NAWTEC17-2315

DESIGN OF A HIGH TEMPERATURE CHAMBER FED BY A PLASMA TORCH FOR THERMAL REMOVAL OF TARS

Alice Fourcault, Europlasma, www.europlasma.com, 21 rue Daugère, 33520 Bordeaux , France.
+33 559 407 816, alice.fourcault@etud.univ-pau.fr

Frédéric Marias, Laboratoire Thermique Energétique et Procédés, ENSGTI, Université de Pau et des Pays de l'Adour, rue Jules Ferry, BP 7511, 64075 Pau Cedex, France. +33 559 407 809, frederic.marias@univ-pau.fr

Ulysse Michon, Europlasma, www.europlasma.com, 21 rue Daugère, 33520 Bordeaux , France.
+33 556 497 000, +33 687 603 663, umichon@europlasma.com

Abstract

Biomass is one of the most important sources of renewable energy. One aim of Biomass gasification is to convert a solid feedstock into a valuable syngas for electricity or liquid fuel production. Actual industrial auto-thermal gasification processes achieve a production of syngas mainly polluted by products such as dust, nitrogen oxides, sulfur dioxide and tars. Tars remain, one of the main drawbacks in using the gasification process since they are capable of condensing at low temperature. This could lead to fouling, corrosion, attrition and abrasion of downstream devices such as gas turbines or engines. Tars are often removed from the syngas, decreasing the internal energy of the syngas itself. These tars are heavy aromatic hydrocarbons whose treatment remains difficult by thermal, catalytic or even physical methods. They can condense or polymerize into more complex structures, and the mechanisms responsible for their degradation are not completely identified and understood.

Turboplasma© is a thermal process, proposed by Europlasma. The main principle of operation relies on the use of thermal plasma for the cracking of tars inside a syngas produced in an auto-thermal gasification step. Basically, it consists of a degradation chamber where the syngas is heated by a plasma torch. The plasma plume provides a high temperature gas (around 5000K) to the system and enables heating of the incoming stream (above 1300K) and also generates high temperature zones (above 1600 K) inside the device. Due to both high temperature and long residence times of the syngas in the vessel, cracking of the tars occurs. Finally, the species released are mainly CO and H_2, leading to an increase in the Lower Heating Value of the syngas. The work presented here describes the design of a high temperature gasification system assisted by thermal plasma. It was performed using a CFD computation implemented with a full chemical model for the thermal degradation of tars. The objectives were to understand the aerodynamic behavior of the vessel and to propose enhancement in its design. We present here some results of this study.

Keywords : tars cracking, plasma torch, CFD, modeling, gasification

1. Introduction

Europlasma SA holds the patents for non-transferred plasma torch technology. This technology has been developed by EADS-LV (ex-AEROSPATIALE, French national aerospace company) to simulate the intense heat encountered by missiles and spacecraft during atmospheric re-entry. Europlasma designs and manufactures plasma heating systems for which high temperature can be used in civil applications such as steel-making industry, waste destruction, high temperature gasification, coal power plant starter. At Present time Europlasma is developing a multi-stage gasification process named CHO-Power which relies on an auto-thermal gasification improved by a high temperature stage: Turboplasma©. Its principle components are depicted on Figure 1. Secondary gasification using high-temperature produced by the plasma transforms the waste into a high-purity BioSynGas that can be supplied to a gas turbine/engine which produces electricity, with an end-to-end electrical yield that may reach 40%. The incoming fuel is refuse-derived fuel from a commercial waste sorting facility. RDF is mainly composed of wood, paper, clothes and thin plastics. Nearly 80% of the RDF mass is similar to biomass. The CHO-Power process involves a preparation of RDF into a CHO-Fuel, removing extra metal, non-ferrous compounds and minerals After a preparation treatment, this waste enters into the auto-thermal gasification unit. This unit is of the fixed bed cross flow reactor type that has been selected for it stability variation in the CHO-Fuel feedstock. First, the material is dried at 200°C and then converted into a product gas in the range of 850-1500K. This operation is carried out with an air supply lower than the stoichiometric requirement, involving a partial combustion which yields heat for the thermal organic conversion of material (C,H,O) into the desired product gas (CO, H_2, CH_4). This is the principle behind the steam gasification process. At the output of the gasification unit, the product gas is mainly composed of carbon monoxide and hydrogen, but it also includes tars. These make the syngas unsuitable for direct supply to turbines or engines because of the low dew points of the condensable volatiles. Tars create process-related problems in the end use devices, such as fouling, corrosion, erosion and abrasion, and thus, it is necessary to clean this gas We have chosen to use plasma torch technology using Turboplasma equipment patented by Europlasma. The non-transferred arc plasma torch delivers a very high temperature gas. Plasma chemical properties are not used, it is the high temperatures that allow the thermal cracking of tars.
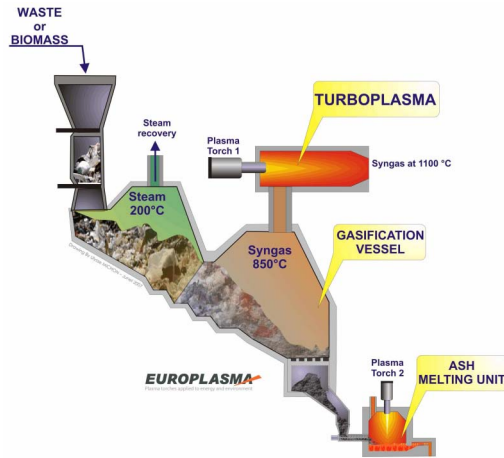

Figure 1 : C.H.O. Power unit

The purpose of this paper is the description of the CFD model that was developed to describe this thermal cracking in the Turboplasma. The first part is devoted to the tars characterization with the objective to specify a tar cracking kinetic model. This kinetic model is then implemented in a Completely Stirred Tank Reactor Model in the second part. This model is then included in the more general CFD model of the Turboplasma, in order to improve its design. Finally, some results are shown.

2. Tars characterization

The term "tar" refers to many substances. In the literature many definitions can be found [1, 2, 3]. The most general definition is : "The organics produced under thermal or partial-oxidation regimes (gasification) of any organic material are called "tars" and are generally assumed to be largely aromatic." Since the meeting of Brussels in 1998, benzene is excluded; tars are hydrocarbons with a molecular weight higher than that of benzene.

Formation of tars begins at low temperature, cellulose and lignin molecule bonds are broken to form primary tars. Then with increasing temperature these tars are transformed into secondary and tertiary tars [2]. The composition

of tars depends upon the transformation process as well as upon the nature of material being gasified. T.A. Milne and R.J. Evans [2] compiled a review that updates the currently available information about gasification tars. One of their main conclusions is that these tars are mainly composed of secondary and tertiary structures.

Jun & Heejon in 2006 [4] divided the tar removal technologies into five groups: mechanical methods; self-modification (selecting optimal operation parameters for gasifier or using a low tar gasifier); Catalytic cracking; Thermal cracking and Plasma methods. The first three methods still remain either relatively complex or expensive. Thermal cracking seems to be interesting provided that the temperature is raised sufficiently high. The drawback of the method is the dilution of the exogenous molecules (like N_2 present in air) that decrease drastically the LHV of the syngas. Performance of these gas clean up process's is evaluated by the tars dew point [1,5].

To design a tar cracking kinetic model, model compounds have to be chosen. In the case of gasification, temperatures can be higher than 600°C. Lopamudra Devi *et al*. [3] discussed many results concerning observations of tar cracking that appear in the literature. It appears that at temperatures higher than 600°C, primary tars are immediately cracked into benzene. Secondary tars, often represented by toluene [6, 7, 8], may be partially cracked, while for tertiary tars, often represented by naphthalene, may not undergo cracking since they required higher temperatures or the presence of a catalyst. Naphthalene and toluene have been chosen as model compounds. Naphthalene is a PAH (Polycyclic Aromatic Hydrocarbon) that is very difficult to crack in comparison to other tertiary tars. In gasification, tertiary aromatics (like naphthalene) are predominant. [9, 6, 3, 10]. Toluene is a good representative of its class because of it represents a stable aromatic structure found in tar formed during high temperature processes [3, 7, 6, 8, 10]. Primary tars are assimilated to benzene.

In the case of thermal cracking, a small amount of data related to kinetics is available. Van Paasen et and al. [2] have identified usable kinetic data. In the Turboplasma equipment the temperature is higher than 900°C. To formulate a CFD model, Arrhenius law kinetic data were employed. Three review articles are available in the literature (O. S. L. Bruisma [11, 12], and A. Jess [6]). However, the work of Jess is the only one that provides information on the products issuing from thermal degradation. Following an experimental results analysis, Jess presents a reactive system for tars thermal removal in an atmosphere of hydrogen and steam. In the case of naphthalene, the main products of degradation are soot, benzene, methane and carbon monoxide. Dealing with benzene, its decomposition mainly leads to methane and carbon monoxide whereas for toluene, they are mainly benzene and methane. Another study was made by Nozaïc [13] to specify, from the case of naphthalene and benzene, which reactions are thermodynamically favorable. This study shows that in our case, reforming reactions need to be taken into account.
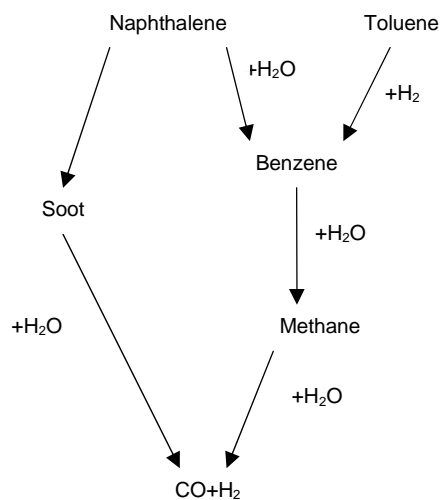

Figure 2 : Tar cracking kinetic model

As thermal cracking products are known, naphthalene and benzene reactions can be set up. Thus, a simple reaction scheme for tar cracking has been established (Figure 2). Kinetic data required for the final derivation of the kinetic model are summarized in table 1. Soot is represented by solid carbon.

3

$C_{10}H_8 \xrightarrow{r_1} 10C + 4H_2$	$r_1 = k_1[C_{10}H_8]^2 \cdot [H_2]^{-0,7}$	$k_1 = 5,56.10^{15} \exp\left(\dfrac{-3.6\times10^5\,(J/mol)}{RT}\right)$	[6]
$C_{10}H_8 + 4H_2O \xrightarrow{r_2} C_6H_6 + 4CO + 5H_2$	$r_2 = k_2[C_{10}H_8] \cdot [H_2]^{0,4}$	$k_2 = 1,74.10^{12} \exp\left(\dfrac{-3.24\times10^5\,(J/mol)}{RT}\right)$	[6]
$C_7H_8 + H_2 \xrightarrow{r_3} C_6H_6 + CH_4$	$r_3 = k_3[C_7H_8] \cdot [H_2]^{0,5}$	$k_3 = 1,04.10^{12} \exp\left(\dfrac{-2.47\times10^5\,(J/mol)}{RT}\right)$	[6]
$C_6H_6 + 5H_2O \xrightarrow{r_4} 5CO + 6H_2 + CH_4$	$r_4 = k_4[C_6H_6]$	$k_4 = 4,4.10^8 \exp\left(\dfrac{-2.2\times10^5\,(J/mol)}{RT}\right)$	[14]
$C + H_2O \xrightarrow{r_5} CO + H_2$	$r_5 = k_5[C] \cdot [H_2O]$	$k_5 = 3,6.10^{12} \exp\left(\dfrac{-3.1\times10^5\,(J/mol)}{RT}\right)$	[6]
$CH_4 + H_2O \xrightarrow{r_6} CO + 3H_2$	$r_6 = k_6[CH_4] \cdot [H_2O]$	$k_6 = 3,101.10^3 \exp\left(\dfrac{-1.247\times10^5\,(J/mol)}{RT}\right)$	[13]
$H_2 + \frac{1}{2}O_2 \xrightarrow{r_7} H_2O$	$r_7 = k_7[O_2] \cdot [H_2]$	$k_7 = 1,08.10^{10} \exp\left(\dfrac{-1.255\times10^5\,(J/mol)}{RT}\right)$	[15]
$CO + \frac{1}{2}O_2 \xrightarrow{r_8} CO_2$	$r_8 = k_8[CO] \cdot [O_2]^{0,25}[H_2O]^{0,5}$	$k_8 = 3,165.10^{12} \exp\left(\dfrac{-1.8\times10^5\,(J/mol)}{RT}\right)$	[16]
$CO + H_2O \xrightarrow{r_9} CO_2 + H_2$	$r_9 = k_9[CO] \cdot [H_2O]$	$k_9 = 2,778.10^2 \exp\left(\dfrac{-1.256\times10^4\,(J/mol)}{RT}\right)$	[16]
$CO_2 + H_2 \xrightarrow{r_{10}} CO + H_2O$	$r_{10} = k_{10}[CO_2] \cdot [H_2]$	$k_{10} = 1,263.10^4 \exp\left(\dfrac{-4.729\times10^4\,(J/mol)}{RT}\right)$	[16]
$CH_4 + 2O_2 \xrightarrow{r_{11}} CO_2 + 2H_2O$	$r_{11} = k_{11}[CH_4]^{0,3} \cdot [O_2]^{1,3}$	$k_{11} = 1,3.10^5 \exp\left(\dfrac{-2.025\times10^5\,(J/mol)}{RT}\right)$	[15]
$CH_4 + \frac{1}{2}O_2 \xrightarrow{r_{12}} CO + 2H_2$	$r_{12} = k_{12}[CH_4]^{0,7} \cdot [O_2]^{0,8}$	$k_{12} = 4,996.10^{13} \exp\left(\dfrac{-2.026\times10^5\,(J/mol)}{RT}\right)$	[16]
$C_6H_6 + \frac{15}{2}O_2 \xrightarrow{r_{13}} 6CO_2 + 4H_2O$	$r_{13} = k_{13}[C_6H_6]^{-0,1} \cdot [O_2]^{1,25}$	$k_{13} = 1,783.10^1 \exp\left(\dfrac{-1.255\times10^5\,(J/mol)}{RT}\right)$	[15]
$C_6H_6 + 3O_2 \xrightarrow{r_{14}} 6CO + 3H_2$	$r_{14} = k_{14}[C_6H_6] \cdot [O_2]$	$k_{14} = 1,58.10^{15} \exp\left(\dfrac{-2.026\times10^5\,(J/mol)}{RT}\right)$	[16]
$C_7H_8 + 9O_2 \xrightarrow{r_{15}} 7CO_2 + 4H_2O$	$r_{15} = k_{15}[C_7H_8]^{-0,1} \cdot [O_2]^{1,25}$	$k_{15} = 1,426.10^1 \exp\left(\dfrac{-1.255\times10^5\,(J/mol)}{RT}\right)$	[15]

Table 1 : Kinetic data for the Turboplasma CFD model.

3. Global kinetic model

The syngas is composed of N_2, H_2, H_2O, CO, CO_2, CH_4 and tars, while the gas injected in the plasma torch is air. Dealing with this set of species, literature yields much information concerning kinetic data, that needs to be taken into account. Table 1 summarizes the information that was used in our model. Before introducing this model into the more general CFD one, a simpler mathematical model had been written. A completely stirred tank reactor is considered. The inputs were the syngas (temperature, flow rate and composition) and the air plasma (temperature and flow rate). The output gives composition, flow rate and temperature of the gas. The problem is illustrated Fig. 3. Equations formulating the problem are :

- Species balance :

$$x_i^{Syn} F^{Syn} + x_i^{Plas} F^{Plas} + \sum_j \nu_{i,j} \cdot r_j \cdot V = x_i^{Out} F^{Out}$$

(1)

- Enthalpy balance :

$$H^{Syn} + H^{Plas} = H^{Out} \qquad (2)$$

- Model for enthalpy :

$$\overline{H}^{loc} = \sum_{i=1}^{NS} y_i^{loc} \left(h_{f_i}^0 + \int_{T_{ref}}^{T^{loc}} C_{p_i}(T) dT \right) \quad (3)$$

The enthalpy is evaluated using fifth order polynomial for heat capacity and using formation enthalpy as reference.

- Mass balance :

$$\sum_i^{NS} x_i^{Out} = 1 \qquad (4)$$

This resulting algebraic system is solved using a Newton-Raphson method.

Calculations were carried out for a normal reactor volume for which, because of confidentiality reasons, we are unable to provide information. Results are shown in Figure 4. Tar compositions are not represented because of the low values, having concentrations are about 9 mg/Nm^3, with 50% being naphthalene and 50% toluene . The kinetic model is compared in the case of an infinite volume to an equilibrium calculation (Gibbs minimization). Outlet compositions are quite similar, offering a partial validation of the kinetic model.
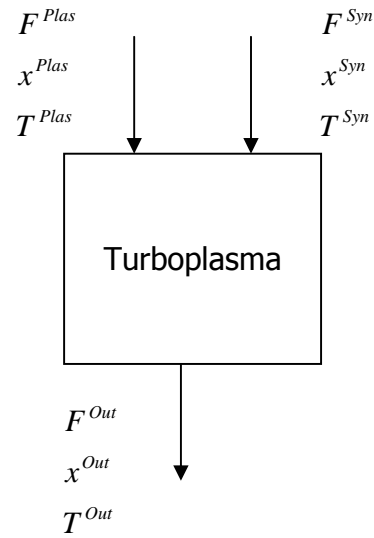
Figure 3 : Recapitulative scheme of the mathematical model

The gas composition obtained is what might be expected given a sufficient temperature and residence time, so that a great part of the tars are cracked, with a reduction rate of about 80%. These results from the foundation upon which the CFD model can be built.

5
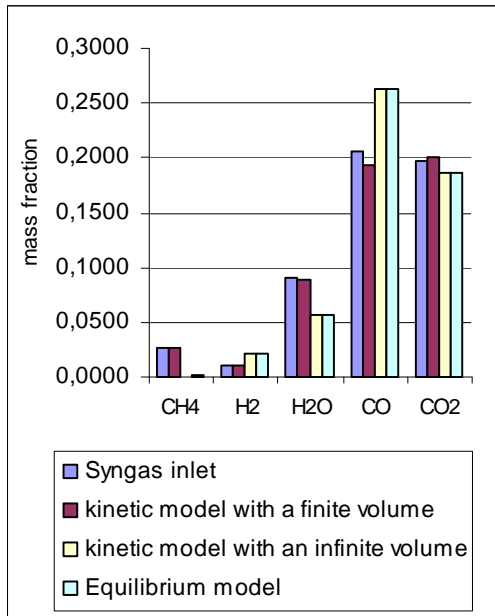
Figure 4 : Comparison between the syngas mass composition at the inlet and outlet mass compositions for calculations carried out with a finite volume, an infinite volume and with an equilibrium model.

4. The CFD model

For a simple Turboplasma geometry three-dimensional calculations were carried out using the FLUENT code. Conservation equations for momentum, energy and chemical species were solved. The standard k–ε model for turbulence and a discrete-ordinates (DO) model for radiation were selected. Mass flow inlet and out flow are chosen as boundary conditions. The radiation absorption coefficient is calculated as a function of characteristic cell size and gas concentrations (see FLUENT manual for details).

Specific properties of the high temperature air plasma are introduced into the software.

Two new species are created which are not in the FLUENT database, naphthalene and toluene. Their properties are calculated thanks to data available in "The properties of gases and liquids" [17].

To have a good convergence, species relaxation factor are reduced, but not too much in order to optimize computational time.

The inputs of the problem are the same as previously.

Inlet temperature of the plasma can be higher than 5000K, it depends upon power of the plasma torch. Temperature of the syngas is about 950K.

5. Results

Figure 5 presents the temperature profile and mass fraction of naphthalene, toluene, benzene, soot and methane. For confidentiality reasons, we are unable to provide any geometrical data about the industrial device under study.

The light area in the temperature profile represent the plume of the plasma. With the mix of the syngas and the plasma gas, temperature can reach values about 1500K and higher. This temperature is high enough to let tars removal occurring, even for tars like naphthalene.

Species mass fraction profiles clearly illustrate the tars cracking process. High mass fraction value fit to light areas. Where mass fraction of naphthalene is low, areas of high mass fraction of soot correspond. Soot is formed from naphthalene removal, and after it is removed. Temperature is high enough to let soot cracking occur. Also, this area with a low mass fraction of naphthalene corresponds to the second area of high mass fraction of benzene and methane. Both reactions are significant. Dealing with toluene, it disappears earlier than naphthalene, as it is explain by A.Jess [6]. Toluene removal occurs at lower temperature than naphthalene. The beginning of the dark area, where mass fraction of toluene is very low, corresponds to the first area of high mass fraction of benzene and methane, as it could be expected according to the tars cracking model.

6. Conclusion

The thermal degradation of tars in a chamber fed by a plasma torch is examined studying this study. After a bibliographic review, naphthalene and toluene are chosen as model compounds. They are good representatives of tertiary and secondary tars, and they are present in the gas leaving the gasification unit. Their thermal cracking process are similar to the other tar components, which can be more complex. A kinetic scheme of this thermal degradation has been developed.

In order to obtain information about the availability of the kinetic model, two numerical studies have been carried out.
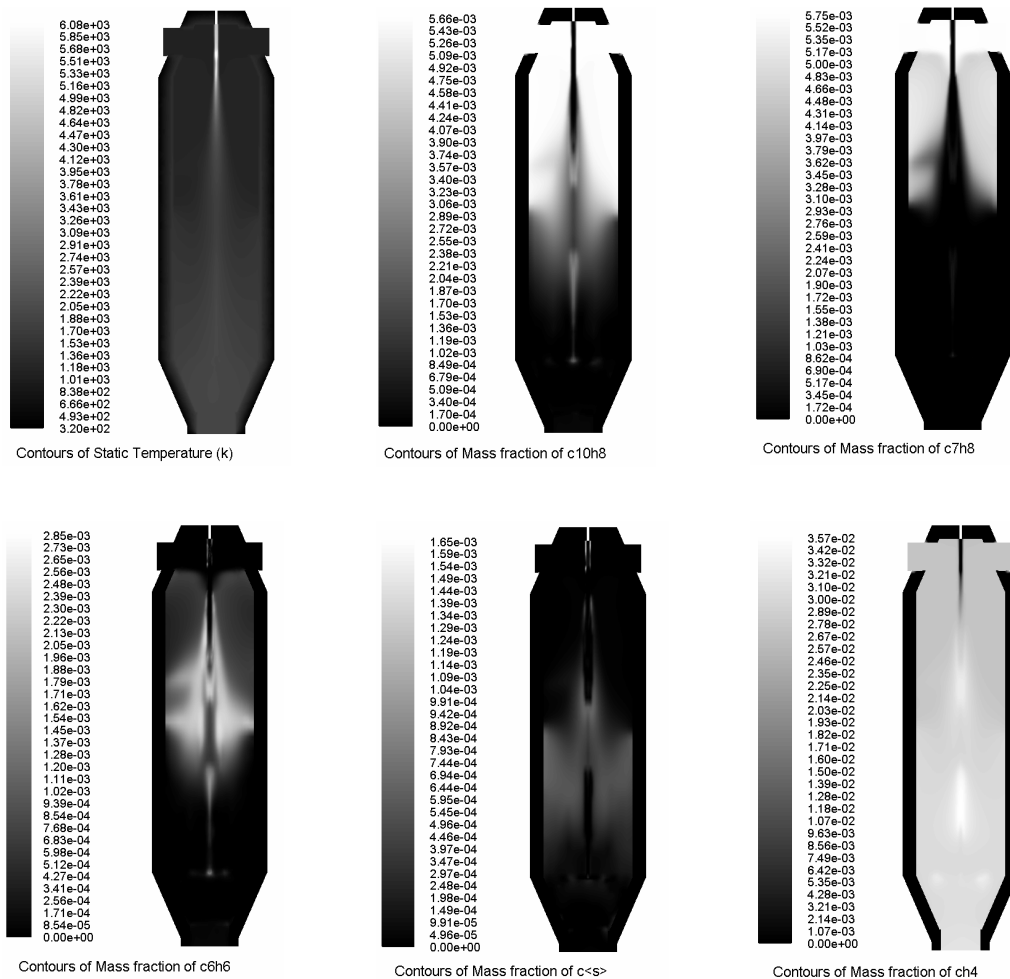
Figure 5 : Contours of temperature and species mass fraction.

The first one is a simple mathematical model, where the Turboplasma is
considered as a completely stirred tank reactor. This model gives information about mass composition at the outlet, and about the temperature/residence time coupling necessary to crack tars. Thus, it is possible to estimate a volume necessary for thermal degradation. According to this volume, a three dimensional geometry was formulated and integrated into Fluent Software. Also, specific properties of the plasma gas, as well as the kinetic model for tars degradation were introduced into the model. Results of these simulations result in a large amount of information concerning the behavior of the Turboplasma equipment. A very hot plasma gas plume is formed, which raises the temperature of the gas to be cleaned, and that in

turn promotes tar removal. The route by which naphthalene and toluene are cracked is well illustrated by mass species fraction profiles. Furthermore CFD calculations give information about velocity profiles, that is necessary to evaluate maximum wall velocities and subsequent abrasion. The Turboplasma geometry can be optimized, in order to obtain the best temperature/residence time coupling, as well as obtain a good compromise for high operational time.

The next step of this work, will be to carry out CFD calculations using this optimized geometry, while integrating dust, that is present in the syngas.

At this stage, the different markets for high quality of syngas use have not been fully addressed, neither mass nor energy balances are

7

disclosed in this paper; authors prefer to prevent from any misunderstanding about specific case applied as an general case. As usual the main drawback that will be raised by concurrent technology (oxygen, wet scrubbers, catalysis) will be energy consuming of plasma.

The first answer that could be provided is to avoid technology to technology brick. Main focus shall highlight the global benefit on the whole process in term of availability, no by-products to handle, limited environment pollution risk Europlasma master its plasma torch models with an energy yield of 85% (Electric Power - Heat lost = Plasma Jet Power). Europlasma philosophy is to consider "one Turboplasma reactor = one plasma heating system". Thanks to its different plasma torch models, Europlasma is able to address product gas flowrate from 3, 000 to 40, 000 Nm^3/h. Restriction of using only 1 plasma Heating System per Turboplasma reactor is a way to limit CAPEX (capital expenditure) related to the multiplication of Plasma Heating system. Finally, the availability rate obtained by Europlasma during 20 years of cupola heated by plasma torch, is about 96%. At last it can be mentioned that for Turboplasma case, the electric energy is transferred to the syngas in manners. The first one is extra steam production for addressing steam turbine. The second one is the major reinforcement of syngas LHV by transferring TAR to CO and H2. It can be noticed that tar removal processes consume a certain level of electricity for removing about 20% LHV (Lower Heating Value) from the syngas

7. Acknowledgments

8. Nomenclature

C_p Heat capacity (J/(mol K))

F Flow rate (mol/s)

$\overline{H}$ Enthalpy (J/mol)

H Enthalpy (J/kg)

$\overline{h_f^0}$ Standard formation enthalpy (J/mol)

NS Species number

R Ideal gas constant (J/(mol K))

r Reaction rate (mol/(m^3 s))

T Temperature (K)

T_{ref} Reference temperature (K)

x Mass fraction (kg/kg)

y Mol fraction (mol/mol)

Superscripts

loc Local

Out Output

$Plas$ Plasma gas

Syn Syngas

Indices

i gas species

j reaction number

9. References

[1] "Tar formation in a fluidised bed-gasifier : impact of fuel properties and operating conditions", *S. V. B. van Paasen, J. H. A. Kiel*, ECN-C-04-013, 2004.

[2] "Biomass Gasifier "Tars": Their Nature, Formation, and Conversion", *T. A. Milne and R. J. Evans,* NREL/TP-570-25357, 1998.

[3] "A review of the primary measures for tar elimination in biomass gasification processes", *Lopamudra Devi, Krzysztof J. Ptasinski, Frans J.J.G. Janssen,* Biomass and Bioenergy 24 125 – 140, 2003.

[4] "The reduction and control technology of tar during biomass gasification/pyrolysis: An overview", *Jun Han, Heejoon Kim,* Renewable and sustainable energy reviews, 2006.

[5] "Tar property, analysis, reforming mechanism and model for biomass gasification—An overview", *Chunshan Li, Kenzi Suzuki,* Renewable and Sustainable Energy Reviews, 2008.

[6] "Mechanisms and kinetics of thermal reactions of aromatic hydrocarbons from pyrolysis of solid fuels", *A. Jess,* Fuel 75 1441-1448, 1996.

[7] "Study of steam reforming of toluene used as model compound of tar produced by biomass gasification", *Dariusz Swierczynski, Claire Courson, Alain Kiennemann,* Chemical Engineering and Processing, 47 508–513, 2008.

[8] "Steam reforming of tar from a biomass gasification process over Ni/olivine catalyst using toluene as a model compound" *D. Swierczynski, S. Libs, C. Courson , A. Kiennemann,* Applied Catalysis B: Environmental, 74 211–222, 2007.

[9] "Tar reduction through partial combustion of fuel gas", *M.P. Houben, H.C. de Lange, A.A. van Steenhoven,* Fuel 84, 817–824, 2005.

[10] "Decomposition of Naphtalene as a Biomass Tar over Pretreated Olivine: Effect of gas decomposition, Kinetic Approach, and Reaction Scheme", *Lopamudra Devi, Krzysztof J. Ptasinski, Frans J.J.G. Janssen*, Ind. Eng. Res. 44, 9096– 9104, 2005.

[11] "Gas phase pyrolysis of coal related aromatic compounds in a coiled tube flow reactor, 1. Benzene and derivatives", *Odolphus S. L. Bruinsma, Rob S. Geertsma, Pim Bank and Jacob A; Moulijn,* Fuel 67, 1998.

[12] "Gas phase pyrolysis of coal-related aromatic compounds in a coiled tube flow reactor. 2. Heterocyclic compounds, their benzo and dibenzo derivatives", *Bruinsma O.S.L., Tromp P.J.J., de Sauvage Nolting H.J.J., Moulijn J.A.,* Fuel 67 1988.

[13] "Production de gaz de synthèse par interactions à haute température du gaz, des goudrons et du résidu carboné issus de la pyrolyse de biomasses", *F. Nozahic*, Phd thesis of the University of Toulouse, 2008.

[14] "Thermal hydrogasification aromatic compounds", *Virks P. S., Chambers L. E., Woebcke H. N.,* Advances in chemistry series 131, 1974.

[15] "An Introduction to Combustion, Concepts and applications", *Stephen R. Turns,* 1996.

[16] "Experimental investigation and modeling of gasification of sewage sludge in the circulating fluidized bed", I. Petersen, J. Werther, Chemical Engineering and Processing, 44 717–736, 2005.

[17] "The properties of gases and liquids", fourth edition, Robert C. Reid, John M. Prausnitz, Bruce E. Poling, 1987.