Formation and Decay of Hydrocarbon Intermediates in an Entrained Flow Gasifier

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Abstract

The paper is concerned with entrained flow gasification of biomass based suspension fuels like pyrolysis oil and char used in the bioliq® process [1] developed at KIT. Experiments carried out under atmospheric conditions with model fuels mixed from glycol and pyrolysis char showed that especially the processes in the main reaction zone near the burner influence process efficiency and syngas quality. Thus a basic understanding of the thermo-chemical processes during reaction of a multi-phase system is essential. Additionally to conventional probe measurements determining the gas phase composition, laser-optical measurement techniques provide complementary information with the advantage of being non-intrusive and having a high spatio-temporal resolution. Laser Induced Incandescence, LII, measurements were successfully applied during gasification of biomass based suspension fuels. The resulting information on soot concentration and primary particle size provides valuable complementary data to conventional gas phase measurements for a better understanding of the gasification process.

1. Introduction

High pressure entrained flow gasification is an efficient technology for the conversion of biomass and low rank fuels into high-quality synthesis gas, which can be further converted to liquid fuels of the 2nd generation or other chemical products. In the bioliq® process developed at KIT [1], straw and other abundant ligno-cellulosic agricultural by-products are pre-treated by fast pyrolysis. The resulting suspension of pyrolysis oil and char is afterwards converted to synthesis gas by high pressure entrained flow gasification. The major scientific challenge is the basic understanding of the thermo-chemical processes during reaction of a multi-phase system at high pressure and temperature. The basic steps of the gasification process are atomization of the fuel, fast heating up and evaporation of the droplets, thermal

decomposition of the fuel, as well as fast combustion and slow gasification reactions. Under ideal conditions the syngas contains only H_2, CO, CO_2 and H_2O, whereby the relation between these species can be described by the water-gas-shift equilibrium reaction [2]. In technical systems, however, due to non-ideal process conditions resulting from atomization, incomplete mixing, residence time distribution and heat loss, intermediate species will reach the reactor outlet, influencing the efficiency of the process. Experiments carried out under atmospheric conditions showed that especially the processes in the main reaction zone characterized by a highly turbulent flame influence process efficiency and syngas quality. With standard gas phase analytics the concentration of permanent gases and gaseous hydrocarbons can be determined using conventional sampling probes. However, besides gaseous hydrocarbons also soot or tar may be formed depending on the operational conditions and fuel specification. Laser-optical measurements have the advantage to be non-intrusive and having a high spatio-temporal resolution. Thus they provide valuable complementary information to conventional gas phase measurements with sampling probes.

2. Experimental Set-up

Experimental investigations are carried out at the laboratory Research Entrained Flow Gasifier REGA (thermal load 60 kW) under atmospheric conditions. Figure 1 shows an axial cut through the reactor. In Figure 2 the cross section used for the measurements is depicted.

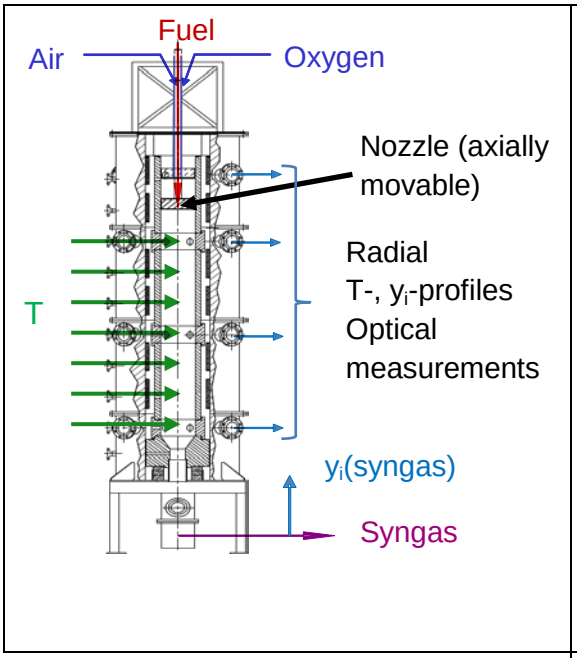

Figure 1 Axial cut through Research Entrained Flow Gasifier REGA.

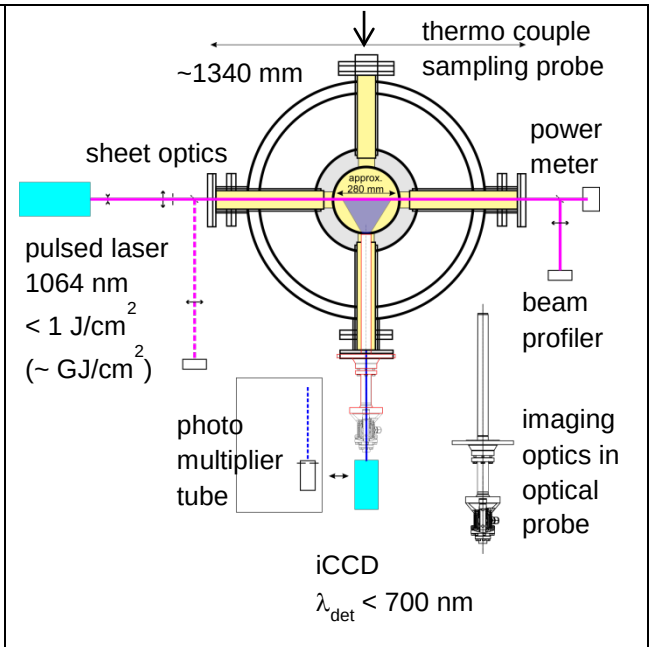

Figure 2 Cross section used for the measurements.

Heat loss is minimized by electrical heating in order to perform the experiments under technically relevant temperatures up to 1500 °C. Liquid or suspension fuels are fed to the reactor by twin-fluid nozzles, using air with variable oxygen enrichment as atomization and gasification medium, which allows for the independent variation of stoichiometry, process temperature and atomization parameters. The reactor provides access for conventional sampling probes as well as for optical measurements. With a vertical movable burner construction, radial temperature or gas phase composition profiles can be measured at variable burner distance, providing a complete data map of relevant quantities inside the reactor. [3]

For the experiments reported here, model fuels like glycol and slurries mixed from glycol and 10 wt% beechwood or straw char were used. The concentrations of permanent gases and gaseous hydrocarbons were determined by standard gas phase analytics and a µGC, using conventional sampling probes. Temperature profiles were measured applying type B double bead thermocouples. In order to investigate the formation of soot, laser-induced incandescence (LII) was applied through an endoscope with a wide angle optic allowing for a field of view of approximately 2/3 of the reactor diameter. LII permits the quantitative determination of soot concentration and primary particle size. The soot particles are rapidly heated up to sublimation temperature by a pulsed laser beam. The incandescence of the particles is measured using collection optics and photodetectors. The soot concentration can be calculated from the peak intensity, whereas the decay behavior of the LII signal is a measure for the primary particle size. [4, 5]

3. Results and Discussion

In Figure 3 radial profiles of hydrocarbon concentration and gas temperature are shown measured 300 and 680 mm downstream from the burner tip for slurry mixed from glycol and 10 wt% beechwood char. With increasing distance from the burner the concentration of hydrocarbons and the temperature decrease due to gasification reactions. At 300 mm both the gas concentration and temperature show a maximum on the reactor axis, whereas at 680 mm gas temperature and gas concentration are distributed homogeneously. This shows the end of the main reaction zone where mixing and reaction are almost completed.

Figure 4 compares the concentration of gaseous intermediates along the reactor axis for glycol and a slurry mixed from glycol and 10 wt% beechwood char. The values are normalized by the respective concentration at 300 mm downstream of the injector. For both fuels there is a fast degradation of intermediates in the main reaction zone up to 680 mm.

For the slurry the methane concentration is higher at the end of the reactor, as intermediates are still formed downstream the main reaction zone due to gasification of char and soot.

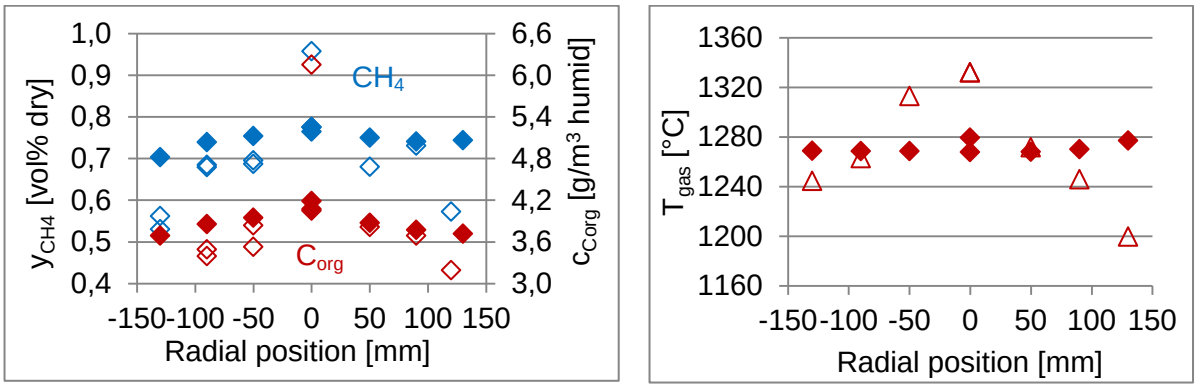

Figure 3 Radial profiles of gas phase composition and temperature
Slurry (glycol + 10 wt% beechwood char), symbols: open: 300 mm / filled: 680 mm downstream from burner)

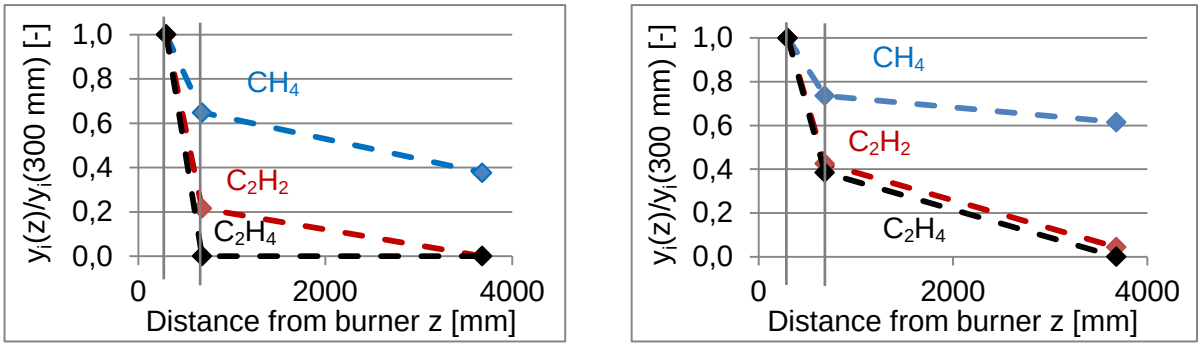

Figure 4 Axial profiles of gaseous intermediates
Left: glycol / right: slurry (glycol + 10 wt% beechwood char)
vertical lines showing position of LII measurements (see Figures 5 and 6).

In the following the results from LII measurements for two types of slurries (glycol with beechwood and straw char) are discussed. LII has the advantage to monitor soot particles of nanometer size while being insensitive to the much larger char particles in the µm size range if adequate laser fluence is employed.

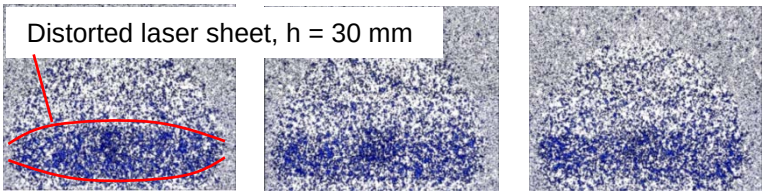

Figure 5: Spatial distribution of LII signal
(with laser excitation, exposure time 60 ns)
slurry (glycol +10 wt% straw char), 680 mm downstream from burner

In contrast to conversion of pure glycol, soot in the size range of 15 to 20 nm is formed during the gasification of slurry. The soot is detected in very low concentrations with homogeneous spatial distribution as visible in Figure 5. It

shows three instantaneous LII images of 60 ns exposure time, with the laser exited region labelled by red lines. The laser-excited region appears distorted due to the wide angle optics employed in the endoscope used for the detection optics and is characterized by very homogeneously distributed signal levels close to the background level. Distinct soot filaments known from rich combustion processes [6] are not identified, at least not in the location of optical access starting 300 mm downstream from the burner. In contrast to soot, char particles travel in larger lumps through the measurement volume (yellow-red signatures in Figure 6). The round field of view of the endoscope optics measures approximately 200 mm, the opposite sampling port appears in darker blue, with a tiny light blue feature indicating the opposite probe. The char particles may be identified by detecting their luminosity when hotter than the reactor ambience with an intensified CCD camera. Visible without laser excitation, char particle cloud luminosity appears spatially unresolved in the line of sight of the camera.

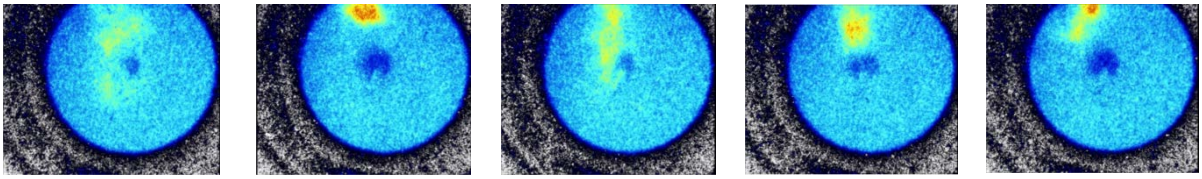

Figure 6: Reactor luminosity (without laser excitation, exposure time 1 µs):
Slurry (glycol + 10 wt% beechwood char), 300 mm downstream from burner.

4. **Summary**

From standard gas phase analytics the end of the main reaction zone is characterized by homogeneous distribution of temperature and gas phase composition 680 mm downstream from the burner. Axial profiles of hydrocarbon intermediates show a fast degradation within the main reaction zone. As compared to glycol, the hydrocarbon concentration was higher at the end of the reactor for the slurry due to gasification of char and soot. The measurements proved the applicability of LII for soot detection under gasification conditions. Soot was only detected for slurry gasification (glycol + 10 wt% pyrolysis char) in the main reaction zone up to 680 mm downstream from the burner. Char lumps can be identified by optical diagnostics if they are hotter than the adjacent reactor walls. The char cannot be quantified.

5. References

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