Final report: Catalytic decomposition of tar from biomass gasifiers

Sammenfatning på dansk

I projektet er udviklet et reaktorsystem, kaldet en tjærereformer, hvor tjæren fra biomasseforgasningsgas kan nedbrydes. I laboratorieforsøg er det bevist, at det er muligt at nedbryde toluene og napthalene, og ved samme temperatur minimere omdannelsen af metan til kulmonooxid og brint.
Der er i første del af projektet gennemført laboratorieforsøg med tjærereformering på den opbyggede tjærereformer på Teknologisk Instituts laboratorium i Taastrup. Derefter er tjærereformeren blevet flyttet til Skive Fjernvarmes fluidiseret bed forgasser, hvor en sidestrøm fra hovedforgasseren er blevet etableret. Via sidestrømmen har det været muligt at udtage en strøm på op til 15 Nm3 forgasningsgas pr. time, som er blevet filtreret for støv og aske i et højtemperaturfilter og derefter sendt igennem tjærereformeren.

Abstract

In this project, a reactor system, called a tar reformer, has been developed to enable tar from biomass gasification gas to be decomposed. Laboratory experiments have shown that it is possible to decompose toluene and naphthalene, and at the same temperature minimise the reforming of methane into hydrogen and carbon monoxide.
Laboratory experiments have been conducted on the tar reforming of the constructed tar reformer in the Danish Technological Institute's (DTI) laboratory in Taastrup. Subsequently, the tar reformer was moved to the bubbling fluidised bed gasifier at Skive Fjernvarme, where a side stream was taken out from the main gasifier and passed through the pilot tar reformer. It was possible to pass up to 15 Nm3 gasification gas per hour through this side stream, where the gas was filtered for dust and ash and then passed through the tar reformer.

Introduction

In the following, a description of the progress in the different work packages of the project "Catalytic decomposition of tar from biomass gasifiers" partly financed by EUDP is provided.

The project tasks were divided between the three partners; the Danish Technological Institute (DTI), Haldor Topsøe A/S (HTAS) and ChimneyLab Europe (CLE). The project is a success regarding the progress and the results and has continued in a second phase, where the design of the main tar reformer at Skive Fjernvarme will be redeveloped and a more thorough understanding of tar reforming, with focus on the monolithic catalytic units used at Skive Fjernvarme, will be investigated.

WP1: Catalyst development (HTAS)

Various materials and chemicals for the manufacturing of catalysts were successfully tested, both in the form of coatings for monoliths and pellets of varying shape and size. Tests of catalytic activity and deactivation in synthetic biomass gasification gas were performed successfully under industrial process conditions for a number of catalyst formulations. A batch of pellet-based catalyst was delivered to DTI for testing in the developed reactor system in Taastrup and later field tests at Skive Fjernvarme.

WP2&WP3&WP4: Construction, development and laboratory testing of catalytic tar reformer

A design for the tar reformer was made with specification of the flow through the reformer and inner tube diameter of the reformer. It was important to get a linear velocity in the reaction bed that would be the same as in a large scale reactor to properly resemble large scale conditions. The residence time in the reactor should also be close to the residence time of a large scale reactor, and this resulted in a design where the reaction bed was approximately two meters long.
The reactor system constructed in the laboratory setup is constituted of a gas- and liquid delivery system, a reactor tube and gas analysis, where we used a gas chromatograph with online sampling possibility. A sketch of the combined laboratory system is provided in the PI diagram in Figure 1.

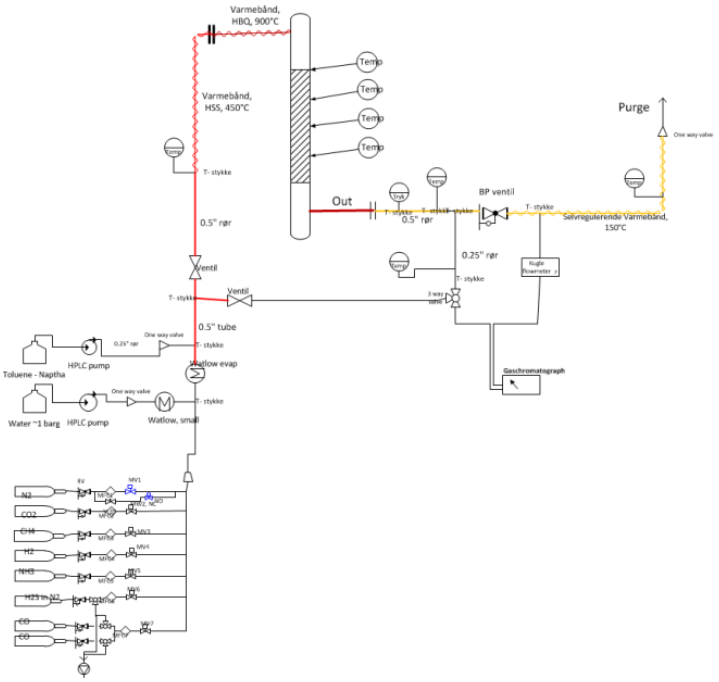

Figure 1: PI diagram of the laboratory setup

The gas- and liquid delivery system consists of five gas mass flow controllers and two liquid pumps that can blend a gas resembling biomass gasification gas, see Figure 2.

Figure 2: Gas supply system of CO, CO2, N2, N2 and CH4 (left) and toluene-solution pump (right)

The pilot reactor is an approximately three meter long steel tube, in which the tar reforming catalyst is placed. The reactor is heated by eight heating elements attached to the reactor, as seen in Figure 3.

The catalyst is based on nickel, and in the project we have performed experiments in order to predict the catalyst's ability to reform tar at different reactor temperatures and flow rates with the specific reformer. The main purpose of the test was to verify that the reformer was capable of degrading naphthalene and toluene at the highest flow rates required, and to test if the preheating of the gas upstream the catalyst was sufficient. These pre-tests were important in order to be prepared for the field test experiments, which were the primary aim of the project.

Figure 3: Pilot reactor with visible heating elements

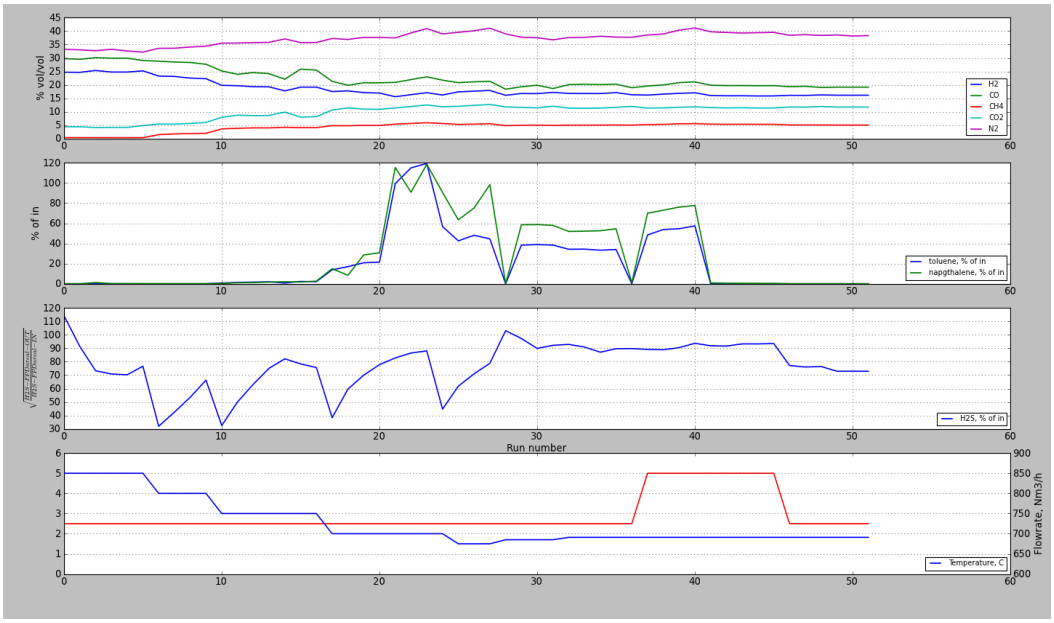

Figure 4: Results of laboratory test with pilot reformer

Figure 4 shows the gas composition after the reformer, flow rate and reformer temperature from a number of experiments performed in October 2012 at DTI in Taastrup. The experiments showed that the catalyst in the reformer could efficiently remove naphthalene and toluene at the desired flow rate and in an acceptable temperature range. These results confirmed that the complete reformer system, including catalyst, preheating and downstream gas cooling, was suitable for the field tests at Skive Fjernvarme.

WP5: Field test at Skive Fjernvarme

The aim of the initial tests at Skive Fjernvarme was to pass a side stream of gasification gas from the main tar reformer through the pilot tar reformer and reach an acceptable level of tar removal. The operation time was aimed at ten days.

Our main concern was that the high amount of dust in the gas would be accumulated in the pilot reformer and thereby increase the pressure loss to a critical level and eventually block the gas flow.

To minimise the amount of particles in the gas, the side stream was taken out in a tube that was in a cut angle of 45°, and placed in the main gasification flow transfer line and turned, so that the 45° hole was pointing away from the flow direction. Secondly, a cyclone was placed upstream the reformer, and a dust measurement showed that this reduced the dust load by more than 90 %.

Figure 5: Filter element and filter house (left) and bottom of the reformer. Both photos are from the field test facility at Skive Fjernvarme

At three hour intervals, the gas at the outlet from the reformer was passed through the Petersen Column and the amount of tar was found using a UV photometer measurement.
Table 1 shows the results of the initial tar reforming experiments, carried out from 17 to 20 December 2012, and the conclusion was that the tar reformer was capable of running without clogging for four days, and the catalyst in the reformer could remove over 95 w/w% tar in the raw gas.

Sample no.	1	2	3	4	5	6
Position	Inlet Pilot (Raw gas)	Outlet pilot	Outlet pilot	Outlet pilot	Outlet pilot	Outlet pilot
Date	17-12-2012	17-12-2012	18-12-2012	18-12-2012	20-12-2012	20-12-2012
Time	16:44-18:00	16:12-16:24	12:02-12:16	12:27-12:40	11:22-11:37	11:44-12:00
Tar, mg/Nm3	3785	66	100	134	116	113
% tar removal	-	98	97	96	97	97

Table 1: Results of the initial tar reforming experiments

After having evaluated the results from December 2012, it was decided to run a comprehensive experimental programme, which comprised a parameter study where the catalyst performance was to be tested at different conditions.
The parameter study included changing the gas flow rate, reformer temperature and changing the gas composition by adding additional synthetic tar, a mixture of toluene and naphthalene, water and also H_2S to the gasification gas. The side stream setup was also equipped with a filtration unit, where the raw gas was filtrated using a candle filter placed in a filter house, see Figure 5 (left). Upstream the reformer, an

automatically controlled high temperature needle valve was installed in order to control the gas flow rate. The complete modified setup is showed in Figure 6.

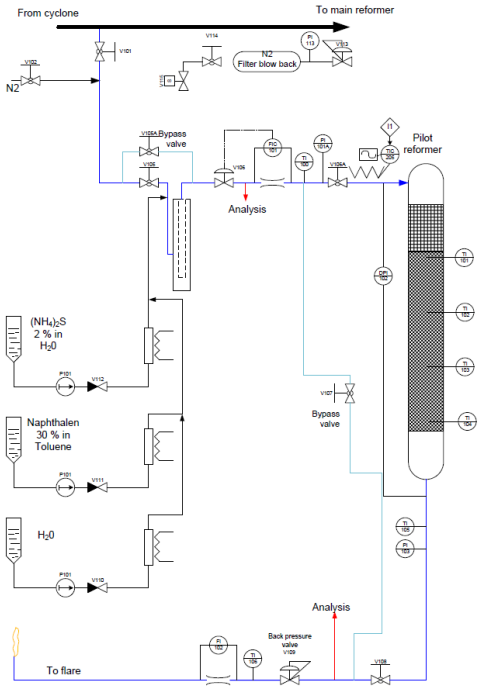

Figure 6: PI diagram of the side stream reformer setup in the field test facility at Skive Fjernvarme

To measure the effects of the changing parameters of the tar reforming, the online gas chromatograph used in the laboratory experiments in Taastrup was moved to Skive Fjernvarme and then equipped with magnetic solenoid valves in order to measure the gas composition before and after the pilot reformer, see Figure 7.

Figure 7: Gas chromatograph for online sampling of gasification gas

The setup shown in Figure 6 ran for more than 1,500 hours and provided HTAS with valuable data on the catalyst performance on a real industrial grade gas.

Commercial aspects of the project

The setup, its capabilities, and the many hours of successful operation at the Skive Fjernvarme sidestream has, among other things, demonstrated long term stability also for HTAS pellet-based catalyst tar reforming technology, at a minimum on-par with the performance of HTAS monolith-based catalyst and technology utilised in the Skive Fjernvarme main tar reformer. Moreover, the extended test programme with a number of critical parameter variations has allowed for the necessary development of pellet-based tar reforming kinetics for industrial biomass gasification gas. The project has also greatly improved the partners' know-how regarding handling and analysis of industrial tar containing gas streams, and this now allows for increasingly industrial-like and complex tar feed stocks to be used for in-house testing. Taken all together, HTAS now has pilot scale data proving the long-term robustness of the pellet-based tar reforming technology, greatly improved kinetic models for industrial design, and expanded know-how for in-house testing using complex tar compositions. It is certain that the project has further strengthened HTAS in relation to competitors, and ensured the continued position of HTAS at the very forefront of suppliers of tar reforming catalysts and technology.

Conclusion

According to the partners, the project has been a great success. Through a 1,500 hour demonstration test, it was demonstrated than HTAS' tar reforming catalyst can effectively remove tar from biomass gasification gas. In the project, a reformer system for handling dust filled gasification gas and tar reforming has been constructed, including a setup for gas analysis using an online gas chromatograph.
With financial support from EUDP, the project has now continued into a second phase, where the main tar reformer at Skive Fjernvarme will be reconstructed and fundamental studies on soot formation and catalyst regeneration will be investigated.