Research article

Modeling of tar thermal cracking in a plasma reactor

F. Marias [a,*], R. Demarthon [a], A. Bloas [b], J.P. Robert-arnouil [b]

[a] Laboratoire de Thermique Energétique et Procédés, Université de Pau et des Pays de l'Adour, Pau, France
[b] Europlasma, Pessac, France

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ABSTRACT

This paper deals with the theoretical modeling of a high temperature reactor devoted to the thermal cracking of tars contained in a gas coming from a biomass gasifier. The aim of this paper is to give an insight into the chemical reactions that take part in this conversion but also into the reactions that may occur in such environment. The investigation is carried on using the simplest continuous reactor configuration that exists (completely stirred tank reactor), which allows to address the effects of chemical reactions without taking into account the mixing. This paper presents the complete set of reactions taken into account. It can also be noticed that this model also describes possible gasification of char particles entering the reactor. An in-depth analysis of the weight of the involved reactions is proposed for the nominal conditions of the reactor operation. The results of the model are also compared to the results of a previous one, highlighting the benefits of the actual model. These results are also compared to values obtained during operation of a pilot plant. Finally, the influence of five of the operating parameters of the reactor is theoretically investigated. It shows that these parameters can have an important impact on reactor operation, but also that conditions can be found that always lead to a conversion of at least 95% of the incoming tars.

1. Introduction

Because of the fossil resource depletion and because of the increasing carbon dioxide content within the atmosphere, the use of alternative fuels for the production of heat, electricity and conventional fuels is expected to increase in the coming future. In order to convert this alternative fuel into more conventional and standard energy carriers, gasification is often used as a preliminary step to convert the initial solid and heterogeneous supply into a synthesis gas that could in turn be burnt into boilers, internal combustion engines, gas turbines or used as a feedstock for other molecule synthesis (methanol, liquid fuels, methane, hydrogen …). However, depending on the technology used for gasification, the gas resulting from this step may contain important amount of tars that need to be reduced before being used.

Europlasma Company is developing a multi-stage gasification process named CHO-Power, which relies on a fixed bed where gasification of the incoming solid material (waste, biomass) is processed and on a reactor where tars held in the gas are converted into lighter molecules. This upgrade is based on the use of high temperature produced by the plasma, which transforms the incoming and low quality gas into a high-purity BioSynGas. Whereas in conventional cleaning gas processes the calorific value of the tars is extracted from the cleaned gas, it is kept in the present process, since heavy organic molecules and possible unreacted solids are converted into lighter fuel molecules. This

conversion thus leads to an increase in the calorific value of the output gas. This reactor is called Turboplasma® [1]. The design of this reactor mainly relies on the use of CFD, combined with a chemical model that describes the transformation of a product gas containing main species such as CO, CH_4, N_2, CO_2, but also tars such as naphthalene, toluene and benzene at high temperatures [2–4]. The use of plasma state to reach the high temperature required for this thermal cracking has also been investigated by Advanced Plasma Power (APP) in the UK, and Plasco Energy Group Inc., in Canada and is still under theoretical investigation [5–6]. The system presented in that study differs from AAP's one since the torch which is in use in Europlasma's Process is of the non transferred type whereas it is of the transferred type in the case of APP.

The scope of this paper is to present an evolution of the former chemical model that was used in the design procedure of the reactor [2–3]. The improvement of this chemical model has been performed in three main directions:

- Inclusion of the chemical pathway that leads to the formation of soot from thermal degradation of methane,
- Inclusion of phenol as a model compound in the mix of tars coming from the gasifier and of its degradation,
- Inclusion of char solid particles in the gas coming from the gasifier and of its gasification reaction.

In the first section of the paper, the general motives that have led us to modify the first model are presented. Then, in the second section, the

* Corresponding author.
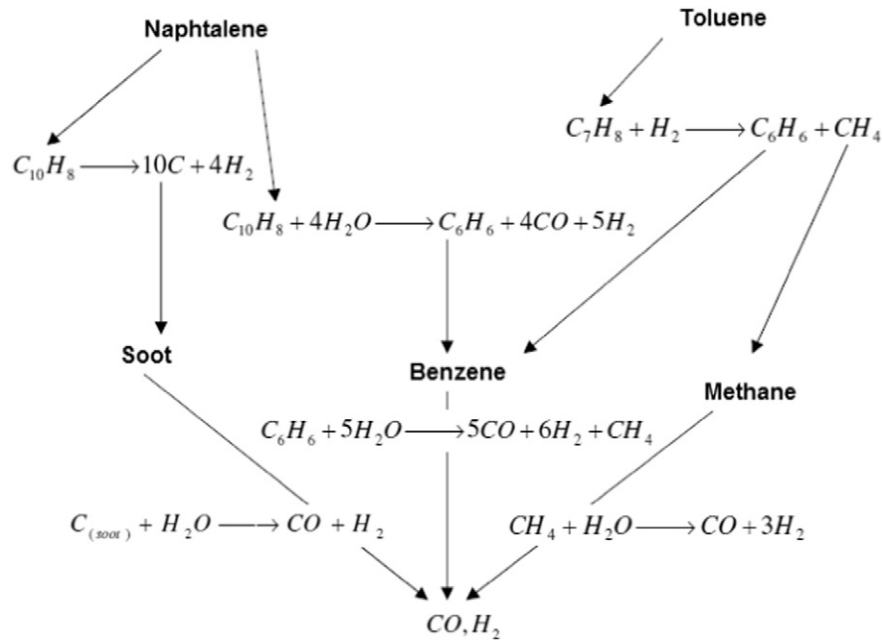 E-mail address: frederic.marias@univ-pau.fr (F. Marias).

Fig. 1. Reactions taken into account in the first model to represent the thermal cracking of tars [2–3].

evolutions of the chemical model will be presented and detailed. The overall set of reactions taken into account as well as the associated kinetics will be given. The reactions will then be introduced into an ideal model of reactor, the Completely Stirred Tank Reactor (CSTR) and the corresponding equations will be derived at this point. Some information regarding the solving procedure will be given in the third section and then, in the fourth section, the results of the model will be presented. In the case of nominal operation, the main differences between the first model and the improved one will be explained, and then, an in-depth analysis of the results of the new model will be presented. The results of the actual model will also be compared to experimental ones obtained at pilot plant scale. The influence of the operating parameters on the reactor operation will also be discussed and finally a conclusion will be presented.

2. Motives

Plasma state can drastically influence the kinetics of any reaction because of the unique properties of the reacting atmosphere it creates (free radicals, ions, excited molecules, high temperature). Hence its benefits on tar cracking are expected to be important. However, in the Turboplasma reactor, it is not possible for the gas to be upgraded to interpenetrate the plasma jet because of the high speed of the plasma leaving the torch. This is the reason why we have chosen to neglect

the chemical effect of the plasma and chosen to take into account the high temperature effects only.

As mentioned in the Introduction, the model, which is presented here, is an evolution of a former one [2–3]. The modifications can be classified into two categories: the ones concerning the reactions occurring within the homogeneous gas phase (even though they may produce soot) and the others associated to the presence of small solid and reactive particles of char entering the reactor with the gas to be cleaned.

2.1. Homogeneous reactions

One of the main drawbacks of the first model is associated to the fact that the soot produced by the thermal degradation of methane is not taken into account. Indeed, even though methane is a stable molecule, its thermal degradation has been widely studied in the literature [7–14]. In order for the model to be used as a design tool for industrial reactors, this possible degradation must be taken into account since it may also lead to the generation of soot that can prevent further downstream use of the gas.

In the first model, the tars that may be present in the product gas coming from the gasifier were lumped into three model compounds: naphthalene, toluene and benzene. Naphthalene was chosen as a representative of the third class since it is a Polycyclic Aromatic Hydrocarbon very difficult to crack in comparison to other tertiary tars; also it appears that it is often the main species found in tertiary tars resulting from

Table 1

Reactions and reaction rates used in the model Part 1: Tar degradation (concentration in $kmol \cdot m^{-3}$, rate in $kmol \cdot m^{-3} \cdot s^{-1}$, R in $J \cdot mol^{-1} \cdot K^{-1}$).

Reactions	Reaction rates	References
$C_{10}H_8 \rightarrow^1 10C_{(s,soot)} + 4H_2$	$r_1 = k_1[C_{10}H_8]^2 \cdot [H_2]^{-0.7}$ $k_1 = 5.56 \times 10^{15}, \exp(\frac{-3.6 \times 10^5}{RT})$	Jess [18]
$C_{10}H_8 + 4H_2O \rightarrow^2 C_6H^6{}_6 + 4CO + 5H_2$	$r_2 = k_2[C_{10}H_8] \cdot [H_2]^{0.4}$ $k_2 = 1.58 \times 10^{12}, \exp(\frac{-3.24 \times 10^5}{RT})$	Jess [18]
$C_7H_8 + H_2 \rightarrow^3 C_6H^6{}_6 + CH_4$	$r_3 = k_3[C_7H_8] \cdot [H_2]^{0.5}$ $k_3 = 1.04 \times 10^{12}, \exp(\frac{-2.47 \times 10^5}{RT})$	Jess [18]
$C_6H_6 + 5H_2O \rightarrow^4 5CO + 6H_2 + CH_4$	$r_4 = k_4[C_6H_6]$ $k_4 = 4.4 \times 10^8, \exp(\frac{-2.2 \times 10^5}{RT})$	Virks et al. [19]
$C_{(s,soot)} + H_2O \rightarrow^5 CO + H_2$	$r_5 = k_5[C] \cdot [H_2O]$ $k_5 = 3.6 \times 10^{12}, \exp(\frac{-3.1 \times 10^5}{RT})$	Jess [18]