

Calculation results of chemical thermodynamic equilibrium of produced gas

José Luiz Marão Junior

*Lithuanian Energy Institute,
Breslaujos g. 3,
LT-44403 Kaunas, Lithuania
E-mail: jose.marao@mail.lei.lt*

The chemical thermodynamic behaviour of gas tars under temperature changes in the system was evaluated. The initial composition and calorificity of the mixture were determined according to biomass and waste gasification. The chemical composition was simulated applying the Gibbs free energy thermodynamic equilibrium calculation with the help of a computational program. The obtained results were compared with the results found in the literature, identifying tar conditioning systems' characteristics and the impact of initial mixture changes at a varying air equivalence and steam-to-carbon ratios. It was found efficient to use water vapour at temperatures of 900–1050 K, whereas at lower temperatures a more intensive oxidation should be used.

Key words: gasification, tar, gibbs energy, thermodynamic equilibrium

1. INTRODUCTION

Recently, gasification of non-food biomass and waste has gained a new potential as one of the new energy sources that reduce dependence on fossil fuels. Gasification is a simple and reliable way to produce a calorific fuel. However, gasification systems need to meet equipment and environmental requirements to avoid unwanted byproducts such as tars, particulates, alkali, sulfur and ammonia [1]. In the present study, the role of particulates and tars in gas producers was investigated. Table 1 shows tar and particulate level requirements of fuel characteristics according to equipments and end use devices.

In the literature, there are several definitions of tars. In this study, tars were considered as condensable organic compounds with a viscous black or dark brown liquid aspect. It is mainly formed by a mixture of aromatics such as toluene, phenol, two- and more ring polycyclic aromatic hydrocarbons (PAH) such as naphthalene and anthracene [2, 3].

On the one hand, separation of tar and particles from synthetic fuels to achieve end-use requirements can be done with

mechanical separators such as cyclones, bag filters, scrubbers and electrostatic precipitators. On the other hand, when tars are eliminated from synthetic gases, the fuel heating value can be drastically reduced; this means that these losses may not justify the use of such equipment. So, there is a need to find methods and processes to re-use the heating value of tars by chemically changing its composition, cracking them into smaller fractions such as permanent gases which are better burnable, do not recombine at temperature changes and do not damage end-use devices.

The present work considers a thermodynamic evaluation process to study the tar-conditioning behaviour. The chemical kinetic models of gaseous phase hydrocarbons can be generalized into three types: empirical, molecular and mechanistic [4]. Empirical investigations have a disadvantage due to time and cost factors and the level of uncertainty of the available equipment. Molecular models can in some cases offer quick and reliable approaches. However, only mechanistic models can represent properly a real chemical phenomenon with a high level of accuracy. But, creating reliable mechanistic models for large hydrocarbon species is very difficult and requires very extensive experimental work (depending on the number and size of species to be analyzed). Thus, considering this limitation, in this work we chose a molecular model for determining the thermodynamic equilibrium of a gas phase mixture of hydrocarbon, nitrogen and tar species and its relation to temperature.

Table 1. End-use devices and process equipment requirements [1, 2]

End-use	Tar, mg/Nm ³	Particulate, mg/Nm ³	Particulate size, μm
Internal combustion engine	10–50	50	–
Gas turbine	5	15	5
Synthetic gas production	–	0.02	–
Compressors	50–500	–	–

2. METHODOLOGY

To solve the problem of chemical equilibrium, the program code *Cantera* was chosen [5] which uses the Villars–Cruise–Smith algorithm. It was chosen because it's well situated to handle multiphase problems [6, 7] by adding and removing condensed species from the simulation at each step of calculation. It solves the Gibbs minimization energy $G(\xi)$ problem with constant pressure and temperature as a function of reaction-extent variables or stoichiometric-vector multipliers ξ :

$$\frac{\partial G}{\partial \xi} = 0. \quad (1)$$

This equation is the same as the equilibrium condition chemical formulation:

$$\Delta G \equiv N^T \bar{\mu}(\xi) = 0, \quad (2)$$

where $\bar{\mu}$ is the chemical-potential vector with entries μ_i , and N^T is the transposed N stoichiometric matrix:

$$N = N_s \times N_r, \quad (3)$$

where N_s is a table with entries v_{ij} representing the stoichiometric coefficient of species i ($i = 1, 2, \dots, N_s$) in the stoichiometric vector j ($j = 1, 2, \dots, R$), and N_r is a column of stoichiometric vectors,

$$R = N'_s - N_e, \quad (4)$$

N'_s is the number of species, excluding inert species, and N_e is the number of atomic elements.

A linear transformation to relate reaction variables to composition variables which constrain the mass conservation of the atomic elements with N is

$$n = n^* + N\xi, \quad (5)$$

where n^* is a known set of mole numbers initiated with guesses.

The equilibrium composition n and the minimum $G(\xi)$ are the results of m iterations using a second-order variation scheme ($\partial^2 G / \partial \xi^2$) for a previously selected set of gaseous, liquid and solid species. The mole number of these species is predicted by a simplex calculation satisfying mass constraints.

Basically, a quadratic approximation of the functions $Q(\xi)$ to $G(\xi)$ is constructed, matching them in terms of first derivatives $G(\xi)$ with respect to ξ and n . When the minimum of $Q(\xi)$ is achieved, it is possible to create a set of N_r linear equations represented by the Hessian matrix $H: N_r \times N_r$ in its transposed form:

$$\partial \xi = H^{-1} \mu_r. \quad (6)$$

So equations (6) and $\partial n = N \partial \xi$ can be solved; then the results of $\xi = \xi^* + \partial \xi$ and equation (5) represent the minimum $Q(\xi)$. When the new calculated values ξ and n are getting closer to the previously calculated ξ^* and n^* , it means that the minimum $G(\xi)$ is up to be achieved. Thus, a repetition of this procedure converges the solution of the equilibrium composition equivalent to the minimum $G(\xi)$. A more detailed information about this procedure is presented by Smith and Missen [8].

2.1. Problem formulation

The gas inlet for this investigation was assumed a constant source with a higher heating value (HHV) fuel 5 MJ/Nm³ including the heat of the combustion of tars. This value was chosen because it represents a typical heating value for a biomass and tire gasification unit [9].

Accordingly, the tar fraction was assumed to be a value which completes the fixed HHV of the fuel, and the nitrogen fraction refers to the amount of gas to complete the volume of the mixture. Besides, the tar species in the inlet gas was considered, to be the two-ring aromatic hydrocarbon naphthalene (C₁₀H₈).

The molar percentage of H₂ per CO in the producer gas in all investigations was assumed to be 7.1% and 9%, respectively, according to experimental results of tire gasification under the sub-stoichiometric air ratio $\alpha = 0.2$ [9]. These values were chosen to give a more realistic aspect to the tar case simulation and because they represent a case in which permanent gas fraction corresponds to about 40% of the HHV of the mixture. In such circumstances, a conditioning system is essential to achieve the optimal output in the process that uses these gases to produce electricity, for example, through an internal combustion engine.

Thus, we investigated the behaviour of tar species changing three process characteristics: thermal cracking (temperature variations), steam reforming (variations of steam to carbon ratio – H₂O/C) and partial oxidation (variations of the air equivalence ratio ER).

In addition, the following assumptions were adopted in this simulation:

- adiabatic process;
- a multiphase problem was considered, i. e. soot formation was taken into account in the calculations;
- sulfur compounds were not considered.

Besides, there is an international standard for tar sampling and analyzing [10]; it is very difficult to determine the fractions of each tar species in producer gases. So, the tar species included in this model were considered the same as tire pyrolysis experiments identified by Chen et al. [11]. Table 2 shows the chemical species included in the models.

In the model, soot was considered as an unwanted byproduct of combustion, represented by large PAH (C/H < 2) species and solid carbon. Due to this simplification, the output tar and soot were analyzed together as both are unwanted calorific products.

Table 2. Chemical species considered in the model

Group	Compounds
Hydrogen and oxygen compounds	H, H ₂ , O, O ₂ , OH, H ₂ O, HO ₂ , H ₂ O ₂ , HCO
Nitrogen compounds	N, N ₂ , NH, NH ₂ , NH ₃ , N ₂ H, NO, NO ₂ , N ₂ O, HNO, CN, HCN, H ₂ CN, HCNH, HCNO, HOCN, HNCO
Hydrocarbons	CH, CH ₂ , CH ₃ , CH ₄ , C ₂ H, C ₂ H ₂ , C ₂ H ₃ , C ₂ H ₄ , C ₂ H ₅ , C ₂ H ₆ , C ₃ H ₇ , C ₃ H ₈ , C ₄ H ₉ , C ₄ H ₁₀
Hydrocarbon – tars	C ₆ H ₆ , C ₆ H ₅ OH, C ₇ H ₈ , C ₇ H ₆ O, C ₈ H ₁₀ , C ₉ H ₈ , C ₁₀ H ₈ , C ₁₂ H ₁₀ , C ₁₃ H ₁₀ , C ₁₄ H ₁₀ , C ₁₆ H ₁₀ , C ₂₀ H ₁₂ , C ₂₂ H ₁₄ , C ₂₄ H ₁₂
Other organic compounds	CH ₂ O, CH ₂ OH, CH ₃ O, CH ₃ OH, HCCO, CH ₂ CO, HCCOH, CH ₂ CHO, CH ₃ CHO
Inorganic carbon compounds	C(s), CO, CO ₂

2.2. Program code and thermodynamic database

As mentioned before, the thermodynamic equilibrium solver used in this work was the *Cantera* program code – an open source code written in *Python* – which uses the Villars–Cruise–Smith algorithm to solve the Gibbs chemical equilibrium problem. The relative error tolerance considered was 1×10^{-9} and the log level = 4. *Microsoft Excel* was used as a post-processor.

The database evaluated in the calculations was the *Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion* [12], containing thermodynamic properties of 508 molecular species; however, only those presented in Table 2 were considered important for this investigation. Originally this database is not on the format used in *Cantera*, so it had to be converted to this format by the author of this paper.

3. RESULTS AND DISCUSSION

The thermodynamic equilibrium results were calculated according to several reactor-simulated temperatures varying from 600 K and 1600 K. These temperatures were chosen because usually tar mixtures condense at temperatures below 600 K, and higher temperatures are limited by the process economic and reliability factor. The expected tar cracking re-

actions should occur due to the process called thermal cracking [3, 13, 14], which can be represented as:



It was observed that the maximum HHV remained stable after reaching certain temperatures. The beginning of heat value peaks was identified in the range 900–1000 K and 900–1100 K in the cases of enhancing thermal cracking with H₂O/C and ER, respectively. Furthermore, these values range from 4.5 to 5 MJ/Nm³ and from 2 to 4.5 MJ/Nm³, respectively, in H₂O/C and ER cases. The maximum HHV value is conversely proportional to the process H₂O/C and ER (Figs. 1 and 2).

From the point of view of cracking tars, ER cases eliminate tars considerably at temperatures of 900–1000 K (Fig. 3), while H₂O/C cases present similar results in temperatures of 900–1050 K (Fig. 4). Increasing the ER ratio resulted in an expressive tar fraction reduction at temperatures up to 800 K, while increasing the H₂O/C ratio showed a weaker influence.

Steam reforming positively enhances the fraction of permanent gases. Comparing the cases of H₂O/C ratios 0.1 and 0.3, the fractions of H₂, CO and CH₄ increased, respectively, from 23.5% to 80%, from 10.8% to 28.5% and from 22.9% to 63.8%, depending also on the equilibrium temperature.

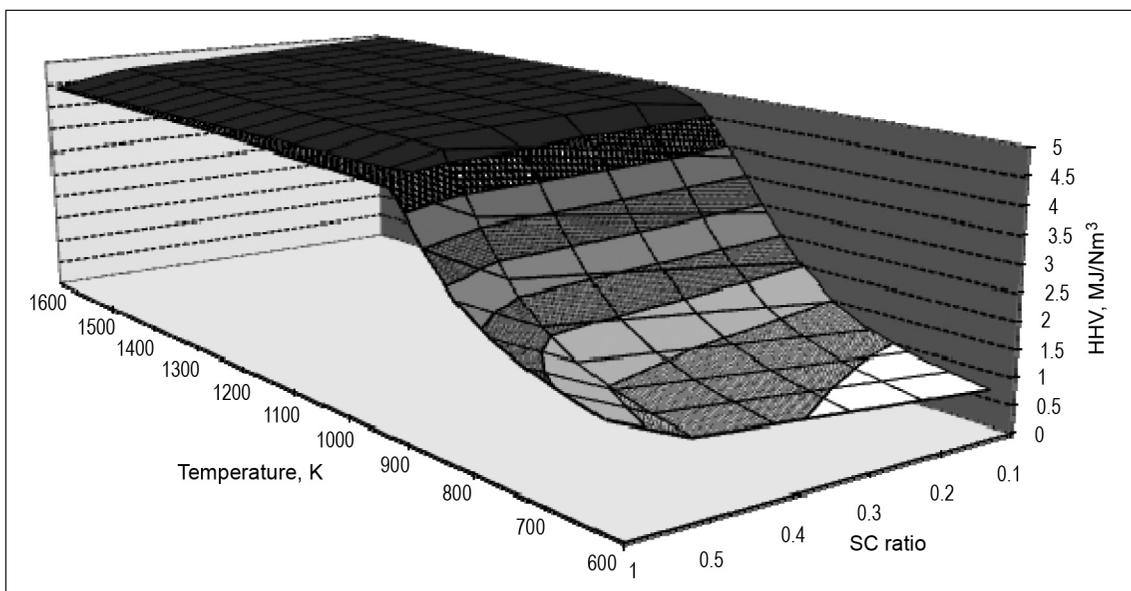


Fig. 1. The effect of H₂O/C ratio on HHV (discounted HHV from tars as a function of temperature)

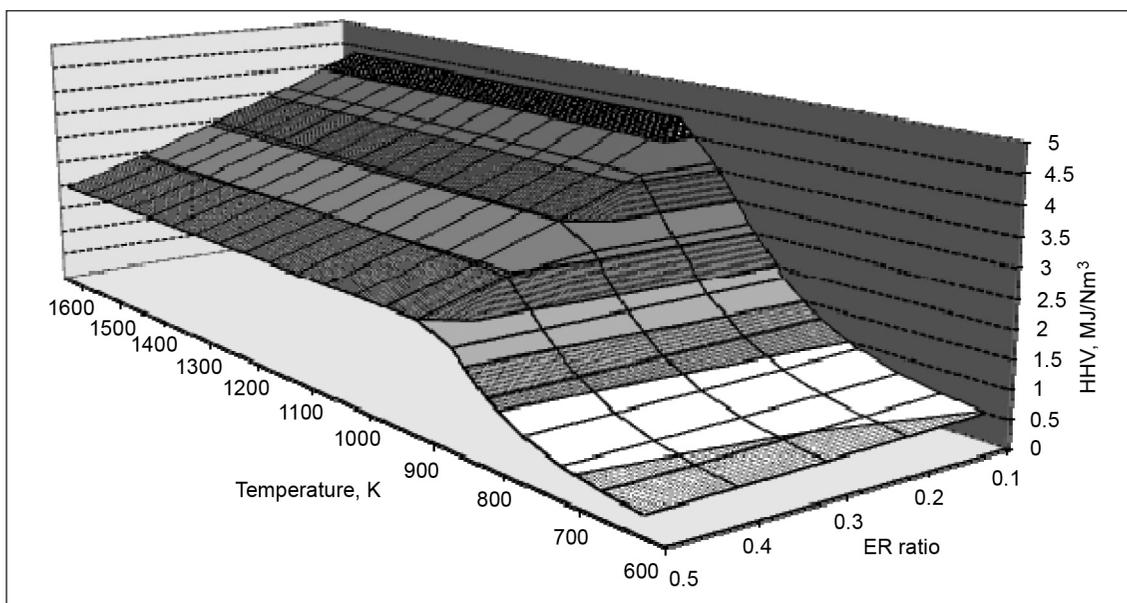
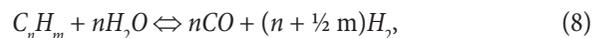


Fig. 2. The effect of ER ratio on HHV (discounted HHV from tars as a function of temperature)

At lower temperatures, the use of steam in cracking seems to enhance the gas calorific value; however, an analysis of a similar gas composition without steam shows a higher HHV when the cracking process proceeds at higher temperatures. This can indicate that steam can be used to enhance tar cracking (equation 8) and gas calorific enhancement at lower temperature tar conditioning systems. This effect is known as a water shift reaction and was discussed by several authors, e. g., by R. Zevenhoven [3] and A. Jess [14]. As this reaction is relatively slow, carbon monoxide conversion is rather promoted by a water shift reaction (equation 9) which has an equilibrium on the right side of the equation. This situation is favorable for producing H_2 -

rich synthetic gases to be used, for example, in fuel cells together with CO_2 capture mechanisms. The tar and carbon monoxide water shift reaction can be represented by the following reactions:



A significant aspect of steam reforming is that it presents a temperature zone in which it may produce optimal results for tar cracking. Such perception is important to define the ranges in which each process can operate.

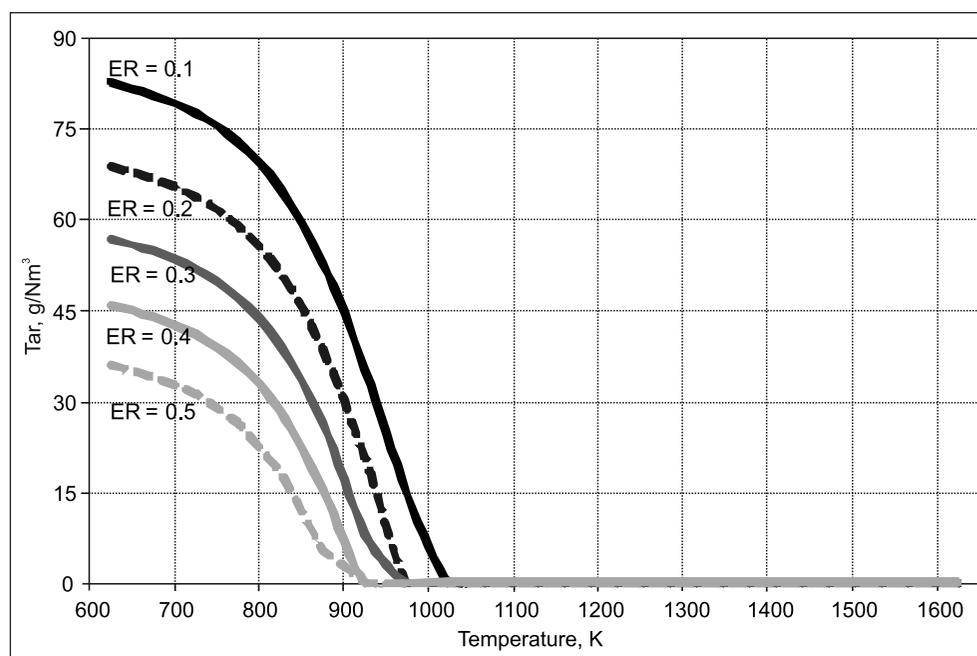


Fig. 3. Effect of ER ratio at the sum of tar species in equilibrium state as a function of temperature

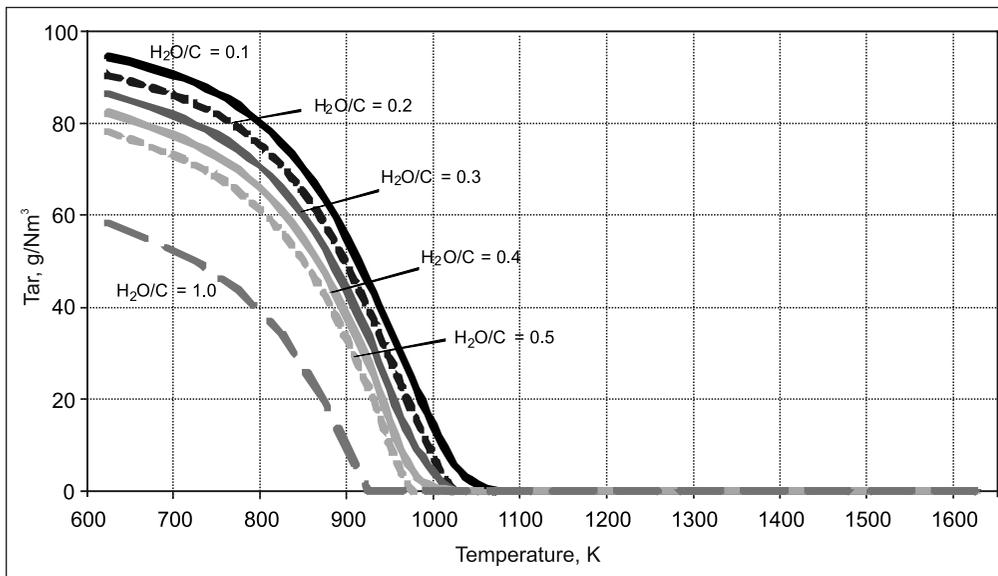


Fig. 4. Effect of H_2O/C ratio at the sum of tar species in equilibrium state as a function of temperature

In Fig. 5, it is possible to identify the possible influence of steam on hydrocarbon polymerization. At a temperature up to 800 K, steam influences tar cracking, while at temperatures higher than 950 K a tendency of polymerization of hydrocarbons into heavier species and soot is observed. The polymerization of tars is identified by polycyclic aromatic hydrocarbon growth through the HACA (hydrogen abstraction and C_2H_2 addition) mechanism [15]. This reaction releases H_2 and consumes acetylene. At temperatures over 1350 K, tars start cracking again; however, these temperatures are not reliable for conditioning systems from the economical point of view.

Formation of heavy tars represented by PAH polymerization and soot formation was observed in the mixtures investigated when the CO_2 fraction in the initial gas was zero (Figs. 5, 6). Depending on the application, such event can be positive for the system, as it consumes hydrocarbons and releases H bonds, resulting in a cleaner gas after mechanical separation, which can increase the lifetime of the equipment,

especially of internal combustion engines and turbines. However, in case of the direct use of producer gas in furnaces, it is clear that polymerization will promote a decrease of the calorific value and system output. Steam reforming in cases with CO_2 absence in the initial gas showed evidences of promoting hydrocarbon polymerization and soot formation at temperatures higher than 1000 K (Figs. 5, 6) and decreasing the equilibrium gas heating value. This may indicate that CO_2 plays an important role in the process and thus should be an optimal point between ER and H_2O/C ratios that represent the best results for the heating value and tar reduction. This may also represent cases when gasification and tar cracking are done in a single stage, using both steam and air as oxidants.

Partial oxidation, investigated by M. P. Houben [13] and other authors, can be a less expensive alternative for tar reduction than others previously mentioned, as it releases heat and consequently requires lower amounts of external heat to promote tar cracking. However, in this investigation it seemed to

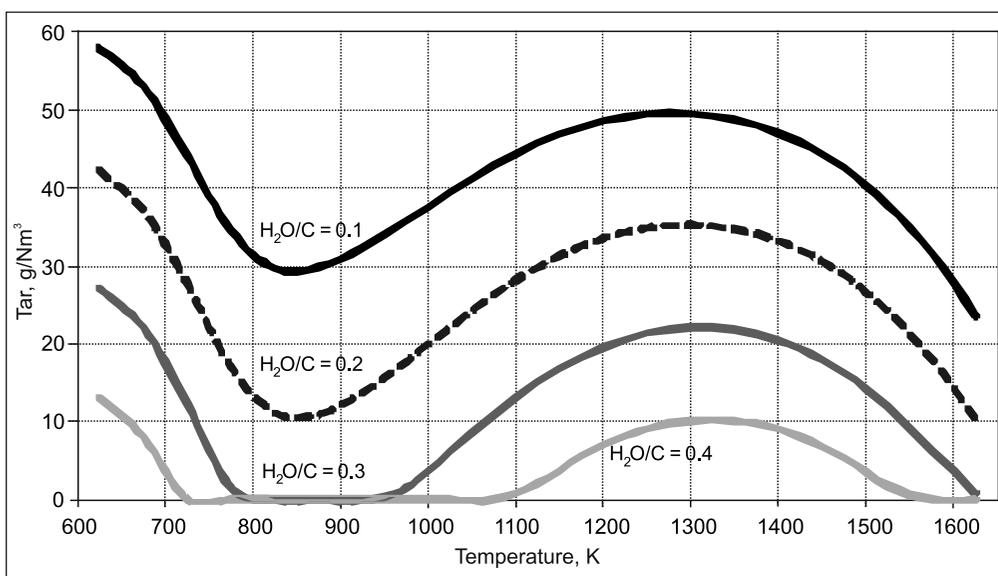


Fig. 5. Effect of H_2O/C ratio at the sum of tar species in equilibrium state as a function of temperature (case with zero initial CO_2 fraction)

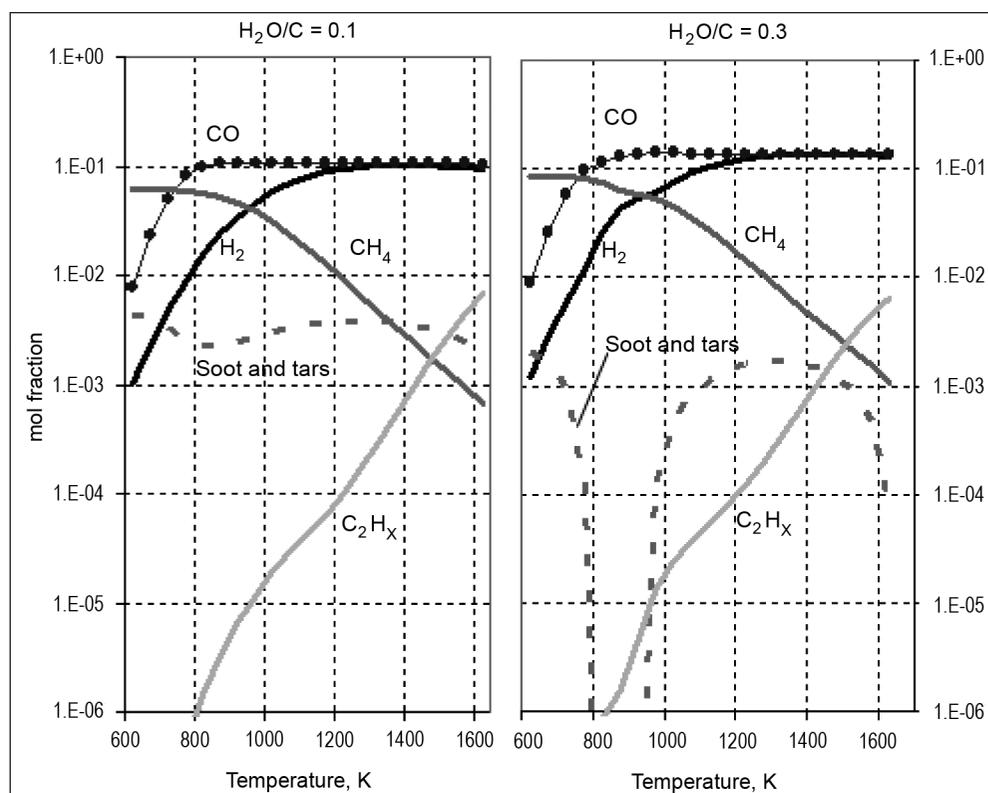


Fig. 6. Equilibrium state of product gas composition (case with zero initial CO_2 fraction)

be not reliable as it reduced considerably the heat value of the gas (Figs. 2, 3). However, before making the anticipated conclusions, it was necessary to investigate economically and compare the losses from partial oxidation with the heat necessary to run the thermal cracking reactor. Probably a life cycle cost analysis would present interesting results in this case [16].

In order to analyze the economy of each system, it is also necessary to consider the residence time required for each scenario to reach the equilibrium or close to it. With this information, it is possible to dimension the equipment and to estimate material and power consumption.

Further investigations should be done using experimental data and the Arrhenius reaction rates in order to enable a more realistic timeline-based solution with the possibility of a better estimation of costs involved in the processes.

There are also some cases, such as the use of producer gas in cement and lime kilns, when no tar treatment is required because it is used as a secondary fuel in processes with long residence times and at the temperatures that are able to crack heavier hydrocarbon and tars. Nevertheless, in the case of utilization as a fuel in internal combustion engines and turbines, tar conditioning is essential to enhance gas quality and equipment lifetime.

4. CONCLUSIONS

The chosen program code and algorithm showed to be adequate for a predictive simulation of producer gas composition behaviour over three processes: thermal cracking, steam reforming and partial oxidation.

According to the equilibrium model studied, partial oxidation, represented by the air equivalence ratio, showed a good capability of reducing tar; however, when analyzing the gases after equilibrium state, the gas calorific value (HHV) was much lower than of the input gas even at a temperature equilibrium over 1000 °C, which may indicate that this alternative is not reliable enough as compared with other alternatives for tar cracking.

Steam utilization in thermal cracking reactors gave the best simulated results for the calorific value discounted the heat from remainder tars. Besides, tar levels are among the highest in the analyzed cases. In cases with a higher $\text{H}_2\text{O}/\text{C}$ ratio ($\text{H}_2\text{O}/\text{C} = 1$), the calorific value of the gas increased at lower equilibrium temperatures, but at higher temperatures it decreased.

Depending on fuel utilization, the polymerization observed in the case of steam reforming can be positive, as it increases the H_2 fraction and consumes carbon.

Abbreviations

HACA – hydrogen abstraction Acetylene absorption,
 HHV – high heating value, MJ/Nm^3 ,
 ER – air equivalence ratio,
 $G(\xi)$ – gibbs minimization energy,
 PAH – polycyclic aromatic hydrocarbon.

Received 4 March 2010

Accepted 21 May 2010

References

1. Rezaian J., Cheremisinoff N. P. *Gasification Technologies: a Primer for Engineers and Scientists*. USA: CRC Press, 2005. P. 165–265.
2. Milne T. A. et al. *Biomass Gasifiers "Tars": Their Nature, Formation and Conversion*. NREL/TP-570-25357. USA, 1998.
3. Zevenhoven R., Kilpinen P. *Control of Pollutants in Flue Gas and Fuel Gases*. 2nd edn. 2002. P. 6.16–6.19.
4. Ranzi E. et al. *Progress in energy and combustion science*. 2001. Vol. 27. P. 99–139.
5. Goodwin D. *Cantera: Chemical Kinetics Software Package*. California Institute for Technology – Caltech. www.cantera.org (accessed in December 2008).
6. Klimczyk P., Benko E., Lawniczak-Jablonska K., Piskorska E., Heinonen M., Ormaniec A., Gorczynska-Zawislan W., Urbanovich V. S. Cubic boron nitride–Ti / TiN composites: hardness and phase equilibrium as function of temperature. *Journal of Alloys and Compounds*. 2004. Vol. 382. P. 195–205.
7. Staniewicz-Brudnik B., Majewska-Albin K., Trybalska B. The effect of Ni, ZrB₂ and MoS₂ additives on certain physico-chemical and mechanical properties of special glasses in the ZnO–PbO–B₂O₃–SiO₂ system. *Journal of Materials Science*. 2005. Vol. 40. P. 2541–2546.
8. Smith W. R., Missen R. W. *Chemical Reaction Equilibrium Analysis. Theory and Algorithms*. New York: Wiley-Interscience, 1982; reprinted, with corrections, Malabar: Krieger, 1991.
9. Schmidths H. The pre-combustion chamber for secondary fuels – development status of a new technology. *Proceedings of the Cement Industry Technical Conference*. IEEE-IAS/PCA. P. 207–218.
10. Van de Kamp W. et al. Tar measurement standard for sampling and analysis of tars and particles in biomass gasification product gas. *Proceedings of the 14th European Biomass Conference & Exhibition*, France, 2005.
11. Chen S. J. et al. Emissions of polycyclic aromatic hydrocarbons (PAHs) from the pyrolysis of scrap tires. *Atmospheric Environment*. 2007. Vol. 41. P. 1209–1220.
12. Burcat A., Ruscic B. *Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion with Updates from Active Thermochemical Tables*. Argonne National Laboratory, USA; Technion, Israel Institute of Technology, September 2005.
13. Houben M. P. et al. *Tar Reduction Through Partial Combustion of Fuel Gas*. doi:10.1016/j.fuel.2004. 2005. Fuel 84. P. 817–824.
14. Jess A., Depner H. Thermische und katalytische Aufarbeitung von Rohgasen der Vergasung und Verkokung fester Brennstoffe. *Chemie Ingenieur Technik*. 1997. Vol. 69. P. 970–973.
15. Frenklach M., Wang H. *Soot Formation in Combustion*. Berlin: Springer-Verlag, 1994. P. 165.
16. Barringer H. P. A life cycle cost summary. *Proceedings of International Conference of Maintenance Societies*. Australia, 2003.

José Luiz Marão Junior

GENERATORIŲ DUJŲ CHEMINĖS TERMODINAMINĖS PUSIAUSVYROS SKAIČIAVIMO REZULTATAI

Santrauka

Šiame straipsnyje įvertintas dervos lašelių generatoriaus dujose cheminis skaidumas, kintant temperatūrai sistemoje. Remiantis literatūra apie biomasės ir atliekų dujų fiksaciją buvo pasirinkta pradinio mišinio sudėtis ir kaloringumas. Programiniu paketu skaičiuojant termodinaminę pusiausvyrą cheminė sudėtis buvo modeliuojama, taikant Gibbso laisvosios energijos minimumą. Skaičiavimai atlikti esant skirtingiems oro pertekliaus koeficientams ir vandens garo kiekiams. Gauti skaičiavimo rezultatai, nustačius dervos lašelių charakteristikas ir pradinio mišinio pokyčio įtaką esant skirtingam oro pertekliaus koeficientui ir garo / anglies santykiui, buvo palyginti su literatūroje aptiktais rezultatais. Gauta, kad vandens garų efektyvu naudoti esant 900–1050 K temperatūrai, o žemesnėse temperatūrose tikslingiau intensyvinti oksidaciją.

Raktažodžiai: dujų fiksavimas, dervos lašelis, Gibbso energija, termodinaminė pusiausvyrą

Жозэ Луиз Мароо Джуниор

РЕЗУЛЬТАТЫ РАСЧЕТОВ ХИМИЧЕСКОГО ТЕРМОДИНАМИЧЕСКОГО РАВНОВЕСИЯ СИНТЕТИЧЕСКОГО ГАЗА

Резюме

В этой статье оценивалось химико-термодинамическое расщепление капель дегтя при разных температурах в системе. Согласно литературе, анализируя образцы газов, обретенных при газификации биомассы и отходов, были определены изначальный состав и теплота сгорания смеси. Для расчета термодинамического равновесия программным кодом было проведено моделирование химического состава, применив минимум свободной энергии Гиббса. Полученные результаты расчетов были сопоставлены с опубликованными результатами других авторов, идентифицируя характеристики системы кондиционирования капель дегтя и влияние изменения изначального состава смеси при разных коэффициентах избытка воздуха и отношениях пар / углерод. Получено, что применение водяного пара наиболее эффективно при температурах 900–1500 K, а при более низких температурах целесообразно использовать более интенсивное окисление.

Ключевые слова: газификация, капелька дегтя, энергия Гиббса, термодинамическое равновесие