Modeling of Reverse Flow Partial Oxidation Process for Gasifier Product Gas Upgrading

Per Tunå, Helena Svensson, Jan Brandin,*

Abstract

Biomass gasification is one of the alternatives to producing liquid fuels and chemicals from biomass residues. The gas produced in gasification contains CO, H₂, H₂O, CO₂, light hydrocarbons and tars. Depending on the gasifier type, operating conditions and fuel, the light hydrocarbons can contain as much as 50% of the total energy contents in the gas. The gas also contains catalyst poisons such as sulfur, as H₂S and COS. This paper presents simulation work of a reverse flow partial oxidation reformer that reaches efficiencies approaching conventional catalytical processes. Furthermore, different reactor designs and parameter variations such as pressure are investigated. For comparison, natural gas simulations are included which clearly show the benefits of using reverse flow operation with lean gases such as gasifier product gas.

Keywords: Reverse Flow Operation, Partial Oxidation, Gasification

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>H</td>
<td>Gas enthalpy, kJ/kg</td>
</tr>
<tr>
<td>G</td>
<td>Gas mass flow, kg/s</td>
</tr>
<tr>
<td>k</td>
<td>Heat transfer coefficient, kJ/m².K</td>
</tr>
<tr>
<td>S</td>
<td>Solid Specific Surface area, m²/m³</td>
</tr>
<tr>
<td>λ</td>
<td>Solid phase heat conductivity, kJ/m.K</td>
</tr>
<tr>
<td>i</td>
<td>Mass flow of specie i, kg/s</td>
</tr>
<tr>
<td>j</td>
<td>Stoichiometric coefficient for specie i in reaction</td>
</tr>
</tbody>
</table>

1. Introduction

Second generation bio-fuels utilize non-food crops for the production of fuels, which means that agriculture waste, forest residue and energy crops become useful for fuel production [1]. One important process for utilization of cellulose rich biomass is gasification. Gasification is a well proven technique for processing of fossil fuels and has been used extensively and has recently been used on biomass feed stocks. During the gasification, the coal containing material is oxidized in contact with air/oxygen and/or steam that convert the solid fuel into a gas and an ash fraction. Gasification is an endothermic reaction and heat has to be supplied, either directly or indirectly.

The produced gas contains as major components CO, CO₂, H₂, H₂O (and N₂ if air is used for the gasification). The composition depends on gasifier type, operating conditions and fuel. However, it may also contain some lower hydrocarbons, C₁-C₃, tars and a multitude of smaller amounts of contaminates such as H₂S, COS, NH₃, HCN. A large portion of the Lower Heating Value (LHV) of the gas can be bound in the lower hydrocarbons (CH₄ + C₂-C₃), up to 50% depending on gasifier type, feed stock etc., while the tars can contain about 10% of the LHV. If the goal is to produce synthesis gas, these hydrocarbons need to be converted.

Because of the contaminants present in the gas, mainly sulfur, conventional technology, such as steam reforming, cannot be used to convert the hydrocarbons to synthesis gas, at least not the methane. Other techniques such as auto-thermal reforming and catalytic partial oxidation, might work, due to higher operating temperature, but have not yet been proven. These techniques all rely on a catalyst, which is highly susceptible to sulfur poisoning, to function effectively. The alternative then is to use a non-catalytic process, for instance partial oxidation. The problems associated with non-catalytic partial oxidation (POX) are mainly related to the high temperature needed for the reactions to occur and the loss of chemically bonded energy in the gas. The temperature is typically 1200-1400°C [2]. In order to deal with this problem and make the process more energy efficient a regenerative reverse flow reactor can be utilized.

In a regenerative reverse flow reactor, heat is transferred between a fluid and a stationary phase. Usually streaming hot gas heats a bed of granular material, while the gas cools down. One of the most important parameters for the thermal buffer is the heat storage capacity and the mass of the solid packing material. The stored heat in the bed can be utilized by flowing cold gas in the opposite direction, heating the gas...
and cooling the bed. The reason for using such a device is the thermal efficiency that can be achieved. It is not unusual with up to 95% efficiency [3]. This is partly due to the large heat transfer area that can be obtained in a bed of granular material, and partly to the high heat transfer coefficients that can be obtained in a packed bed with a proper choice of grain size and gas flow rate.

The forced unsteady-state conditions that occur during reverse flow operation have been shown to have a positive influence on several catalytic processes [3-5]. The main advantages of this reactor operation mode are the absence of a catalyst that can be deactivated, the high thermal efficiency, due to the heat recuperation, and that an optimal temperature profile can be achieved in the reactor so as to benefit the reactions [6-9]. Blanks et al [7] demonstrated the concept of CPO, with Ni-catalyst, and POX of natural gas first in laboratory scale with a natural gas flow of 3 Ndm$^3$/min using air as oxidant. Since then several simulation and laboratory investigations have been performed predominantly on CPO [10-13].

2. Modeling

The regenerative reformer is modeled as a tank-series. The simulations were performed in a C++ program as the performance advantages over scripted programs such as MATLAB are very noticeable. A third party library, Cantera, is utilized to calculate kinetics and thermodynamics. Cantera uses GRI-Mech 3.0 [14] for the kinetics. GRI-Mech 3.0 contains 53 species and 325 reactions and was originally designed to model combustion of natural gas.

2.1. Heat and Mass Balances

The heat and mass balances for the system is described with the following ordinary and partial differential equations:

Energy balance for the gas phase

\[ \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \frac{1}{\rho} \frac{\partial \rho H}{\partial x} \right) + m_{\text{in}} H_{\text{in}} + m_{\text{out}} H_{\text{out}} + \Delta H_{\text{reaction}} + \dot{Q} \left( T_{\text{inlet}} - T_{\text{outlet}} \right) \]  

Energy balance for the solid phase

\[ \frac{\partial T}{\partial t} = \frac{1}{\rho_{s}} \frac{\partial}{\partial x} \left( \alpha \frac{\partial T}{\partial x} \right) + m_{\text{in}} a_{\text{in}} + m_{\text{out}} a_{\text{out}} \]  

Mass balance for the gas phase

\[ \frac{\partial n}{\partial t} = m_{\text{in}} H_{\text{in}} + \sum_{i} \dot{N}_{i} \]  

The solid phase is not modeled as a tank series and therefore it needs boundary conditions. The Partial Differential Equation (PDE) for the solid heat balance has the following boundary conditions:

\[ \frac{\partial T_{\text{wall}}}{\partial x} \bigg|_{x=0} = \frac{1}{\lambda} \left( T_{\text{inlet}} - T_{\text{wall}} \right) \]  

\[ \frac{\partial T_{\text{wall}}}{\partial x} \bigg|_{x=L} = 0 \]

2.2. Pseudo Steady-State

Evaluating the results from simulation of a forced unsteady state system such as the regenerative reactor requires additional programming to determine when pseudo steady-state is achieved. The evaluation algorithms store the temperature profiles in the reactor during the simulation and when sufficient number of cycles shows the same profile over the reactor it evaluates the efficiency and conversion of methane. We allowed a deviation of 5K between the profiles during our simulations. After five almost identical cycles the system was deemed to be in pseudo steady-state and the results could be evaluated.

2.3. Reactor Design

The design of the reformer started as a straight pipe but soon evolved. The need for increased residence times was apparent, but reactor length in excess of one meter was undesired. That resulted in increased reactor diameter. But increasing the diameter also increases the mass of the bed material. This had a negative effect as the inlet gas could no longer cool the inlet of the reactor before the next switch and the consequence was that the temperature at the end points of the reactor reached the same temperature and the system failed.

In order to avoid too much heating of the end points the diameter at the ends was reduced by two thirds. This design was further improved by leaving 50% of the large section hollow for an additional increase in residence time.

The original concept had the oxygen inlet in the centre of the reactor. This has the advantage of only using one inlet, but a clear disadvantage is that only half of the reactor volume can be utilized. Adding oxygen to the inlet gas stream enables the whole volume of the reactor but it heats the inlet at the same time resulting in a system failure due to end point temperature as mentioned above. The ideal solution lies somewhere in between and it was decided to add oxygen at the beginning of the large section and at the end of the large section. Only the oxygen inlet closest to the reactor inlet is in use and when the flow direction switches the active oxygen inlet switches as well.

2.4. Evaluation Criteria

Two different cases were tested to evaluate the capabilities of the regenerative reformer, natural gas and synthesis gas from gasified biomass. Efficiency calculations were defined as:
Table 2: Gas composition used in the simulations.

<table>
<thead>
<tr>
<th>Component</th>
<th>Natural Gas</th>
<th>Gasifier Product Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.5 %</td>
<td>-</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.5 %</td>
<td>27.8 %</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>4.5 %</td>
<td>-</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>2.5 %</td>
<td>-</td>
</tr>
<tr>
<td>CH₄</td>
<td>92 %</td>
<td>8.1 %</td>
</tr>
<tr>
<td>CO</td>
<td>-</td>
<td>11.8 %</td>
</tr>
<tr>
<td>H₂O</td>
<td>-</td>
<td>37.6 %</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>-</td>
<td>3 %</td>
</tr>
<tr>
<td>H₂</td>
<td>-</td>
<td>11.7 %</td>
</tr>
</tbody>
</table>

For natural gas, the enthalpy of the additional steam is added to LHV_{total} in. Both the methane conversion and the efficiency in the reactor have to be considered when determining the effect of different parameters. When the steam/carbon-ratio in the gas is too low, the reforming becomes equilibrium constrained and yields too low methane conversion. Since the efficiency calculations include the energy in the steam and because additional steam is needed for the natural gas reforming the efficiency figures for natural gas are overall lower. Therefore it is difficult to compare a methane rich gas, such as natural gas, to a lean gas such as gasifier producer gas as the requirements to maximize efficiency are different.

All simulations were run with the properties presented in Table 1.

Table 1: Properties for the reactor during simulations.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor length</td>
<td>0.6 (m)</td>
</tr>
<tr>
<td>Reactor diameter (thickest)</td>
<td>0.1 (m)</td>
</tr>
<tr>
<td>Diameter ratio (max/min)</td>
<td>3</td>
</tr>
<tr>
<td>Inlet gas flow</td>
<td>6 Ndm³/min</td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>873 K</td>
</tr>
<tr>
<td>Switch-temperature</td>
<td>1000 K</td>
</tr>
<tr>
<td>Particle size</td>
<td>1x1 mm spheres</td>
</tr>
</tbody>
</table>

The composition for the natural gas and the gasifier product gas is given in Table 2.

3. Results

Fig. 3 shows the typical profile for gas temperature and component mole fractions for a simulation. The temperature of the solid is the same as the temperature for the gas and is therefore omitted. There are three sections of the reactor, two heat buffers and a reaction zone. Following the inlet from left to right in Fig 3, the inlet gas cools the first heat buffer in the reactor before entering the oxidation zone (first peak) were the temperature is increased. After the oxidation zone the temperature decreases due to the endothermic reactions. The second peak is the oxidation zone for operation in the opposite direction. As the gas exits the reactor and goes through the second heat buffer, it heats the bed which effectively moves the heat from the first heat buffer to the second. When the flow is reversed, the heat is moved back to the first heat buffer and a cycle is completed.
Fig. 4 shows the performance figures for gasifier product gas reforming with varying oxygen inlet amount. There is a clear trend for increased oxygen amount as the methane conversion increases which raises the efficiency. However, there is a point at which further increase of oxygen decreases the efficiency. Adding more oxygen to the gas will oxidize more of the feed gas towards carbon dioxide and water which increases temperature and lowers efficiency.

Varying the reactor pressure, while keeping the inlet flow constant, as can be seen in Fig. 5, also varies the residence time (top X-axis in Fig.5 shows the residence time in seconds). The low residence time for atmospheric pressure, results in low conversions of methane and higher temperature as the endothermic reforming reactions are less evident. Increasing the residence time increases the reforming which lowers reactor temperatures. Lower reactor temperatures decrease the reforming which explains the drop in methane conversion at higher residence times.
Fig. 6. Reactor efficiency and conversion of methane as a function of steam/natural gas-ratio.

Fig. 6 shows the reactor efficiency and the conversion of methane as a function of the steam/natural gas-ratio. The simulations were run using a constant oxygen/natural gas-ratio and the result is a decrease in the reactor temperature, $T_{\text{max}}$, due to the decrease of energy input, which has a negative effect on the conversion. Increasing the steam/natural gas-ratio is however better for the equilibrium which explains why the conversion is not linear as a function of steam/natural gas-ratio. Increasing the steam/natural gas-ratio has a negative effect on the efficiency as more steam is required. The efficiencies, with and without steam, in the figure can be considered to be two extreme points. In an industrial application, the heat in the exit gas can be utilised and the efficiency goes up somewhat for the gas with higher steam ratio.

Fig. 7. Methane conversion and reactor efficiency as a function of added oxygen.

Fig 7 shows the conversion of methane and the reactor efficiency as a function of the added oxygen in percent of the total inflow of reactants. There is a clear trend that increasing the oxygen amount increases the temperature and methane conversion, which results in higher reactor efficiencies. But when too much oxygen is added (16 %), the temperature in the oxygen-inlet zone gets too high, over 1723 K, which is considered the maximum temperature for safety reasons.

4. Conclusion

When natural gas is used as feed, additional steam must be added in the inlet in order to achieve an acceptable conversion of methane. The synthesis gas contains a relatively low amount of methane and higher hydrocarbons and a sufficient amount of steam for high methane conversion. It is also necessary to increase the residence time when the concentration of methane increases.

The regenerative reformer seems well suited for reforming of methane in gasifier product gas. The same system is however not equally suited for reforming of natural gas and further research is required.

The two most important parameters for the reforming of methane are residence time and temperature. Both parameters are dependent on a number of other parameters such as the oxygen inlet flow, reactor dimensions, reactor pressure etc.

Cycle times for the gasifier product gas simulations were in the range 5-6 minutes and 7-8 minutes for natural gas. The systems can not, however, be compared with each other as the temperature in the reactors differ. Natural gas reforming requires more energy, in absolute terms, as it contains more methane, which lowers the temperature after the oxidation zone. The temperature falls faster as more methane is present in the gas. The lower temperature requires longer residence times, or higher reactor temperatures. It is however not realistic to increase the temperature beyond 1700-1800 K as it is approaching the melting point of the bed. Higher reactor temperature also consumes more of the chemically bonded energy in the outgoing gas and thus lowers the efficiency.

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References


