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Modeling of Soot Formation during Partial Oxidation of Producer Gas

Svensson, Helena^a; Tunå, Per^b; Hulteberg, Christian^c; Brandin, Jan^d

- a) Corresponding author
Department of Chemical Engineering, Lund University, Box 124, 221 00 Lund, Sweden; Tel: +46 46 222 93 13; Fax: +46 46 14 91 56; E-mail: helena.svensson@chemeng.lth.se
- b) Department of Chemical Engineering, Lund University, Box 124, 221 00 Lund, Sweden; E-mail: per.tuna@chemeng.lth.se
- c) Department of Chemical Engineering, Lund University, Box 124, 221 00 Lund, Sweden; E-mail: christian.hulteberg@chemeng.lth.se
- d) Bioenergy Technology, Linnaeus University, 351 95 Växjö, Sweden; E-mail: jan.brandin@lnu.se

Abstract

Soot formation in a reverse flow partial oxidation reactor for reforming of gasifier producer gas has been studied. The process was modeled using a detailed reaction mechanism to describe the kinetics of soot formation. The numerical model was validated against experimental data from the literature and showed good agreement with reported data. Nine cases with differing composition was simulated in order to study the effect of water content, hydrogen content and methane content of the gas. The CO and CO₂ content was also varied to study its effect on soot formation as well as the tar content of the gas. The results show that steam and hydrogen content of the inlet gas had lower influence on the soot formation than expected. The methane content greatly influenced the soot formation. Results also showed that increasing the CO₂ content of the gas reduces the amount of soot formed and gives a higher energy efficiency and methane conversion. For the case with no tars in the ingoing gas the soot formation was significantly reduced. It can be concluded that removing the tars in an energy efficient way, prior to the partial oxidation reactor, will greatly reduce the amount of soot formed. Further investigation of tar reduction is needed and experimental research of this process is undergoing.

Keywords: gasification, reforming, partial oxidation, reverse flow operation, synthesis gas, modeling

1. Introduction

The need to replace liquid fuels, such as gasoline and diesel, produced from crude oil resources has given rise to much research in the area of biofuels. Liquid fuels in this area can be for instance ethanol, methanol and bio-diesel produced from different types of biomass using various methods. Fischer-Tropsch diesel produced from synthesis gas (CO and H₂) derived from renewable resources is a growing area of research [1-4].

Traditionally the synthesis gas used for the Fischer-Tropsch process was produced via coal gasification. Lately research has been focused on how to produce synthesis gas by utilizing gas produced via biomass gasification [4-10]. The gas produced by the gasifier is often referred to as producer gas. The producer gas contains CO, CO₂, H₂ and H₂O as well as CH₄ and higher hydrocarbons, including some tar compounds. There are also small amounts of contaminants present in the syngas, such as NH₃, H₂S, COS and HCN. The composition of the producer gas and the range and amounts of contaminants is largely dependent on the type of biomass and gasifier that is used for the production of the producer gas.

In order to upgrade the producer gas into synthesis gas, which can be used to e.g. produce liquid fuels, a reforming process is necessary. Many alternatives are available and have been the focus of much research, such as steam reforming, (SR), autothermal reforming, (ATR) and catalytic partial oxidation, (CPO). The main problem with the mentioned techniques is that they rely on catalysts which are highly susceptible to sulfur poisoning [11-14]. Although much research has been devoted to finding suitable catalysts for this area no clear alternative has yet emerged. An alternative would then be to use a non-catalytic process such as partial oxidation, (POX). The main drawbacks of POX are related to the high temperature needed to reform methane. This results in a less energy efficient process compared to the catalytic alternatives and a loss of chemically bonded energy in the gas. One way of addressing these problems, making the process more energy efficient, is to use a reverse-flow POX reactor. The reverse-flow reactor consists of a vessel filled with a granular material with high thermal capacity acting as a heat buffer. As the gas flows through the packed bed, heat produced by the reactions is transferred from the gas to the stationary phase. When the flow direction is reversed the heat stored in the bed is used to heat the incoming cold gas. Eventually a pseudo steady-state temperature profile is established with a high temperature in the middle of the reactor while the inlet and outlet are kept at a lower temperature. This concept has been previously studied and proven highly effective for reforming of hydrocarbon fuels [15-17]. The reverse flow POX reactor has been modeled in previous work and shows potential in handling the unique qualities of the producer gas that makes it difficult to reform using conventional techniques [18]. However some issues still remain to be resolved. Because of the high temperature required for POX, and the general composition of the producer gas, soot formation is likely to occur during reforming. This is further emphasized by the fact that soot precursors, such as ethylene, acetylene and tars, are present in the producer gas [19-21]. Since the reverse-flow reactor consists of a packed bed it is vulnerable to blockage if soot formation is too extensive.

In order to evaluate the reverse-flow partial oxidation reactor for reforming of producer gas it is of the outmost importance to establish how much of the incoming carbon that is likely to be converted into soot and explore ways of reducing the formation of soot, while maintaining an energy efficient process and high methane conversion.

Because of the inherent difficulties in measuring and analyzing soot formation in different locations of the reactor, modeling of the process was undertaken as a first step in this investigation. The aim of the investigation was to examine the extent to which soot is likely to form and possible ways of counteracting such formation. The results were evaluated from the viewpoint of synthesis gas energy efficiency and methane conversion as well as soot reduction.

2. Modeling

The reverse-flow POX reactor is an example of a forced unsteady-state system because of the reversal of flow direction during operation. In order to describe the dynamic behavior of the system, a numerical model of the reverse flow reactor was developed in earlier work [18]. This model was used to investigate how the reverse flow concept could be applied to reforming of a producer gas. For the sake of evaluation a pseudo steady-state for the reactor had to be achieved during simulation. The time the system is operated in each direction is called the cycle time. For different conditions the cycle time of the system will vary. In order to determine when pseudo steady-state was achieved the temperature profiles of each cycle were evaluated. A deviation of 5 K between the temperature profiles of the cycles was allowed. After five cycles with a temperature difference of 5 K or below the system was considered to be in pseudo steady-state.

The simulations were performed in a C++ program and a third party library, Cantera, was used to calculate thermodynamics and kinetics. Cantera uses the GRI-Mech 3.0 mechanism for the kinetics [22]. The mechanism was originally designed to model combustion of natural gas. This mechanism has been shown to give results that closely agree with experimental data for reforming processes [6]. However, this mechanism does not include the formation of tars and soot. For the purpose of studying the soot formation another mechanism is needed to describe the kinetics. A mechanism that describes conventional gas phase reactions and particle growth was therefore chosen [23, 24]. The mechanism, together with the corresponding thermodynamic and transport property data, is available on-line [25]. This mechanism was developed to describe formation of polycyclic aromatic hydrocarbons, (PAH), and soot in fuel-rich benzene flames. Because the mechanism that describes soot formation is much larger than the GRI-Mech 3.0 mechanism it was not possible to use it within the dynamic model of the reverse flow reformer previously described. For this reason a simplified numerical model was developed for the evaluation of soot formation in the reverse flow POX reactor [26].

Figure 1. Schematic description of the tank series employed in the model and example of temperature profile over the length of the reactor.

The simplified model can be described as a static model. The principle of the static model is described in figure 1. The model consists of a series of reactors. The reverse flow reactor is divided into segments and each segment is modeled as a separate reactor. The residence time of each reactor corresponds to the residence time of the reverse flow reactor-segment modeled. The temperature profile over the reactor series is determined at pseudo steady-state for each case modeled, with the more extensive dynamic model previously described. In each reactor the temperature and pressure is kept constant. The outgoing composition from each reactor is used as the ingoing composition in the following reactor in the reactor series. The oxygen inlet is placed 0.2 m from the gas inlet. The solid phase is not included in the model. The static model has been validated against the more extensive dynamic model in previous work [26]. The results showed that the simplified model gives an accurate description of the reactions to occur during reforming of a producer gas in a reverse flow partial oxidation reactor.

2.1 Validation of numerical model

Soot formation during reforming of hydrocarbon fuels has been observed in several studies [5, 10, 15, 16, 27]. These mainly concerned the partial oxidation of methane-air mixtures although ethane and propane was also studied [15]. Experiments were performed in packed bed reactors, some operated in reverse-flow mode [15, 16]. The formation of higher hydrocarbons was noted in all studies at high equivalence ratios although the soot onset limit varied due to differences in experimental setup. In some cases the size of the packing material affected the soot formation with smaller particle-packings showing less soot formation [5, 27]. The bed material itself should be inert and not participate in the gas phase reaction. An explanation for such a particle-size dependency could be that the void space between the particles also increases with increased particle size. When the free distance in the void exceeds the quenching distance for the actual local gas mixture, the gas can be ignited in the void space. This gives rise to a locally high temperature in the flame and effects the formation of soot. When the free void distance is below the quenching distance, the reaction proceeds via a homogenous gas phase reaction instead.

Soot formation was observed by Valin et al [10] when reforming a producer-gas-like gas. In this work the methane conversion of a simulated producer gas during thermal reforming at high temperatures (1273-1773 K) and varying residence times was investigated. The gas mixture consisted of CO, CO₂, CH₄, H₂ and H₂O. No higher hydrocarbons or tars were included. The experiments were performed in the PEGASE reactor, a down-flow isothermal plug-flow reactor. The reactor was designed to study the conversion of methane, light hydrocarbons and tars at high temperature. The reactor was heated by Kanthal heating elements and consisted of a preheating zone and an isothermal reaction zone. The reacting gas was injected into the reactor and preheated to the desired temperature in the preheating zone before entering the reaction zone. The gas was then cooled to 1173 K and maintained at that temperature until it left the experimental setup [10]. Soot formation was observed during the experiments but not measured quantitatively. However, qualitative comparisons were made regarding the amount of soot formed at various experimental conditions. The results of this study regarding soot formation are summarized in table 1. A peak in soot formation was observed between 1363 K and 1645 K. The hydrogen content of the gas was observed to have great influence on the soot formation. More hydrogen in the gas was observed to significantly reduce the amount of soot formed. This is in agreement with prior research that hydrogen represses soot formation due to tar cracking [28, 29].

Table 1. Soot formation during thermal reforming of bio-syngas [10].

Case	Gas composition (mol-%)					Temperature (K)	Residence time (s)	Soot formation
	CO	CO ₂	CH ₄	H ₂	H ₂ O			
1	19	14	7	16	25	1363-1645	2.1	A peak in soot formation was observed between 1356 K and 1645 K.
2	19	14	7	16	25	1783	3.5	Soot formation was relatively low.
3	19	14	7	16	15	1453	2.1	Soot formation was relatively high.
4	19	14	7	32	15	1453	2.1	Soot formation was considerably reduced compared to case 3.

Because of the difficulty in finding experimental data on reverse flow POX of a bio-producer-gas-like gas it was decided to validate the simplified numerical model presented in this work with the experimental data obtained by Valin et al. for the thermal reforming of producer gas using the PEGASE reactor [10]. The reactor setup described in the numerical model was modified to the PEGASE reactor setup, with three reactors representing the preheating zone, reaction zone and cooling zone. The main difference between the two setups (the PEGASE and reverse-flow reactors) is that the PEGASE reactor is isothermal and operated in a unidirectional way, meaning that the flow direction is not reversed during operation. The results obtained with the numerical model after simulation of the experimental conditions was then compared to the experimental data. The results are presented in figure 2 and 3.

Figure 2. Concentration profiles in the reactor as a function of temperature with residence time 2.1 s. Experimental (symbols) and calculated (lines) values; (a) CH₄:7 mole% and (b) CH₄:14 mole% (H₂O:25 mole%; H₂:16 mole%; CO:19 mole%; CO₂:14 mole% in both cases) [10].

Figure 3. Concentration out of the reactor as a function of residence time. Experimental (symbols) and calculated (lines) values; temperature 1453 K; CH₄:7 mole%; H₂O: 25 mole%; H₂:16 mole%; CO:19 mole%; CO₂:14 mole% [10].

Figure 2 shows the output gas composition as a function of temperature in the reaction zone. It can be seen that the numerical model shows an overall good correlation with experimental data. At higher temperatures the concentration of CO is underpredicted and the concentration of H₂O is overpredicted by the numerical model. This is a result of a loss of carbon that is transferred to soot in the reaction mechanism used. This loss of carbon is higher in the numerical model than in the experimental work. The main reaction controlling the relative relation of CO and H₂O is the water gas shift (WGS) equilibrium described below.

If the carbon that is transferred to soot is mainly coming from reactions involving CO this concentration would be lowered, shifting the WGS equilibrium to the left. As a result of this more H₂O would be formed which would explain the results obtained with the numerical model. The results for the higher hydrocarbons, C₂H₂, C₂H₄ and C₂H₆, are well in range of those obtained during the experiments with levels below 0.6% by volume. There does however seem to be a slight over-prediction of the C₂H₂ in the case of low carbon content in the gas (figure 2a) and also in the production of ethane in the high carbon case (figure 2b). It can be concluded from the results of the numerical model that the soot formation will probably be somewhat overpredicted as too much carbon is incorporated in the soot particles. This behavior has been noted in previous work where the concentrations of CO, CO₂, H₂O and H₂ were found to be affected by the soot formation as a result of the incorporation of carbon in the soot particles [26]. However, the results for the concentrations of CH₄, CO₂ and H₂ correspond very well with the experimental data over the entire temperature range. The deviations of the model from the experimental data for CO and H₂O only occur at higher temperatures.

As a conclusion the results from the numerical model is found to show good agreement with the experimental data. However the outcome of the numerical model should not be interpreted as absolute values but as a basis for comparison of different operational alternatives.

3. Simulations

Simulations were performed with varying ingoing gas composition in order to determine the extent to which certain species affect the soot formation. The results of the simulations were evaluated on synthesis gas energy efficiency and methane conversion as well as soot reduction. Because the ingoing gas composition will vary for the different cases the temperature profile over the reactor will also be affected as well as the amount of oxygen that needs to be added. Therefore all temperature profiles for the different cases and the amount of oxygen needed for each case were determined prior to the simulations with the dynamic model previously described. All simulations regarding soot formation were performed with the static model described in the modeling section.

One base case was modeled and eight cases with deviations from the base case were then carried out. The cases are summarized in table 2.

Table 2. Composition of ingoing gas for the modeled cases, mole-%, and the amount of oxygen added to the process, mole-% of total incoming gas flow.

Component	Base case	1	2	3	4	5	6	7	8
CH ₄	7	7	7	7	4	10	7	7	7
C ₂ H ₄	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	4
CO	19	19	19	19	19	19	12	19	19
CO ₂	14	14	14	14	14	14	14	24	14
H ₂	16	16	16	32	16	16	16	16	16
H ₂ O	25	15	35	25	25	25	25	25	25
C ₁₀ H ₈	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0
N ₂	17	27	7	1	20	14	24	7	15
Added O ₂	5	5	5	5	4	5	5	5.5	5.5
Total carbon in (g/m ³)	77	77	77	77	72	82	66	93	77
LHV (total in) MJ/Nm ³	7.85	7.85	7.85	9.41	6.88	8.82	7.04	7.85	8.17
MJ/kg	8.37	8.02	8.74	12.22	7.22	9.55	7.50	7.83	8.90

In case 1 and 2 different water contents in the gas was investigated. In case 3 the hydrogen content in the gas was doubled to study the effect of hydrogen on soot formation. As has been previously observed the hydrogen content has a great influence on the amount of soot formed but it is not known how this will affect the synthesis gas energy efficiency and methane conversion. In case 4 and 5 the methane content of the gas is studied. The effect of carbon monoxide content in the gas is studied in case 6 and in case 7 the influence of carbon dioxide content on soot formation is further investigated. Through these cases it will be possible to deduce which gas component is the most influential with respect to soot formation or whether the total carbon level is more important. In case 8 the effect of tar content is studied. All the naphthalene, model compound for tar, was considered reformed to ethylene and the effect of this on the soot formation was determined.

The synthesis gas energy efficiency was calculated according to eq. 2.

$$\eta = \frac{LHV_{CO+H_2_{out}}}{LHV_{total\ in}} \quad (\text{eq. 2})$$

The soot formation is reported as the amount of carbon in the soot as a percentage of the ingoing total carbon content in the gas. The amount of ingoing carbon is not equal for all simulations, table 2.

4. Results and Discussions

The results of the simulations are summarized in table 3, where the synthesis gas energy efficiency, methane conversion and soot formation is reported. This is also illustrated in figure 4. The relatively low synthesis gas energy efficiency reported for the simulations performed is mainly attributed to the, albeit high, but not full conversion of methane and of course to the formation of soot. A substantial amount of energy is left in the unconverted methane.

Figure 4. The results of the base case compared to the modeled deviating cases 1-8. Energy efficiency and methane conversion is given in % and the soot formation is given in mass-% of ingoing carbon.

Table 3. Summarized results for the modeled cases. Energy efficiency and methane conversion is given in % and the soot formation is given in mass-% of ingoing carbon. The normalized soot formation is normalized with respect to the amount of ingoing carbon as this varies for the different cases.

	Base case	1	2	3	4	5	6	7	8
Synthesis gas energy efficiency	74	73	75	77	75	70	71	76	81
Methane conversion	95	96	95	92	94	97	96	97	94
Soot formation (mass-% of ingoing carbon)	11.1	11.5	10.7	10.9	10.6	12.2	13.0	8.9	6.6
Soot formation (normalized mass-%)	8.6	8.9	8.3	8.4	7.7	10.0	8.6	8.3	5.1

Not surprisingly lowering the water content of the gas increased the amount of soot formed and vice versa, see figure 4 a. However the effect of water content on the soot formation was not as significant as anticipated. It seems that, at the concentrations studied, the water content of the gas only has a minor effect on the amount of soot formed. The synthesis gas energy efficiency and methane conversion for these alternatives were also insignificantly affected. For both case 3 and 4, figure 4 b, soot formation is reduced. This is consistent with previous findings that increasing the hydrogen content of the gas reduces soot formation [28, 29], and also that methane seems to have a negative effect on soot formation. The lower the methane content of the gas the less soot is formed. The increase of hydrogen content in the gas did not affect the soot formation as much as expected. It might be that there is a threshold effect for the hydrogen and this effect should be investigated further. The results of the simulations show that the hydrogen content in the outgoing gas is not increased as much for case 3 as for case 4 or the base case. These results indicate that there is a threshold effect that influences the soot formation. Both synthesis gas energy efficiency and methane conversion is of course greatly affected by varying the methane and hydrogen content of the gas. For the cases with less CO and more CO₂ in the gas, cases 6 and 7 in figure 4 c, it was found that decreasing the CO content of the gas gave rise to an increase in soot formed. The opposite was observed when the CO₂ content of the gas was increased as has been reported in previous studies [26]. This is not surprising since it is well known that CO₂ can act as an oxidizing agent in this type of reactions, donating oxygen and thus forming CO [30, 31]. Both the synthesis gas energy efficiency and methane conversion was increased in case 7. Case 6 has the lowest concentration of CO in the outgoing gas and case 7 has the highest. It seems that the concentration of CO in the outgoing gas is somehow correlated to the amount of soot formed. This is believed to be connected to the addition of CO₂ as it will work as an additional oxidation agent (forming CO) and thus increase the oxidation potential of the gas mixture, which will suppress the coking further. However the amount of ingoing carbon is not the same for all cases. Therefore it might be more correct to look at the normalized amount of soot formed when comparing the cases, see table 3. In figure 5a it is shown that the amount of soot formed is decreased as the carbon content in the ingoing gas is increased. In terms of actual amount of soot formed this is not entirely true as the normalized soot formation is equal for the base case and case 6. For case 7 the normalized soot formation is somewhat lower than that for the base case and case 6. In figure 5b it can also be seen that the amount of oxidant is the highest for case 7 compared to the base case and case 6. This indicates that the amount of oxidant for each case might be the factor controlling the amount of soot formed for each case.

Figure 5. The results for soot formation as a function of the amount of carbon (a), and amount of oxidant (b) for each modeled case. Square symbols represent the base case, circle symbols represent case 6 and triangle symbols represent case 7.

The figure also shows that other factors but the amount of oxidant does impact the soot formation.

For case 8, depicted in figure 4d, the soot formation was greatly reduced. This is true for the normalized soot formation as well. The synthesis gas energy efficiency of the process was greatly improved, mainly due to a lower loss of energy in the soot. The methane conversion was somewhat lower for this case. The results clearly show that the more soot precursors that are present in the gas the more soot will be formed. It is therefore of great interest to further study ways of cracking the tars in the producer gas in an energy efficient way before reforming the methane and C₂-hydrocarbons.

The results show that the soot formation was significantly reduced for case 2, 4, 7 and 8. For the other cases the amount of soot formed was not affected by the varying compositions as much as anticipated.

5. Conclusions

The aim of the investigation was to examine the extent to which soot is likely to form and possible ways of reducing soot formation. One base case and 8 cases with varying gas composition were simulated and studied. The results were evaluated from the viewpoint of synthesis gas energy efficiency and methane conversion as well as soot reduction. The results showed that neither steam nor hydrogen content of the gas affected the soot formation in any high degree, which is unexpected. The methane content of the gas had a greater impact on the amount of soot formed than both steam and hydrogen content. The amount of soot formed was reduced when more CO₂ was present in the ingoing gas, most likely due to the increased amount of oxidant present. The synthesis gas energy efficiency and methane conversion was also positively affected in this case. The best results regarding soot formation was received for the case when no tars were present in the ingoing gas.

The reaction mechanism used in the numerical model presented in this work was not developed to describe reforming. Instead it has been adapted for combustion of benzene in fuel-rich flames. The model should, according to theory, be valid also for reforming but the deviation from expected behavior may indicate that the model does not perfectly describe the reactions involved. It would therefore be of interest to develop a reaction mechanism that could describe soot formation in reducing environments such as reforming.

From the results obtained it was concluded that in order to reduce the amount of soot formed in the reverse-flow POX reactor it would be of interest to further study ways of reducing the amount of tars in the gas in an energy efficient way. Experimental research of this process is undergoing and will be presented in later work.

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