982, Kinetics and mechanism of CO₂ hydrogenation on nickel, *Journal of Catalysis*, 77, 460-472.
- Web sites: [1] <http://www.eia.doe.gov/neic/infosheets/coalreserves.html>