When biomass is gasified in an air blown gasifier it is not only converted into biomass fuel gas containing mainly a gas mixture of $N_2$, $CO$, $H_2$, $CO_2$, $H_2O$ and $CH_4$, but also trace amount of impurities such as tars, particles, nitrogen compounds and $H_2S$. The removal of tar from biomass gasification gas remains as the dominant problem for broad industrial use of biomass gasification. In previous research in CHIS, it was shown the problem can be solved by using a catalytic $\alpha$-alumina porous candle filter, consisting of a suitable nickel-based catalyst deposited onto the filter pore walls, allowing integration of the high temperature removal of particles and tars from biomass gasification gas in a one-step gas cleaning process. The urea method was used to deposit secondary supports (e.g. $Al_2O_3$ and/or $ZrO_2$) inside the pore of the filter to increase surface area, active Ni metal and promoters in this research. At a temperature of 900 °C, one could successfully clean the fuel gas of tars.

The main goal in this work was to try and lower the necessary operating temperature and as a result to reduce the capital cost of the catalytic filter, while still meeting the stringent specifications demanded by end-use devices and environmental constraints. Small scale nickel-based catalytic filter discs, consisting of approximately 2.5 wt% secondary support $Al_2O_3$, 1.0 wt% Ni and 0.5 wt% $MgO$, were tested on laboratory scale in a broad range of parameters (reaction temperatures, tar concentrations, filtration velocities and $H_2S$ contents) allowing the identification of the best operational region. Whereas in absence of $H_2S$, benzene and naphthalene chosen as tar model compound were completely removed at all filtration velocities and reaction temperatures (except at 6 cm/s and at 750 °C), tar conversion in presence of $H_2S$ was far from complete and was sensitive to temperature.

A detailed kinetic analysis with a simple model (plug flow plus axial dispersion) of the large data set clearly identified the reversible inhibition by strong adsorption on the Ni sites of $H_2S$, effectively poisoning those sites and resulting in a strong drop in activity. The naphthalene conversions in presence of $H_2S$ are practically independent of naphthalene loading as the reaction is first order in the tar component. The reaction temperature could however be reduced to around 830-850 °C, still with satisfactory performance for the optimal catalyst.

Given the dominance of $H_2S$ poisoning on Ni catalysts, even after adequate addition of promoters to limit this deactivation, and the knowledge also $ZrO_2$ can catalyse the tar decomposition (although with poor performance) a study of zirconia as a catalyst support was started. The effect of various secondary supports ($Al_2O_3$, $ZrO_2$ or a mixture of 50 wt% $ZrO_2$/50 wt% $Al_2O_3$) on BET surface areas was studied. The general trend for the surface area ($S_{BET}$) is: $Al_2O_3 > ZrO_2-Al_2O_3 > ZrO_2$. Tar conversion achieved from the three types of supports ($ZrO_2$, $Al_2O_3$ and a mixed $ZrO_2-Al_2O_3$) are generally similar, except at high velocity and low temperature where the mixed support is best. Although some conversion is occurring on the zirconia or mixed supports without deposition of Ni catalyst, the performance is generally poor, but much better than for other similar materials reported in literature. The only way to reach the 100 to 1000 fold reduction of tars is with the Ni catalyst and at high temperature.

Furthermore, the effect of varying the ratio of mixed secondary support $ZrO_2-Al_2O_3$ was investigated. The BET surface measurement indicates that the highest surface is obtained with the disc containing 55 wt% $Al_2O_3$ /45 wt% $ZrO_2$. Comparing the experimental results of two Ni modified discs with different $ZrO_2-Al_2O_3$ contents (50 wt% $ZrO_2$/50 wt% $Al_2O_3$ and 55 wt%...
Al₂O₃/45 wt% ZrO₂) at 900 °C, the better performance is always achieved by the one consisting of 55% Al₂O₃/45% ZrO₂ at different velocities.

The effect of promoters added to limit the influence of H₂S on activity such as MgO, CaO and La₂O₃ with or without secondary supports was determined. The trend of promoter enhancement on Ni catalyst for tar elimination as derived from sulphur deactivation test results follows the order: MgO > La₂O₃ > CaO. Hence, MgO is the preferred promoter for this catalyst.

Additionally, the effect of Ni loading on the performance of the catalytic filter discs was tested with a fixed Ni/MgO weight ratio of 2 and a nickel loading ranges from 0.1 wt% up to 2 wt%. It indicates that the disc with 0.1 wt% Ni can not offer sufficient Ni active sites for tar destruction at 900 °C. At 900 °C, it appears that increasing the nickel loading from 0.5 wt% to 2 wt% caused a very minor improvement of the performance. However, at lower temperature (900 °C), the disc with 0.5 wt% Ni exhibits a slightly better catalytic performance (naphthalene conversion: 96.7%) at 2.5 cm/s than the one with 1 wt% of Ni.

The performance of ZrO₂ catalysts or the monolith Ni reactors was reported in literature to benefit from O₂ addition before the catalyst. Following this idea, low amounts of oxygen (1−3% O₂), were added and resulted in a spectacular improvement of the performance, especially at lower temperatures. With the optimal ZrO₂-Al₂O₃ supported Ni/MgO catalyst, at 2.5 cm/s, 800 °C with 100 ppm H₂S and 1 g/Nm³ naphthalene, the conversion rose from 79.5% (in absence of O₂) to 98.2% (in presence of only 1% O₂), effectively decreasing the tar level from an unacceptable 0.205 g/Nm³ to 18 mg/Nm³, well below the tolerance limit of 50 mg/Nm³, e.g. for a downstream diesel engine. This would in many cases allow operation around 800°C, a typical gasifier outlet temperature and avoid the need for reheating of the gas, either by combustion or indirectly with a heat exchanger.

From a large set of experiments and some thermodynamic equilibrium calculations and dynamic experiments, we can propose a probable mechanism for the influence of oxygen addition. In absence of oxygen, only a fraction of all Ni in the catalyst is available for surface reaction, as most of it is poisoned by strong, but reversible adsorption of H₂S. When oxygen is added, adsorbed H₂S is continuously removed by oxidation on the catalyst followed by release of SO₂. Part is then poisoned again by readsorption of H₂S. This nevertheless frees up an extra amount of Ni sites, and increases activity, hence allows operation in conditions of stronger poisoning such as at lower temperature. This improvement can not possibly come from thermal reactions, either extra decomposition of the tar by direct oxidation or removal of H₂S by direct bulk oxidation, or on the support, but really need the Ni sites for the improvement, as was shown in the empty tube and support experiments.

Long term experiments were performed using different catalytic filter discs in absence or presence of O₂. In absence of O₂, a complete naphthalene conversion is achieved at 900 °C with 100 ppm H₂S, but a slight increase of pressure drop is found during the extended test period. However, at 800 °C, a disc containing 1.73 wt% ZrO₂ + 1.43 wt% Al₂O₃ + 1.03 wt% Ni and 0.47 wt% MgO was tested during 250 hours with 1 g/Nm³ naphthalene, 100 ppm H₂S and 1% O₂. The conversion of naphthalene is ranging from 98.2% to 99.4%, while the pressure drop remained stable over 250 h. Adding a small amount of oxygen to the fuel gas allows almost complete removal of tars at low temperature without significantly modifying the gas composition and resulting in significantly simpler and less expensive equipment, as no reheating of the producer gas coming from the gasifier is needed. The resulting reduction in equipment cost and stable and reliable long term operation should allow application of the catalytic filter and the increased use of biomass gasification, especially on smaller scale.