Development of a Tar Decomposition Model for Application in a Chemical-Looping Reformer Operated with Raw Gas from a Biomass Gasifier

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Abstract

The production of synthetic natural gas (SNG) represents one of the most promising alternatives for biofuel manufacture. The producer gas, from biomass gasification, has to be cleaned from the presence of condensable organic hydrocarbons called tars, as well as from other contaminants. A system for cleaning the producer gas was developed at Chalmers University of Technology, using a Chemical-Looping Reformer (CLR) for catalytic cracking of the tar components. A model of the catalytic decomposition of tars was developed, using experimental data available from this system. A manganese-based catalyst was used in the fuel reactor (FR) at three different operating temperatures. Two oxygen concentrations were used for reforming the catalyst in the air reactor (AR). From implementation of the model, it was possible to verify to what extent the model correctly describes the tar decomposition processes inside the reactor. Also, to get a first impression on how fast the reactions are and how reactions interact among themselves. Experimental data and simulation results only differed by around 15% (maximum). It was possible to observe some trends on the tar decomposition pattern but no simple correlation between operating conditions and cracking processes could be derived. Temperature seems to have a higher influence on the results than the oxygen concentration.

Keywords: Tars; Catalytic Cracking/Decomposition; Manganese-Based Catalyst; Biomass Gasification; Synthetic Natural Gas; Chemical-Looping Reformer

1. Introduction

Natural gas is increasingly important as a primary source. It is used for electricity production, for industrial and domestic heating purposes, as a chemical feedstock and it is gaining importance in the transport sector as compressed natural gas (CHG) [1]. According to BP Statistical Review of World Energy [2] the consumption of natural gas will increase over any other energy source (in absolute numbers). The import dependency in the EU is expected to increase to approximately 70% in 2020 [1,3]. Therefore, a sustainable alternative is required as the natural gas reserves are finite and their use still contributes to GHG emissions [4]. The substitution of natural gas by a renewable equivalent is an interesting option to reduce the use of fossil fuels and the consequent gas emissions. This is called green natural gas and comprises both biogas and synthetic natural gas (SNG) [5].

The production of SNG represents one of the auspicious alternatives for biofuel manufacture. A main advantage of the production of SNG is the large diversity of ready-to-use applications in different sectors, especially in the transport sector [4,5]. It could lead to a smooth transition from fossil fuels to bio, renewable fuels [6], allowing extended security of gas supply, especially for the EU [7]. The process steps to yield SNG, illustrated in Figure 1, are gasification of biomass followed by gas conditioning/cleaning, methanation and gas upgrading of the product gas [3,5,6].

A potential limitation for total substitution of natural gas for SNG in the future is the requirement of large amounts of biomass for gasification [3]. Biomass gasification is recognized as an effective way of converting biomass with low heating value into a combustible gas [8]. The choice of the gasifier,
gasifying medium, such as air, steam or oxygen, and operating conditions depends on both the provided feedstock and the whished quality of the final syngas [5]. The composition of the product gas will vary depending on the operating conditions [5]. However, its constituents are permanent gases, such as N₂, CO, H₂, CO₂, CH₄ and C₂H₆, as well as char, ash, soot, particulate matter, steam, volatile organic compounds and condensable organic hydrocarbons [9], as represented by the following equation:

\[
\text{biomass} + O_2 \text{(or } H_2O) \rightarrow CO, CO_2, H_2O, H_2, CH_4 + \text{other hydrocarbons}
\]

\[
\rightarrow \text{tar} + \text{char} + \text{ash}
\]

\[
\rightarrow HCN + NH_3 + HCl + H_2S + \text{other sulfur gases}
\]  

The condensable organic compounds, called “tars”, start condensing at around 350 °C [10] and tend to cause plugging, fouling and corrosion problems in the equipment [9,5]. Tars can be understood as a complex heterogeneous mixture of organic molecules, such as hydrocarbons from 1- to 5-ring aromatic compounds, oxygen and sulphur-containing hydrocarbons and polycyclic aromatics (PAHs) [11,12]. Although they only account for a small percentage of the product gas, they are the most difficult to eliminate [13]. Therefore, product gas conditioning/cleaning is one of the most critical steps in the whole biofuel production process efficiency and it is attracting a lot of attention. There is a necessity to develop new, optimized and more economic processes [13].

Catalytic tar decomposition is considered the technology with the highest potential to contribute to the solution of the tar fraction problem [14]. It offers several advantages: possibility of thermally integrating the catalyst reactor temperatures with the gasifier exit temperatures, minimizing heat losses; possibility of adjusting the composition of the product gas for the utilization step and steam can be added to the catalyst reactor to ensure complete reforming of tars. Different approaches for integrating catalytic tar destruction into biomass gasification systems and numerous catalysts have been already studied [15]. The system under study in this work is one new alternative for this technology.

2. Chemical-Looping Reforming System at Chalmers

2.1. Description of Experimental Set-up

The system was developed by Chalmers, based on the principle of Chemical-Looping Reforming (CLR), with the objective of reducing the tar fraction in the product gases from biomass gasification processes. It reforms the tar components (CₙHₘ) into useful gas molecules [16,17] through partial oxidation, steam reforming and catalytic cracking of the compounds, using a metal oxide catalyst circulating between the two fluidized bed reactors. The used catalyst particles, M4MgZ1150 (a manganese-based metal oxide), are characterized in Table 1. Operating conditions during the experiments were characterized by a bed material composed of 23 wt% catalyst and 77 wt% silica-sand with operating fuel reactor (FR) temperatures between 700 °C and 800 °C, and two different oxygen concentrations (1% and 2.2%) in the
air reactor (AR). Previous studies at Chalmers demonstrated that the silica-sand has no activity on the tar cracking [18]. The complete system is composed of two fluidized beds and is illustrated in Figure 2.

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>Mn₃O₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt % of the metal oxide</td>
<td>40</td>
</tr>
<tr>
<td>Inert material</td>
<td>Mg-ZrO₂</td>
</tr>
<tr>
<td>Wt % of the inert</td>
<td>60</td>
</tr>
<tr>
<td>Nomenclature</td>
<td>M₄MgZ₁₁₅₀</td>
</tr>
</tbody>
</table>

| Sintering temperature [°C] | 1150 |
| Density [kg m⁻³] | 2260 |
| Porosity | 0.58 |
| Crushing strength [N] | 0.7 |
| Rate index | 4.60 |

Table 1 - Summary of properties of M₄MgZ₁₁₅₀ particles

Both reactors are placed inside an oven and are kept at pressures of 94 to 96 kPa. In the FR the raw gas reacts with the partially oxidized catalyst. The reformed raw gas leaves the system as cleaned producer gas and the reduced catalyst goes into the AR through the inferior loop-seal (ILS). In the AR, re-oxidizing reactions of the metal oxide will occur. The reformed catalyst returns to the FR through a cyclone and the superior loop-seal (SLS). Both loop-seals are fluidized with helium.

2.2. Measurement Techniques

The permanent gases are analyzed by a micro gas chromatograph after passing through a cooling and cleaning (using iso-propanol as a solvent for the remaining tars in the gases) setup.

The complexity of tars makes it impossible to perform an on-line analysis [4]. Therefore, it was used a novel technique – solid-phase adsorption (SPA) on amino-phase for vapor-phase tar sampling. The method includes the SPA on amino-phase, for sampling, followed by liquid chromatographic (LC) group separation and capillary gas chromatography (GC) with flame-ionization detection (FID), for the individual tar compounds analysis [12].

3. Decomposition model

Tar samples were taken every hour or one hour and a half after changes in the operating conditions, so that the system could reach steady-state conditions. These samples were taken in sets of between three to six SPA-samples at the inlet and outlet of the CLR-system. 21 known molecules were chosen to be the representative tar molecules for the whole system. Also, approximately 170 unknown compounds with molecular weights spread between benzene and higher than pyrene were detected.

Grouping these tars took into account three parameters – the individual conversion, the molecular structure and the relative percentage of each tar from the total number of existing tars. The tar concentrations were He-corrected and calculation of their respective conversions was done by:

$$X_i[\%] = \left( \frac{C_{i,0} - C_i}{C_{i,0}} \right) \times 100 = \left( 1 - \frac{C_i}{C_{i,0}} \right) \times 100$$ (2)
In the GC-FID analysis, molecules are identified by their length and polarity while they are being processed. This means that the unknown molecules listed in times between other known compounds, have, most probably, similar sizes and structures to the known molecules adjacent to them. Therefore, it was decided that the unknown molecules would be divided according to their detection position between the known compounds after the grouping of the 21 known molecules was performed. Figure 3 shows the scheme of resulting tar groups.

Group concentrations were calculated by addition of each group component’s individual concentration. Group conversions were calculated by Equation 2. One important thing to keep in mind is that when talking about conversion of a group what is being mentioned is the relative velocity at which tars from the group are being decomposed against the velocity of formation of these same molecules originated from other groups’ own decompositions. For this reason, it was important that the developed model could translate correctly the simultaneousness of the reactions and the interaction between groups.

Grouping of tar samples and grouping of the tars for development of model showed an error below 15%. Exceptions were observed for benzene, which were explained by the possibility of detachment of the molecules from the amino-phase extraction column, due to the high vapor-pressure at which they are submitted.

A model by Corella et al. [19], which divided the tars into six different groups, was considered to be the base of the developed model. It considered that both thermal and catalytic mechanisms occurred simultaneously in the tar decomposing reactions, giving no particular relevance to one or the other. This

![Figure 3 - Tar groups: a) benzene; b) naphthalene; c) branched molecules of 1 and 2 rings; d) non-alternant molecules of 1 and 2 rings; e) polycyclic aromatic hydrocarbons (PAHs) of 3 and 4 rings; f) phenolic compounds](image-url)
was important because thermal cracking was considered insignificant in this work (silica-sand study). Figure 4 illustrates the developed tar decomposition model.

As shown in Figure 4, the amounts of H$_2$, CO, CH$_4$, C$_2$H$_6$ and char should be calculated from the entire reactions network, as they are resulting components from the cracking of each lump and not only from the decomposition of the last group, i.e., benzene. The general cracking reaction can be described as:

$$\text{Tar} \ (C_nH_m) + CO_2 + H_2O \rightarrow C_{n-1}H_m + C + H_2 + CO + CH_4 + C_xH_y$$

(3)

The proposed reaction network has 11 kinetic constants. Therefore, the set of kinetic equations to describe it should be the simplest possible. Thus, first-order reactions with respect to the concentration of the groups considered were chosen:

$$r_j = k_{ij}C_i - k_{ji}C_j$$

(4)

where $r_j$ is the reaction of the $j^{th}$ group, $k_{ij}$ and $k_{ji}$ are the kinetic rate constants (from the $i^{th}$ group to the $j^{th}$ group and forward) and $C_i$ and $C_j$ are the concentrations of each group, respectively. Positive sign means the formation of the $j^{th}$ group from the decomposition of the $i^{th}$ group and negative signs mean the decomposition of the $j^{th}$ group forward to a following $l^{th}$ group.

The reaction of each group can also be interpreted as a first order differential equation because it describes how the concentration of each group varies in time, i.e., the reaction rate. The group of equations that describes the kinetics of the developed model is:

$$r_1 = \frac{C_{1,0}dX_1}{d\tau} = \frac{dC_1}{d\tau} = k_{31}C_3 + k_{41}C_4 - k_1C_1$$

(5)

$$r_2 = \frac{C_{2,0}dX_2}{d\tau} = \frac{dC_2}{d\tau} = k_{42}C_4 + k_{52}C_5 + k_{62}C_6 - k_{23}C_2$$

(6)

$$r_3 = \frac{C_{3,0}dX_3}{d\tau} = \frac{dC_3}{d\tau} = k_{23}C_2 + k_{43}C_4 + k_{53}C_5 - k_{31}C_3 - k_{36}C_3$$

(7)

$$r_4 = \frac{C_{4,0}dX_4}{d\tau} = \frac{dC_4}{d\tau} = k_{54}C_5 - k_{41}C_4 - k_{42}C_4 - k_{43}C_4$$

(8)

$$r_5 = \frac{C_{5,0}dX_5}{d\tau} = \frac{dC_5}{d\tau} = -k_{52}C_5 - k_{53}C_5 - k_{54}C_5$$

(9)

$$r_6 = \frac{C_{6,0}dX_6}{d\tau} = \frac{dC_6}{d\tau} = k_{36}C_3 - k_{62}C_6$$

(10)
The residence time of the raw gas inside the FR and in contact with the catalyst, i.e., the time that the actual catalytic cracking is being performed, is equal to 1 second. The measured volume flow of the raw gas feed was around 2.6 l/min for every operating condition.

Implementation of the model and estimation of the kinetic reaction rate constants was performed using the software MatLab r2009b or r2010b.

4. Results and Discussion

Figure 5 represents the conversions of each group of tars for the different operating conditions. An estimation of the trends of each tar group’s decomposition was performed:

1) Benzene:
   - Seems to be “converted” at 700 °C; this is, all remaining groups have low conversions at 700 °C and the decomposition velocity of benzene is high enough to compensate the molecules’ formation from other tars’ breakdown;
   - However, benzene is produced at a faster rate at higher temperatures;

2) Naphthalene always increases in concentration:
   - For lower oxygen concentrations, the concentration of naphthalene increases with increasing temperature;
   - But with higher oxygen concentrations, the concentration increases with decreasing temperature, meaning that probably higher O₂ and higher temperatures are the most favorable conditions to have higher decomposition of naphthalene, along with/besides the formation from other groups;

3) Branched compounds always breakdown:
   - Increasing temperatures and increasing oxygen concentrations lead to higher conversions, this is, even if there is high formation of these compounds from other molecules, as they have more fragile structures they have a higher tendency to breakdown and compensate the previous effect;

4) Non-alternant molecules behave similarly to the branched compounds;

5) 3 and 4 rings PAHs:
   - Increase concentrations at 700 °C for both oxygen concentrations; this might occur because at 700 °C the unknown molecules from that group, which most probably have larger and branched structures, decompose first (on elemental conversions they have
positive values, meaning cracking) giving formation to the other molecules from the same group;
  o However, for the remaining conditions they decompose with increasing conversion for increasing temperatures and O2 concentrations;

6) Phenolics always decompose with the largest conversions of the whole present compounds in the raw gas, meaning that they are the easiest to decompose, as suggested in previous works [19].

However, no simple correlation between operating conditions and tar conversion was possible to be achieved. This means that, the proportion of tars that enter the system and that are decomposed inside it cannot be linearly related with the working temperatures and oxygen concentrations.

Finding the best kinetic constants (k) for each operating condition was done by manually sorting the range of values that best fitted the concentrations of each tar group, at a residence time equal to 1 second. When a good set of k’s appeared, graphics of the evolution of the tars’ concentrations throughout a determined residence time span were plotted.

![Figure 6 - Evolution of each tar groups’ concentrations at 700 °C and 1% O2 on the considered time span](image)

![Figure 7 - Zoom of the evolution of each tar group’s concentrations at 700 °C and 1% O2 pointing the initial concentrations (at the FR inlet) and concentrations at residence time 1 second (at the FR outlet)](image)
Figure 8 - Evolution of each tar groups' concentrations at 800 °C and 2.2% O2 on the considered time span

Figure 9 - Zoom of the evolution of each tar group’s concentrations at 800 °C and 2.2% O2 pointing the initial concentrations (at the FR inlet) and concentrations at residence time 1 second (at the FR outlet)

Figure 6 to Figure 9 show the evolution of the tar groups' concentrations, both over the considered time spans and the zoom on the residence time inside the FR, for two main operating conditions – 700 °C with 1% O2 and 800 °C with 2.2% O2. Results for these temperatures and different oxygen concentrations as well as for 750 °C were also obtained. Table 2 shows the “intrinsic reactivity rate” of each group for the two operating temperatures shown in the figures. The “intrinsic reactivity rate” can be understood as the relative velocity at which each group is decomposed.

Table 2 - "Intrinsic reactivity rate" of each group of tars

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
<th>G5</th>
<th>G6</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 °C; 1% O2</td>
<td>6.3</td>
<td>0.5</td>
<td>0.85</td>
<td>0.38</td>
<td>0.085</td>
<td>3</td>
</tr>
<tr>
<td>700 °C; 2.2% O2</td>
<td>6.2</td>
<td>0.3</td>
<td>0.96</td>
<td>0.385</td>
<td>0.0013</td>
<td>5.2</td>
</tr>
<tr>
<td>800 °C; 1% O2</td>
<td>9</td>
<td>0.75</td>
<td>3.1</td>
<td>1.08</td>
<td>0.59</td>
<td>16.1</td>
</tr>
<tr>
<td>800 °C; 2.2% O2</td>
<td>9.5</td>
<td>1</td>
<td>4.05</td>
<td>1.56</td>
<td>0.72</td>
<td>37</td>
</tr>
</tbody>
</table>

From Figure 6 and Figure 8, it is verifiable that with increasing temperatures, the necessary residence time in the FR for the complete decomposition of tars is decreasing. This is seen by the curvature of the evolution lines, which increases for increasing temperatures. This means that, with higher operating temperatures, the reforming reactions occur faster as soon as the raw gas enters the FR. As a consequence, bigger conversions are obtained and the necessary residence time is shortened. With
increasing oxygen concentrations this is effect is also present. However, it is not so pronounced. These results are portrayed by the increase in the values of the “intrinsic reaction rates” with increasing operating conditions.

From Figure 7 and Figure 9, it is possible to seen the combined effect of O\textsubscript{2} and temperatures in the slopes of each tar group near the initial time. This is specially verified for the naphthalene (G2) and benzene (G1) curves. With increasing values of the operating conditions, a high peak in the curve is formed when entering the FR. This means that the decomposition of bigger tar groups is so fast that the formation of naphthalene and benzene is very high. However, at these operating conditions the decomposition of naphthalene and benzene is also faster, making the curvatures decrease more sharply. The phenolics (G6) should also be noticed, as the gradient at residence time zero is near 90°, meaning almost immediate total decomposition of these compounds. This is not surprising as the phenolics are the easiest molecules to reform.

From Table 2 it is seen that the differences between the reactivity rates at 700 °C and 800 °C are higher than the differences between different O\textsubscript{2} concentrations for each temperature. This means that, probably, the operating temperature of the FR has a bigger influence on the decomposition process than the oxygen concentration in the AR, as suggested in the figures discussion.

It is important to keep in mind that all these kinetic constants are affected by the simulation errors, which presented a maximum value of around 15%. A small change in one group decomposition velocity can change significantly all other kinetic constants. This happens because the model is a net of interrelated reactions and every change in one group has consequences on the behavior of all the remaining ones. Errors could be derived from the degree of uncertainty that is present in the simulation because of the required manual process of choosing the kinetic values’ range.

5. Conclusions

The decomposition model was developed after tars were grouped according to three criteria – individual conversions, molecular structure and relative percentage in the whole tar amount. A reaction network was developed to represent the relation between tar decompositions inside the fuel reactor.

Naphthalene is always formed at higher rates than it is decomposed, for all operating temperatures and oxygen concentrations. This is confirmed by the positive gradients at low residence times of the evolution of tars’ concentrations and by the low values of the “intrinsic reaction rates”, especially at higher temperatures. For higher temperatures, it is expected the growth in concentration of benzene as it is the last considered stage of decomposition in the developed model. Branched compounds and non-alternant molecules seem to have higher decomposition rates than formation rates at all FR and AR conditions. Phenolic compounds seem to be the easier compounds to breakdown, which is supported by the highest conversions of all tar groups in all situations and the sharpest negative gradients in all simulation results. As expected, general trends were possible to be withdrawn from the conversions and evolution of concentrations of tars but no simple correlation was possible to be made. The proportion of tars that entered the system and that were decomposed inside could not be linearly related with the operating conditions. However, FR operating temperatures seem to have a higher influence on the decomposition process than the AR oxygen concentrations.

Overall, the model seems adequate to represent the reaction network and tar relative decomposition velocity inside the fuel reactor. Hence, from simulation results, conjectures of the behavior of tars with changing operating conditions could be made. It was observed the trend that higher temperatures and higher oxygen concentrations seem to improve the system performance.
References


