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Integrated high temperature gas cleaning: Tar removal in biomass gasification with a catalytic filter

L. Ma, H. Verelst, G.V. Baron [*]

Vrije Universiteit Brussel, Department of Chemical Engineering, Pleinlaan 2, Brussels 1050, Belgium

Abstract

A nickel-based catalytic filter material for the use in integrated high temperature removal of tars and particles from biomass gasification gas was tested in a broad range of parameters allowing the identification of the operational region of such a filter. Small-scale porous alumina filter discs, loaded with approximately 2.5 wt% Al_2O_3, 1.0 wt% Ni and 0.5 wt% MgO were tested with a particle free synthetic gasification gas with 50 vol% N_2, 12 vol% CO, 10 vol% H_2, 11 vol% CO_2, 12 vol% H_2O, 5 vol% CH_4 and 0–200 ppm H_2S, and the selected model tar compounds: naphthalene and benzene. At a typical face velocity of 2.5 cm/s, in the presence of H_2S and at 900 °C, the conversion of naphthalene is almost complete and a 1000-fold reduction in tar content is obtained. Technically, it would be better to run the filter close to the exit temperature of the gasifier around 800–850 °C. At 850 °C, conversions of 99.0% could be achieved in typical conditions, but as expected, only 77% reduction in tars was achieved at 800 °C.

Conversion data can be reasonably well described with first order kinetics and a dominant adsorption inhibition of the Ni sites by H_2S. The apparent activation energies obtained are similar to those reported by other investigators: 177 kJ/mol for benzene and 92 kJ/mol for naphthalene. The estimated heat of adsorption of H_2S is 71 kJ/mol in the benzene experiments and 182 kJ/mol in the naphthalene experiments, which points at very strong adsorption of H_2S. Good operation of the present material can hence only be guaranteed at temperatures above 830 °C mainly due to the strong deactivation by H_2S at lower temperatures.

Keywords: Candle filter; Tar removal; Ni catalyst; Gasification; Biomass

1. Introduction

Power generation by biomass gasification technology has attracted increasing interest because it is a highly efficient and environmentally friendly technology. The advantage of gasification over direct combustion is that a gaseous fuel burns more cleanly than a solid fuel, and can be used in an advanced power cycle in the smaller capacities, such as an engine or turbine power plant.

Biomass gasification yields a producer gas containing CO_2, CO, H_2, CH_4, H_2O and N_2 (in the case of air gasification), but also several undesired contaminants that must be controlled to avoid plugging and damaging of the downstream equipment. The major hurdle in successfully applying gasification is the elimination of tars (to below 50 mg/m^3) and particles. In our previous work [1–5], a novel catalytic candle filter was proposed (Fig. 1) to integrate the high temperature removal of particles and tars from biomass gasification gas in a one-step gas-cleaning process in order to reduce the equipment inventory and meet the specifications demanded by end-use devices and environmental constraints. It consists of a ceramic α-alumina porous filter substrate in which a suitable nickel-based catalyst is deposited onto the pore walls to convert the tars.

Filtration itself is a reasonably well-developed technology and this work is only concerned with the tar removal performance of such a catalytic filter. A large amount of development and optimization work has already been performed, resulting in an optimal catalyst composition: 2.5 wt% Al_2O_3, 1.0 wt% Ni and 0.5 wt% MgO in the porous, preformed alumina filter material. Testing was so far only

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[*] Corresponding author. Tel.: +32 2 6293246; fax: +32 2 6293248.
E-mail address: gvbaron@vub.ac.be (G.V. Baron).

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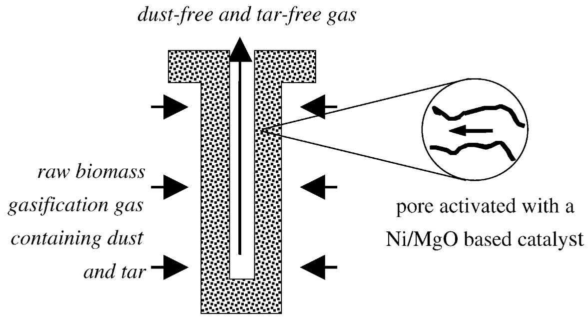

Fig. 1. Schematic representation and operation of the catalytic candle filter.

Table 1
The composition of the filter discs

Disc name	Total content of disc
SD26	2.74 wt% Al_2O_3 + 0.96 wt% Ni + 0.44 wt% MgO
SD27	2.78 wt% Al_2O_3 + 0.87 wt% Ni + 0.40 wt% MgO
SD08	3.18 wt% Al_2O_3 + 0.97 wt% Ni + 0.44 wt% MgO
SDM20	2.59 wt% Al_2O_3 + 0.87 wt% Ni + 0.40 wt% MgO
SD14	3.28 wt% Al_2O_3 + 0.99 wt% Ni + 0.45 wt% MgO

performed at 900 °C and fixed conditions to find the optimal material for those standard operation conditions of catalysts used so far in packed bed or monoliths.

In the present paper, the effects on the tar conversion of several operation parameters are investigated using filter discs containing the optimal catalyst formula in a laboratory-scale set-up. A dust-free simulated biomass gasification gas, based on the typical product gas of an air blown fluidized bed gasifier, is sent over the catalytic discs. In this way, the removal efficiencies of the two tar model compounds in the gas, benzene and naphthalene, can be monitored in varying reaction conditions, such as different reaction temperatures, tar concentrations, gas velocities and H_2S concentrations. Based on these extensive data, some preliminary kinetic parameters have been obtained and can serve as a basis for a more thorough investigation of the catalytic processes involved in tar conversion, or further optimization and comparison of such materials.

2. Experimental

A small-scale porous alumina disc (diameter: 3 cm, thickness: 1 cm), with properties identical to the full-scale catalytic candle filter, is placed in the middle of a pure alumina tube and fixed by means of alumina cement to avoid the potential leak between the disc and the tube walls. Filter discs (Table 1) were reproducibly prepared with the optimal catalyst composition (1.0 wt% Ni + 0.5 wt% MgO + 2.5 wt% Al_2O_3) determined by Engelen et al. [6] using a co-precipitation method with urea in order to investigate the influence of varying experimental parameters on the tar model compound conversions. A detailed preparation procedure of catalytic discs was described in previous publications [1–3]. The laboratory reaction set-up employed for this test was also described in a previous publication [2].

A simulated dust-free biomass gasification gas was used, consisting of 50 vol% N_2, 12 vol% CO, 10 vol% H_2, 11 vol% CO_2, 12 vol% H_2O, 5 vol% CH_4 and 0–200 ppm H_2S, and the selected model tar compounds: naphthalene or benzene. Various initial concentrations of benzene (5, 10 and 15 g/(N m^3)) naphthalene (1, 2.5 and 5 g/(N m^3)) were loaded to the simulated gasification gas to determine the effects on tar conversion efficiencies.

Reaction conditions, such as the gas face velocities (2.5, 4 and 6 cm/s), reaction temperatures (750, 800, 850 and 900 °C) and H_2S content (0, 50, 100 and 200 ppm) were tested in order to determine some preliminary kinetic parameters. In each experiment care was taken to establish steady state conditions, and no deactivation in time was found.

3. Results and discussion

High-temperature generated biomass tar [7] mainly includes highly stable aromatic compounds such as benzene (60–70 wt%), naphthalene (10–20 wt%) and other poly-aromatic hydrocarbons (10–20 wt%), which can amount up to a total tar content of 15–20 g tar/Nm^3. It has, however, been shown that proper operation of the gasifier can strongly reduce these tars, and hence allow their near to complete removal by catalytic processes such as packed beds or monoliths. Our previous test results also indicated that using benzene and naphthalene as model compounds gives a good idea of performance with real biomass gasification gas.

3.1. *Influence of the benzene loading*

Three different feed benzene concentrations (5, 10 and 15 g/(N m^3)) were used to assess the effect on tar

Table 2
Benzene conversions vs. tar and H_2S concentrations and reaction temperatures at 2.5 cm/s

Reaction temperature (°C)	5 g Benzene conversion (%) SD26				10 g Benzene conversion (%) SD27				15 g Benzene conversion (%) SD08			
	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S
900	100	99.6	97.8	91.0	100	99.9	98.9	93.6	100	99.9	99.2	96.1
850	100	89.2	78.8	64.2	100	93.0	79.7	56.8	100	95.4	87.0	75.9
800	100	58.2	45.3	39.8	100	53.2	31.8	21.5	100	71.1	56.0	35.6
750	100	41.3	36.7	29.3	100	22.8	16.0	12.3	100	23.9	20.2	16.9

Table 3
Benzene conversions vs. tar and H_2S concentrations and reaction temperatures at 4 cm/s

Reaction temperature (°C)	5 g Benzene conversion (%) SD26				10 g Benzene conversion (%) SD27				15 g Benzene conversion (%) SD08			
	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S
900	100	97.7	91.7	78.0	100	98.4	91.8	78.4	100	98.7	95.4	87.6
850	100	74.7	57.6	38.4	100	71.9	45.8	33.1	100	82.8	66.4	53.2
800	100	34.7	24.4	19.8	100	29.5	17.4	11.0	100	46.3	27.3	13.2
750	100	22.7	19.8	15.6	99.9	11.5	8.9	4.6	100	9.5	7.4	5.2

Table 4
Benzene conversions vs. tar and H_2S concentrations and reaction temperatures at 6 cm/s

Reaction temperature (°C)	5 g Benzene conversion (%) SD26				10 g Benzene conversion (%) SD27				15 g Benzene conversion (%) SD08			
	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S
900	100	92.4	75.9	55.2	100	95.1	84.3	63.5	100	95.0	86.1	72.3
850	100	58.5	40.3	24.3	100	64.4	38.1	16.4	100	64.8	45.0	34.2
800	100	29.7	22.7	18.0	100	14.8	7.2	5.0	100	25.6	11.4	3.7
750	99.8	20.4	17.2	12.7	99.8	8.5	4.6	1.1	99.5	1.9	1.0	0.1

Table 5
Naphthalene conversions vs. tar and H_2S concentrations and reaction temperatures at 2.5 cm/s

Reaction temperature (°C)	1 g Naphthalene conversion (%) SDM20				2.5 g Naphthalene conversion (%) SD26				5 g Naphthalene conversion (%) SD14			
	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S
900	100	100	100	99.9	100	100	100	100	100	100	100	99.9
850	100	99.9	98.6	92.5	100	99.9	99.0	94.3	100	99.9	99.3	93.2
800	100	91.7	76.0	56.5	100	92.9	77.9	53.6	100	92.8	77.1	55.8
750	100	55.2	38.8	29.5	100	46.8	29.6	20.2	100	49.0	36.9	29.8

Table 6
Naphthalene conversions vs. tar and H_2S concentrations and reaction temperatures at 4 cm/s

Reaction temperature (°C)	1 g Naphthalene conversion (%) SDM20				2.5 g Naphthalene conversion (%) SD26				5 g Naphthalene conversion (%) SD14			
	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S
900	100	99.9	99.7	98.6	100	99.9	99.8	98.9	100	99.9	99.7	98.4
850	100	98.5	94.3	81.3	100	99.1	95.0	82.3	100	98.3	92.7	78.7
800	100	82.3	60.6	41.5	100	82.1	58.5	33.4	100	76.0	54.9	36.0
750	100	36.1	27.9	23.5	99.9	29.0	15.6	8.7	100	26.7	15.2	8.7

Table 7
Naphthalene conversions vs. tar and H_2S concentrations and reaction temperatures at 6 cm/s

Reaction temperature (°C)	1 g Naphthalene conversion (%) SDM20				2.5 g Naphthalene conversion (%) SD26				5 g Naphthalene conversion (%) SD14			
	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S	0 ppm H_2S	50 ppm H_2S	100 ppm H_2S	200 ppm H_2S
900	100	99.7	98.6	94.8	100	99.9	99.2	95.7	100	99.6	98.3	93.3
850	100	95.9	86.5	70.3	100	96.0	85.0	64.5	100	93.5	79.7	59.5
800	100	68.2	49.3	36.9	99.9	65.5	39.0	24.7	100	59.2	33.8	22.5
750	100	31.9	25.7	21.8	99.8	21.5	12.4	6.3	99.9	19.7	9.8	5.9

conversions of gas velocities (2.5, 4 and 6 cm/s), reaction temperatures (750, 800, 850 and 900 °C) and H_2S content (0, 50, 100 and 200 ppm) (Tables 2–4).

3.2. *Influence of the naphthalene loading*

Three different feed naphthalene concentrations (1, 2.5 and 5 g/(N m^3)) were used with the same test conditions as for benzene (Tables 5–7).

3.3. *Discussion*

It should be noted that the H_2S concentration was not changed by the catalyst, and shutting down of the H_2S resulted in all conditions in a fast recovery of the catalyst from its deactivated state to 100% conversion. This points at reversible, but strong adsorption of H_2S. Only at much higher partial pressures, sulphides are formed [8]. At each given H_2S concentration, a fraction of the active Ni sites are lost by adsorption of H_2S, and hence result in a decrease of the tar conversion rate. It can be concluded from the above table that:

- In the absence of H_2S, benzene and naphthalene are completely removed at all gas velocities and reaction temperatures (except at 6 cm/s and at 750 °C).
- When H_2S is added, benzene and naphthalene conversion drops significantly, but less at high temperatures, and the effect is less strong for naphthalene.
- The influence of the amount of benzene added is complex and depends on reaction temperature and H_2S concentration, the highest conversion is achieved at the highest concentration of 15 g/(N m^3) at 850 and 900 °C. At lower temperatures, conversion strongly decreases with loading.
- The naphthalene conversions drop moderately when the naphthalene loading is increased, in contrast with the concentration influence in the benzene conversion.

It is well established that benzene is not a problematic compound in real biomass gasification gas, as its combustion is clean and results in no clogging, so the complete removal of benzene is not required. Naphthalene is a good model for the reactivity of the heavier tars (e.g. phenanthrene and pyrene) that caused the plugging and contamination of the downstream equipment. There are different acceptable limits for the different end-use devices but a common one for a diesel engine is a maximum tar limit of 50 mg/(N m^3) [9]. In typical conditions with a velocity of 2.5 cm/s and, the presence of 100 ppm H_2S and at 900 °C the conversion of naphthalene is 100%. From an energy economy point of view, and considering requirements (and costs) for the materials in the filter vessel, a working temperature of the catalyst close to the exit temperature of the air gasifier around 800–850 °C is to be preferred. At 850 °C, in typical conditions (velocity of 2.5 cm/s, presence of 100 ppm H_2S), conversions of 98.6, 99.0 and 99.3% with a naphthalene concentration of 1, 2.5 and 5 g/(N m^3), respectively, were achieved. This means that only 4, 25 and 35 mg naphthalene/Nm^3 is left in the cleaned gas after the hot-gas cleaning, which is certainly low enough for direct use in a diesel engine. Only 77% reduction in tars is achieved at 800 °C. Still, the reduction by 50 °C, which can be achieved with the catalyst used here leads to significant cost reduction in the equipment and avoids some of the problems, such as sintering ashes that can block the filter. Even better catalysts, also operating at those lower temperatures are now being developed, and they should achieve 98–99% conversion, which does not appear to be readily attained. A deeper understanding of the mechanisms involved in these reactions is needed to guide any attempt to improve them. The present large set of data is certainly insufficient to unravel these, but a simple analysis shows some of the possible effects involved.

4. Kinetic analysis of the catalytic conversion of benzene and naphthalene

The literature contains mainly global performance data on the different catalysts for tar conversion. Few reports with kinetic analyses are available [8,10,11]. They indicate that when the hydrocarbon model compounds, namely benzene and naphthalene, are decomposed by a nickel-based catalyst under high reaction temperatures, benzene and naphthalene are found to follow a pseudo-first order reaction, inhibited by hydrogen sulphide that competes with benzene and naphthalene for the active sites in this reaction, by reversible adsorption at low H_2S concentrations. More elaborate models have been proposed [10,11], but will not be used here.

Assuming ideal plug flow through the porous layer of catalyst, the tar components are gradually converted. Assuming pseudo-first order in benzene or naphthalene,

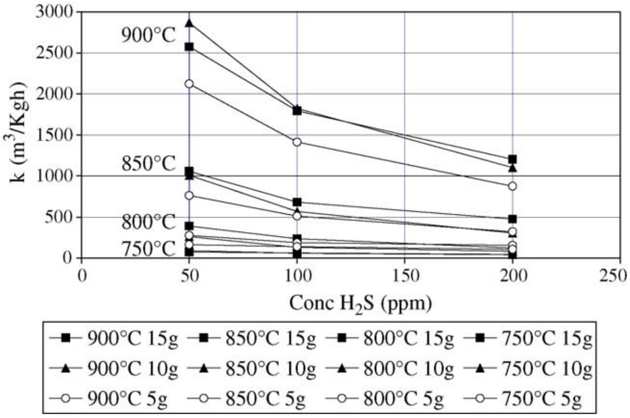

Fig. 2. The apparent rate constants (k_{benzene}) obtained at different benzene loadings as a function of the H_2S content.

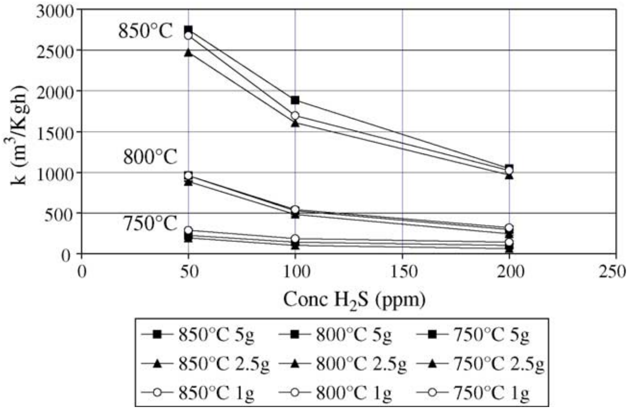

Fig. 3. The apparent rate constants ($k_{\mathrm{naphthalene}}$) obtained at different naphthalene loadings as a function of the H_2S content.

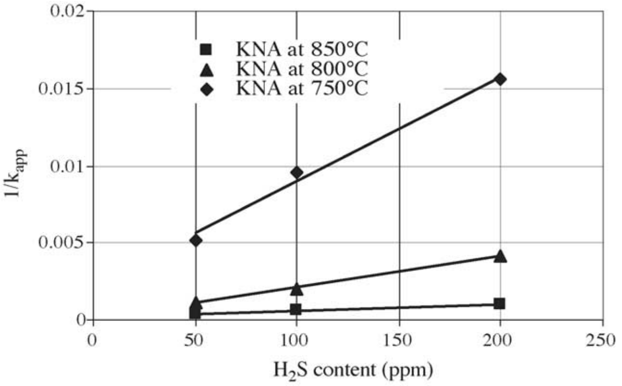

Fig. 4. Langmuir type relation for the H_2S concentration dependence of the apparent rate constant for naphthalene conversion (2.5 g/(N m^3) feed).

the conversion X_{tar} at the exit of the catalyst layer can be converted in a first order rate constant k_{app}:

$$\ln(1 - X_{\mathrm{tar}}) = -k_{\mathrm{app}}\,\tau$$

with $\tau = W/F$, the space time (W weight of catalyst and F volumetric flow rate). This equation remains valid even if the k_{app} is dependent on H_2S, since H_2S is not converted when passing over the catalyst and its concentration is a constant.

In the Figs. 2 and 3, the aparent rate constants are shown as a function of the hydrogen sulphide concentration and the reaction temperature.

These data are in agreement with the results from Depner and Jess [8] and Corella et al. [10] for other Ni based catalysts and Fig. 4 shows that, in a typical case, with increase of H_2S contents, the activity of tar cracking catalyst is reversibly decreased by a Langmuir type adsorption term.

Hence, the influence of the H_2S concentration on the apparent rate constants can be described by an adsorption term

$$k_{\mathrm{app}} = \frac{k_i}{1 + K_{\mathrm{H_2S}}\,p_{\mathrm{H_2S}}}$$

with k_i is the rate constant for naphthalene and benzene, respectively, and with $k_i = k_{i,0}\exp(-E_{\mathrm{a},i}/RT)$, the apparent activation energies and with $K_{\mathrm{H_2S}} = K_{\mathrm{H_2S,0}}\exp(-\Delta H_{\mathrm{H_2S}}/RT)$, the heats of adsorption of H_2S can be obtained. All k_{app} values for benzene and all k_{app} data for naphthalene were fitted to these equations separately. The reasonably good fit with these equations is illustrated in the parity plots for the kinetic constants in Fig. 5.

The apparent activation energies obtained are similar to those reported by other investigators: 177 kJ/mol for benzene and 92 kJ/mol for naphthalene. The estimated heat of adsorption of H_2S is 71 kJ/mol in the benzene experiments and 182 kJ/mol in the naphthalene experiments, which points at very strong adsorption of H_2S. Leaving out some data points resulted in large shifts in the values of activation and adsorption energies, which appeared to be strongly coupled. The values are in the range of those found by others (e.g. Ref. [8]). They clearly indicate the strong

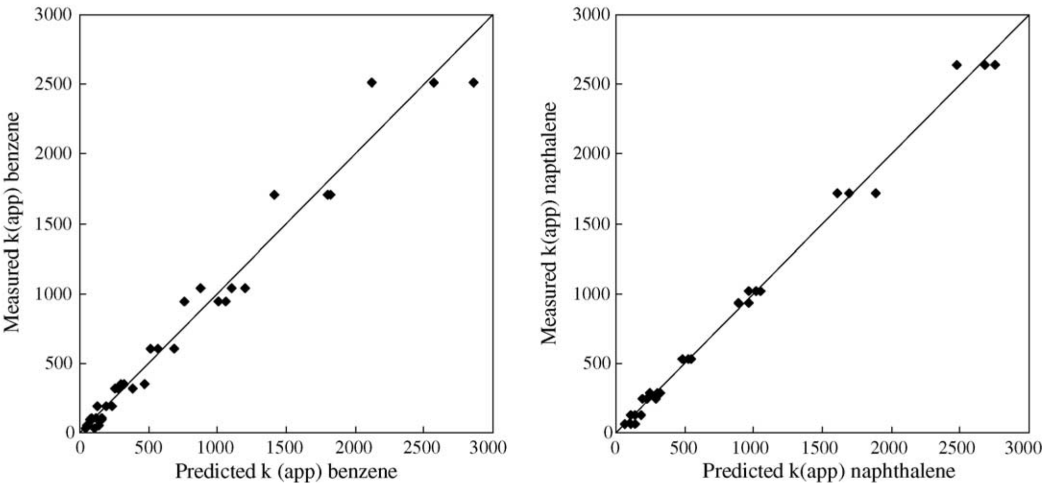

Fig. 5. Parity plots for apparent kinetic constants for benzene and naphthalene.

adsorption of H_2S on the active sites to be a very important factor in the performance. This model does not explain the large spreading in conversion as benzene concentrations are changed. No simple additional terms in the equations could explain those variations.

Hence, the equations presented here are merely to be seen as a means of representing the data, useful for interpolation of the data in design. More accurate modeling and analysis, as well as surface studies of the catalyst, are needed to be able to discuss these data further.

5. Conclusion

When considering that mainly naphthalene and higher tars have to be eliminated in biomass gasification process, and this at concentrations of 1–2 g/(N m^3) when the gasifier is optimally operated, the catalytic filter discussed in the present paper can deliver the performance required to directly feed into a diesel engine after this one-step cleaning process, even when operating at a temperature as low as 830 °C. As particles are filtered out before reaching the catalytic material, they cannot clog the catalyst, which can happen in monoliths. To our knowledge, monoliths are not able to achieve such a performance due to mass transfer problems [12,13] in the wide channels to allow for particle passage. We believe this good performance results from the complete elimination of mass transfer limitations in the 25 μm pores of the material, even though the specific surface of this catalyst is only of the order of 2 m^2/g, a Ni loading of 1% and contact times of typically a fraction of a second. The use of a catalytic filter instead of a filter followed by a catalytic bed or a monolith followed by a filter not only saves on equipment but also takes advantage of the low velocities already available in the filter (face velocities of a few centimetre per second) and the fine structure of the porous filter material for more optimal operation.

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