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The application of homogeneous reactor models to examine the conversion of Polycyclic Aromatic Hydrocarbons in biomass derived fuel gases

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Abstract

The removal of tar from biomass derived fuel gases is considered to be a bottleneck in the widespread application of biomass gasification. Tar is made up of Polycyclic Aromatic Hydrocarbons (PAHs) consisting of fused aromatic rings. Past research has proven the possibility to remove the PAH species naphthalene from producer gas at high temperature by means of introducing a limited amount of oxidizer ($\lambda \leq 0.2$). This process, which also can be regarded as partial combustion, is not yet fully understood. By conducting a fundamental study of the mechanisms involved it will be possible to optimize the process conditions and the reactor geometry. In the work presented here it is examined if partial combustion can be described by homogeneous reactors. The PAH species representing the tar content of the producer gas is naphthalene (in correspondence with the executed experiments). Chemical equilibrium calculations indicate that, if time scales approach infinity, it is possible to convert naphthalene to lighter hydrocarbons at small values of λ (the equivalence ratio). For $\lambda < 0.2$ soot is produced. The influence of chemical kinetics is examined with Perfectly Stirred Reactor (PSR) calculations. The results reveal that the time scales involved in the conversion of naphthalene at small values of the equivalence ratio ($0 < \lambda < 0.2$) are considerable. This leads to the conclusion that the process of tar cracking by partial combustion cannot be described by homogeneous reactors alone. The experimental results are not fully explained by the presented results. This indicates that heterogeneous effects should be taken into account. This requires full 2D simulations in which molecular transport is included.

Introduction

The reduction or decomposition of tar in biomass derived fuel gases is considered to be the bottleneck in the application of biomass gasification [7]. A study of the different methods available to convert or remove tars has led to an interesting observation. All the currently most promising technologies experience a significant increase in tar conversion when small amounts of oxygen are added to the process [2, 3, 7, 8, 10, 12–15, 22, 24, 27].

For instance, when a non-thermal plasma is used to clean producer gas originating from a biomass gasifier, the tar content of the gas is reduced by approximately 70%. Experiments have shown the positive influence of oxygen-radicals on the conversion rate in this process [13, 14]. Also catalysts make use of oxygen/air/steam injection to improve the tar reduction levels [4, 5, 27, 28]. And research has proven more than once that tar is reduced by secondary air or steam injection directly into the gasifier [2, 7, 15].

A study by Houben [8,9] and van der Hoeven [23, 24] demonstrates the possibility to remove the Polycyclic Aromatic Hydrocarbon (PAH) species naphthalene from producer gas at high temperature by means of introducing a limited amount of oxidizer ($\lambda \leq 0.2$). The experimental results indicate the prominent role of oxygen and radicals in partial combustion of contaminated synthetic producer gas. The oxidizer is fed continuously through several nozzles into a reactor creating multiple diffusion flames (see figure 1). The working mechanism behind this heterogeneous process is not yet fully understood. The purpose of

this work is to gain additional knowledge of the working principles behind this process.

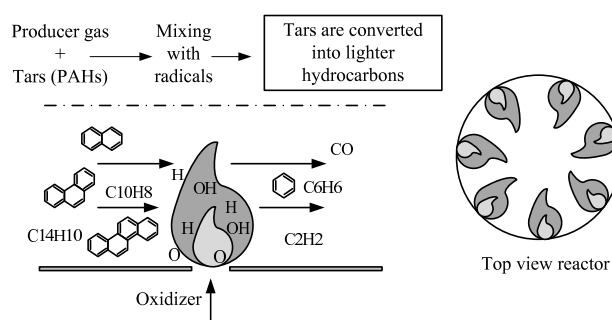


Figure 1: Converting tars by means of partial combustion [8, 23]

Specific Objectives

To gain fundamental knowledge of the process it is important to investigate the separate influence of thermodynamics and chemical kinetics. These phenomena play an important role during partial combustion and therefore several situations are simulated. As a first approach it is assumed that the process can be modeled by homogeneous reactors. The analysis tool applied is the CHEMKIN II chemical simulation package. Chemical equilibrium simulations are conducted to study the thermodynamics of the process. Perfectly Stirred Reactor (PSR) calculations reveal which time scales are involved. Several reaction mechanisms are assessed to give information about the differences in kinetics between the employed mechanisms.

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Table 1: Producer gas composition from the Milena indirect gasification technology

Species	Name	Mole fraction (-)
H ₂ O	Water vapor	0.312
H ₂	Hydrogen	0.212
CO	Carbon monoxide	0.182
CO ₂	Carbon dioxide	0.149
CH ₄	Methane	0.095
N ₂	Nitrogen	0.009
C ₂ H ₂	Acetylene	0.002
C ₂ H ₄	Ethylene	0.031
C ₂ H ₆	Ethane	0.031
C ₆ H ₆	Benzene	0.005
C ₇ H ₈	Toluene	0.0004

Thermodynamic analysis

Chemical equilibrium is the state in which the chemical activities or concentrations of the reactants and products have no net change over time. During this process of rearrangement the enthalpy, pressure and elements are preserved. Determining the chemical equilibrium is an iterative process where the Gibbs energy $G = H - TS$ of the system is minimized. In this relation the enthalpy is represented by H , the temperature by T and the entropy by S . Within the simulation package CHEMKIN II the equilibrium solver EQUIL is applied to execute the simulations. The 159 species (and their thermodynamic data) present in the MSR mechanism are included in the simulations. This mechanism originates from Pope and Miller [16]. It contains 159 species and 773 reactions [20] [21]. The consumption and production of the major species of fuel-rich oxidation of methane can be fairly accurately described with this kinetic model [19]. The growth of PAHs is modeled by HACA (Hydrogen-Abstraction-C₂H₂-Addition) up to pyrene from Appel et al. [1] (the ABF mechanism), further growth by cyclopentadienyl addition from Marinov et al. [11], and combinative growth of aromatics following Böhm and co-workers [19]. For further information the reader is referred to the stated literature. So all major gas species and the aromatic species varying from toluene to pyrene (a 4-ring PAH) are present in this set. To examine the possibility of the formation of fixed carbon this species, along with its available thermodynamic data, is added to the set of species.

Initial Conditions

Since this research project is executed in close collaboration with the Energy Research Center of the Netherlands (ECN) the producer gas of the indirect gasification technology Milena is chosen as the gaseous fuel of interest. Its composition and initial conditions are stated in table 1. The tar content of 28 g/Nm³ is represented by naphthalene (C₁₀H₈), a 2-ring aromatic species.

Several other initial conditions are listed in table 2.

Table 2: Initial conditions EQUIL calculations

Parameter	Value
Pressure	1.0 atm
Inlet temperature	1173 K
Species included	160 (159 +1)
Tar content	28 g/Nm ³
Naphthalene C ₁₀ H ₈	0.52 vol%

The working pressure is atmospheric because an open system is considered. The inlet temperature is based on the temperature of the product gas (fu) after it leaves the gasifier. The parameter of interest is the equivalence ratio φ .

$$\varphi = \frac{1}{\lambda} = \frac{\left(\frac{m_{fu}}{m_{ox}}\right)}{\left(\frac{m_{fu}}{m_{ox}}\right)_{st}} = \frac{\left(\frac{n_{fu}}{n_{ox}}\right)}{\left(\frac{n_{fu}}{n_{ox}}\right)_{st}}, \quad (1)$$

where m represents the mass and n the amount of moles. The subscript _{st} indicates that the conditions within the brackets are to be considered at stoichiometric conditions. The oxygen factor λ is varied from 0 to 0.3. At $\lambda = 1$ complete conversion will take place. Considering the energy cost and the research conducted in the past only small values of λ are considered. The type of oxidizer (ox) is pure oxygen. Indirect gasification produces a gas with a low content of nitrogen. If air is chosen as an oxidizer the product gas would be diluted with nitrogen, which is not desirable.

Results and Discussion

The purpose behind applying partial combustion is to convert the tar content to smaller hydrocarbons. The process of aromatic species growing to soot, which is called polymerization, is undesired. Polymerization is likely to appear at environments of high temperature and where low to no oxygen is present. It is assumed that the summation of all species with a higher molar mass than the added naphthalene can be considered as the soot concentration (excluding fixed carbon). In addition in examining the thermodynamic route from PAHs to soot the creation of fixed carbon is regarded.

The results are presented in figure 2. The upper left figure shows that for every oxygen factor λ all the present naphthalene disappears. Even when no oxygen is added all naphthalene disappears. To investigate if naphthalene undergoes the process of polymerization a summation is made of all bigger species which is referred to as soot. In the upper right figure it can be seen that polymerization does not occur for any value of λ . The figure on the bottom on the left side shows that for a $\lambda < 0.2$ a considerable amount of fixed carbon is formed. Which indicates that the formation of soot actually is favored for small values of λ . Lets consider the results of the major gas species present in the Milena product gas.

The results for four major species (methane, carbon monoxide, hydrogen and carbon dioxide) can be seen in figure 3. The methane present in the product gas disappears even when no oxygen is added. Likely, a big part is

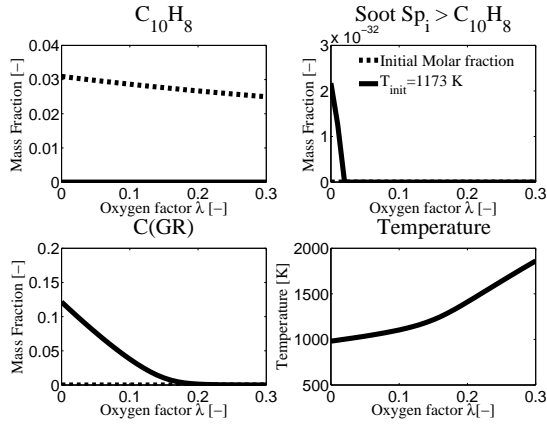


Figure 2: Species Naphthalene $C_{10}H_8$, the formed soot fraction, the concentration of fixed carbon C and the temperature as a function of the oxygen factor λ

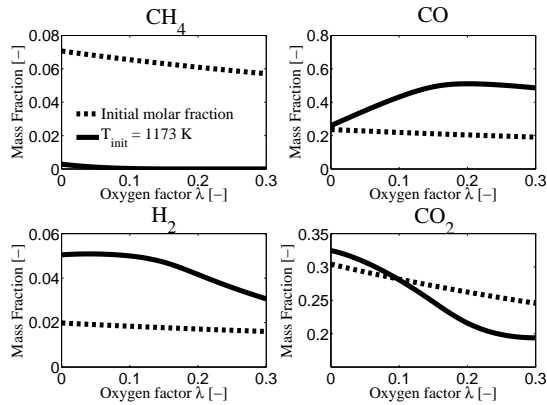


Figure 3: Major species CH_4 , CO , H_2 and CO_2

converted to fixed carbon. For carbon monoxide and hydrogen there is always an increase visible. There is also an increase in carbon dioxide visible for a small range of λ .

The chemical equilibrium results of the other species present in the product gas are now shortly discussed. The concentration of water vapor decreases (in respect to its initial concentration) for the smaller values of the oxygen factor λ . All smaller hydrocarbons C_xH_y are not present at chemical equilibrium. By combining the trends visible in the results it can be concluded that the tar content in the product gas, represented by naphthalene, is converted into fixed carbon (for $\lambda < 0.2$), carbon monoxide, hydrogen and carbon dioxide. This also accounts for the smaller hydrocarbons like acetylene, ethylene and benzene. A critical note must be placed by the type and amount of species included in these calculations. If fixed carbon is not taken into account different results are achieved. For it is not possible to include all species a choice is made to include all major gas species, a range of PAHs and fixed carbon.

Analysis of chemical kinetics

The chemical equilibrium calculations have shown that the thermodynamics of the system favor the path of cracking the naphthalene to lighter hydrocarbons like hydrogen and carbon monoxide, but at the same time a considerable amount of fixed carbon is formed. Of course these calculations describe a model environment where time scales and chemical kinetics do not play a role. To investigate the time scales that are involved Perfectly Stirred Reactor (PSR) calculations are executed. These calculations are performed using the PSR code of the CHEMKIN II software package. A reactor made up of a fixed volume with both a feed and a product stream is considered. When the reactants enter the reactor they are instantaneously mixed. The walls are non-catalytic and insulated. The flow through the atmospheric constant-volume reactor is characterized by a residence time τ . Constant enthalpy is assumed. The following stationary relation for species is solved.

$$\frac{\omega_i \tau}{\rho} = (Y_i - Y_{i,\text{inlet}}) \quad (2)$$

In this relation the change of species i is determined as a function of residence time τ , chemical source term ω_i and the density ρ .

Initial conditions

Since chemical kinetics play the leading part in PSR calculations the applied reaction mechanism determines the outcome. For the first calculations the MSR mechanism is applied. In this case the reaction paths involving fixed carbon are not taken into account, since they were not available. Calculations with other mechanisms have also been performed and will be discussed later on in this section. A short overview of the initial conditions can be seen in table 3.

Table 3: Initial conditions PSR calculations

Parameter	Value
Constant Pressure	1.0 atm
Constant Volume	1.0 cm ³
Constant Enthalpy	-
Inlet temperature	1173 K
Reaction mechanism	MSR
Species included	159
Reactions included	773
Tar content	28 g/Nm ³
Naphthalene $C_{10}H_8$	0.52 vol%

The oxygen factor λ is again varied from 0 to 0.3, using pure oxygen. In addition the residence time is varied from 10^{-6} to 10^4 seconds. A reactor residence time varying from 10^{-3} to 10^{-1} seconds would indicate that the process can be economically feasible. If the residence time would become any longer the required volume increases to unrealistic values. The results are presented in the next section.

Results and Discussion

In figure 4 the PSR results for the added naphthalene and the formed soot can be seen.

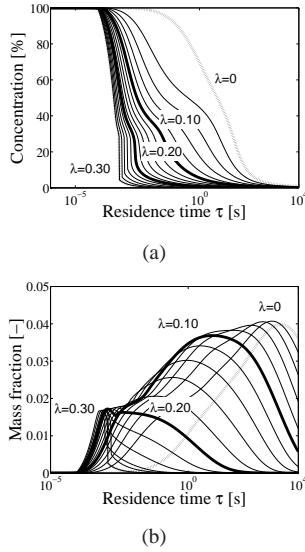


Figure 4: a) Naphthalene b) Soot formed by growth of PAHs

The decrease of naphthalene as a function of the oxygen factor λ and the residence time τ is represented as a percentage of the initial concentration. The initial mass fraction of naphthalene at $\lambda = 0$ is equal to 0.03. Since there is no soot present at $\tau = 0$ the soot concentration is represented as an absolute mass fraction. For all values of λ considered the fraction of naphthalene goes to zero when the residence time τ increases, just as the chemical equilibrium calculations predicted. Figure 4(b) shows that soot is produced and consumed again as a function of residence time. This process is accelerated when more oxygen is added. These results show that, as was indicated by the chemical equilibrium calculations, the concentration of the added naphthalene goes to zero when small amounts of oxygen are added. In the same time soot is produced and consumed again. The results indicate that the time scales which are involved are relatively big to apply the principle of a PSR in reality. Now let's consider the major species (figure 5). The top left figure shows the behavior of methane as a function of λ and τ . In comparison with the chemical equilibrium results an increase of methane for small values of λ can be observed. The fact that the route to fixed carbon is not taken into account explains this effect. When more oxygen is added almost all methane is consumed at large values of τ . Carbon monoxide and hydrogen show an increase, in respect to their initial concentration, under all modeled conditions. The concentration of carbon dioxide decreases for a λ bigger than 0.1 at longer residence times.

As was indicated by the calculations conducted by EQUIL the water vapor content increases at any additional amount of oxygen. Only for the larger time scales involved a decrease in the water vapor content can be

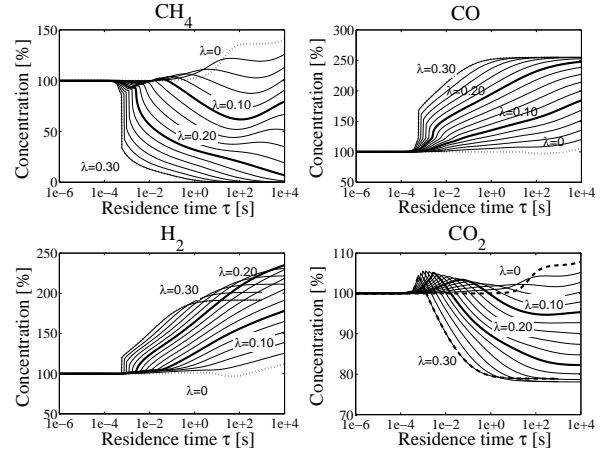
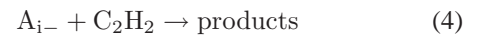
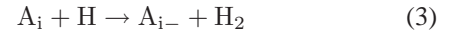


Figure 5: Major species CH_4 , CO , H_2 and CO_2

observed. For acetylene an interesting trend can be noticed. Before the acetylene is consumed at larger time scales an increase up to 1500 percent for $\lambda = 0.3$ is observed. This increase can probably be explained by regarding the nature of the reaction mechanism. The mechanism applied in these calculations is developed to simulate the soot formation during methane oxidation. As was stated earlier the main soot formation submechanism incorporated is the so-called Hydrogen-Abstraction- C_2H_2 -Addition (HACA) mechanism [25] [6]. The growth process is described by the abstraction of hydrogen to activate aromatics (3), followed by adding acetylene (4).



In this case the production of acetylene can thus be regarded as the driving mechanism behind the growth of aromatics to soot. The other smaller hydrocarbons C_xH_y are consumed in time. The addition of more oxygen accelerates this process.

The PSR calculations confirm that naphthalene disappears for small values of λ . The involved time scales are relatively big to apply the principle of a PSR in reality. The route to bigger aromatic species which leads to the formation of soot is also clearly visible in the results. Larger time scales show that the formed soot is consumed again which is in correlation with the chemical equilibrium results. Some remarks must be placed here. First of all, the applied mechanism is developed for soot formation. The results confirm this. Secondly, no soot oxidation reactions are included in the mechanism. The added naphthalene is only able to react with H, OH, C_2H and C_3H . This probably also contributes to the large time scales necessary for the soot to be consumed.

The same PSR calculations are performed with the ABF and the Richter2 mechanism. The ABF mechanism consists of 101 species and 544 reactions and was developed

to model soot formation during natural gas combustion [26]. The Richter2 mechanism is developed by Henning Richter et al. [17] and was initially developed for the oxidation of benzene (C_6H_6) by Shandross et al. [18]. It consists of 158 species (up to three condensed aromatic rings - phenanthrene and anthracene) and 872 reactions. The results have been compared with the results achieved with the MSR mechanism.

Comparison with two other reaction mechanisms

In this section the agreements and differences of the PSR results of the three assessed mechanisms will be discussed. The results of the concentration of added naphthalene for all mechanisms can be regarded in figure 6.

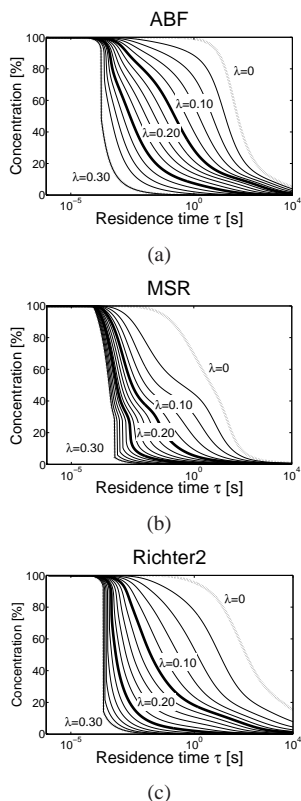


Figure 6: Naphthalene results from the a) ABF mechanism b) MSR mechanism c) Richter2 mechanism

The naphthalene decreases as a function of time. Adding oxygen accelerates this process. This trend is visible in the results achieved with every mechanism. The rate at which this process accelerates does differ. When increasing the oxygen factor λ less time is needed to decrease the naphthalene to zero according to MSR mechanism in respect to the ABF and Richter2 mechanism. The ABF and Richter2 mechanisms also predict the production and the subsequent consumption of soot (see figure 7). Two distinctive differences are noticeable in the results. The absolute mass fraction of the produced soot and the time scales involved in the consumption. The ABF mechanism predicts that less time (in regard to the MSR mechanism) is needed to consume the soot again.

These two variations can also be observed when the results from the Richter2 mechanism are compared to those of the MSR mechanism. In addition to these variations a shift can be seen in the location of the peak values. For the larger values of λ soot is produced and consumed earlier. Furthermore, it can be seen that the effect between adding no oxygen ($\lambda = 0$) and adding little oxygen ($\lambda = 0.1$) is much bigger in respect to the other two mechanisms.

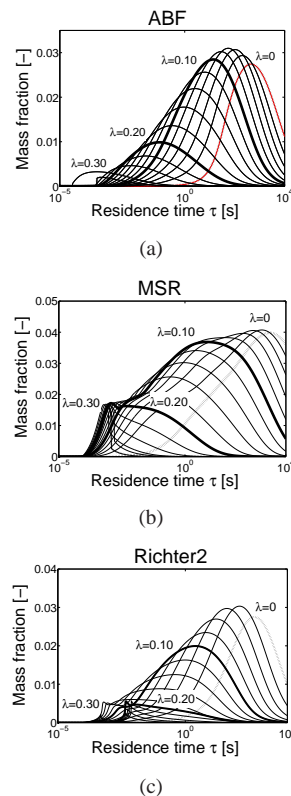


Figure 7: Soot results from the a) ABF mechanism b) MSR mechanism c) Richter2 mechanism

In regard to the major species there are no big differences noticeable. The resulting trends for the major species and the smaller hydrocarbons can be considered to be the same for every mechanism. For benzene and toluene some differences are observed in absolute concentrations, but the general trends can be considered to be the same.

Conclusions

The chemical equilibrium calculations have shown that the thermodynamics favor the cracking of the added naphthalene without the occurrence of polymerization to bigger aromatic species. Although, for $\lambda < 0.2$ a considerable amount of fixed carbon is formed. To investigate the time scales involved Perfectly Stirred Reactor (PSR) calculations have been executed. Results have shown that the time scales involved are relatively big ($10^3 - 10^4$ s), in respect to the desired $10^{-3} - 10^{-1}$ s, to apply the principle of a PSR in reality to convert tars in product gas. In addition to the MSR mechanism two additional mech-

anisms have also been applied, the ABF and the Richter2 mechanism. The results show that all three mechanisms express the same trends. A remark must be made by the fact there are no oxidation reactions present in the three mechanisms. The assessed mechanisms are all developed to model the growth of PAHs to form soot without taking oxidation into account. By including oxidation reactions it can be possible that the time scales involved will change. From the presented results it can be concluded that the process of tar cracking by partial combustion cannot be described by homogeneous reactors alone. The experimental results are not fully explained by the presented results. This indicates that heterogeneous effects should be taken into account. This requires full 2D simulations in which molecular transport is included. These 2D simulations are part of the current work.

Acknowledgements

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