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Catalysis Today 27 (1996) 55–62

CATALYSIS TODAY

Catalytic hot gas cleaning of gasification gas

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Abstract

Gasification gas containing dust can be efficiently purified from tars and ammonia with nickel monolith catalyst. Temperatures over 900°C and residence times of about 1 s (SV 2500 1/h) were needed at 5 bar pressure to obtain complete tar decomposition and 80% ammonia conversion with a feed gas from a pilot scale fluidized bed gasifier. At these conditions deactivation caused by carbon deposition or by H_2S can be avoided. Decline of catalyst activity was not observed during 100 h long test runs. Dolomites and limestones can be used as effective tar decomposing catalysts at lower pressures and around 900°C temperatures, where they stay in calcined form. Low-cost iron containing materials can in turn be applied for catalytic ammonia removal.

Keywords: Catalytic hot gas cleaning; Gasification gases

1. Introduction

Power production from biomass and peat by gasification is the focus of intense research and development in Finland. At the power scale of 50–150 MWe economically the most interesting alternative is the simplified integrated gasification combined cycle (IGCC) process. Most of the process concepts are based on pressurised fluidised bed air gasification and hot gas cleaning (particulate removal) followed by a gas turbine having a steam turbine connected to it to recover the energy of the exhaust gases. At smaller scale biomass derived power can be generated with a combination of a gasifier and an engine. This process can be based on fluidised bed or updraft gasification at atmospheric pressure followed up by a (hot) gas cleaning unit and a set of engines for power generation.

However, in addition to the main gas components (H_2, CO, CH_4, CO_2, H_2O, N_2) gasification gas contains also impurities like tars, ammonia and dust. Tars are harmful because they can easily block up the particulate filters or other downstream units like engine suction inlets by condensing or by polymerising to soot like deposits. Ammonia on the other hand is a source of NO_x emissions when the gas is burned.

These problems can be avoided by using a catalytic gas purification unit to decompose tars and ammonia. The operating temperature of this unit should be close to that of the gasifier outlet temperatures being about 900°C (fluid bed applications). The gas cleaning unit should also tolerate the high particulate content of gasification gas. Various catalytic gas cleaning options have been studied at VTT using laboratory and PDU scale facilities [1–8]. These options include the use of cheap bulk materials such as limestones and dolomites in a separate catalyst reactor or as additives

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SSDI 0920-5861(95)00172-7

in the gasifier as well as a specially designed monolith catalyst reactor. In this paper an evaluation of these studies is given together with the results obtained with the novel nickel monolith catalyst.

2. Experimental

A laboratory scale apparatus consisting of two tube reactors (i.d. 25 mm, fireproof steel) operated in parallel was used for catalyst screening studies. A slip-stream (dust free) from industrial scale updraft gasifier and from a PDU fluidised bed gasifier were used as feeds. Typical compositions of these feed gases are presented in Table 1. Catalyst volume of the reactor was 50 cm^3, gas residence time range studied was 0.1–1.5 s and temperature range 700–1000°C at atmospheric pressure. Temperature of the catalyst bed was measured in these tests from the top and from the bottom of the bed and the indicated test temperature was a mean of these two values. Catalyst particle size was in these tests 2–4 mm [1–5].

For catalyst deactivation and for hot gas cleaning chemistry studies a laboratory scale pressurised tube reactor system was used that was fed by simulated gasification gas mixture made from bottle gases (CO 11%, CO_2 13,5%, CH_4 5%, H_2 10%, H_2O 12%, NH_3 4400 ppm, H_2S 0–500 ppm, toluene 3200 ppm as tar model compound, N_2 balance). The reactor was a quartz tube (i.d. 12 mm) having a 5 cm^3 sample volume. The pressure range studied was 5–20 bar and the temperature range 700–1000°C at 0.5 s residence time. Catalyst particle sizes tested were 0.3–0.35 mm and 0.6–1.2 mm [6–8].

Studied bulk material catalysts were: dolomites, limestones and iron sinter. Studied commercial catalysts and catalyst carriers were: nickel catalysts (Ni/Al_2O_3 and Ni on refractory material), alumina and alumina silicate. Details considering the nickel catalyst are proprietary information. Silicon carbide and alpha-alumina were used as reference materials. The both fixed bed tube reactor systems, used catalyst materials and analytical methods are described in more detail in other publications on this subject [1–8].

A bench scale pressurised reactor was used for monolith catalyst testing using a slip-stream (dust containing) gas from a PDU fluid bed gasifier as feed (Fig. 1). The reactor comprised a pressure vessel, a three zone furnace and the reactor tube proper, within which the gas preheater, the combustion chamber and the monolith catalyst were sited. Ceramic monoliths (Ni/Al_2O_3) of 300×50×50 mm having square channels were used in the tests. Details of the catalyst are proprietary information. Two such monoliths were placed on top of each others. Due to sealing of the elements a cross-sectional area of 31 × 31 mm was

Table 1

Gas composition at the inlet and at the outlet of the catalyst reactor with a nickel catalyst (Ni/Al_2O_3) and calculated equilibrium composition at reaction temperature. Updraft and fluid bed gasifier gas were used as feed, peat as feedstock. Laboratory scale fixed bed tube reactor, mean temperature 900–910°C, residence time 0.2–0.3 s, pressure 1 bar.

Component	Updraft gas	Reactor outlet	Equilibrium	Fluid bed gas	Reactor outlet	Equilibrium
CO, vol.-%	17.2	20.8	21.4	9.8	17.2	18.0
CO_2, vol.-%	8.0	8.7	8.6	14.6	9.6	9.2
CH_4, vol.-%	1.6	<0.1	<0.1	3.6	0.3	<0.1
LHC, vol.-%	0.4	0	0	0.5	0	0
H_2, vol.-%	13.2	27.0	27.4	9.8	18.6	18.3
H_2O^a, vol.-%	25.9	14.4	13.9	13.7	10.9	11.5
N_2, vol.-%	32.6	29.0	28.7	47.4	43.3	43.1
NH_3, ppmv	1700	<10	20	4100	10	10
Tar, ppmv	9800	<10	0	1400	<10	0

[a] calculated from material balance.

LHC = light hydrocarbons (C2–C5).

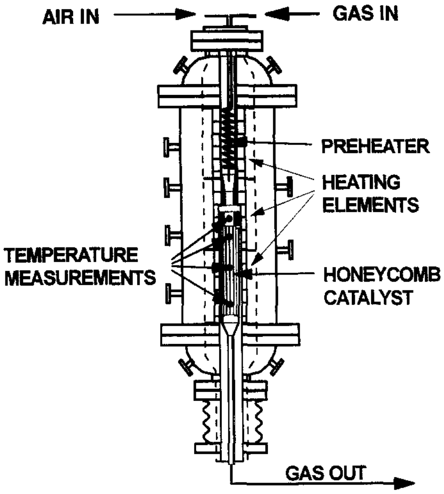

Fig. 1. The monolith catalyst test reactor.

in use. The inside temperatures of the monoliths were measured by three thermocouples placed in the centre channels near the inlet, in the middle and at the bottom part of the monolith assembly. The temperature values presented in this study are a mean of these three thermocouple readings.

Various biomass fuels were used as gasifier feedstocks in the monolith catalyst tests: forest waste wood, bark, wood chips and peat. These yielded feed gases of different compositions (typical gas with peat is presented in Table 1) that contained tar 1–7 g/m^3_n, NH_3 600–6000 ppmv, H_2S 30–250 ppmv and dust 0.6–6 g/m^3_n. The temperature range studied was 880–960°C and the pressure 5 bar. Total gas flow rate (dry) was varied in the range 4.5–32 dm^3/min resulting in residence time range of 0.5–2 s (space velocity 1000–5000 1/h). Three test runs that lasted 45, 95 and 98 h were conducted. Sampling and analytical methods have been described elsewhere [1,3].

Before the first two test run weeks catalysts were pre-reduced in situ with H_2/N_2 mixture. Reduction procedure was as follows: heating rate 50°C/h, total gas flow 10 l/min, heating to 200°C to 700°C in H_2/N_2 mixture (20% H_2), from 700°C to test temperature again in N_2 flow. Reduction directly in gasification gas was applied in the last test run. The catalyst was heated up in N_2 flow (heating rate 50°C/h) to the test temperature (900°C) after which it was exposed directly to gasification gas.

3. Results and discussion

In the first phase of catalytic hot gas cleaning studies catalyst screening tests were performed with the atmospheric laboratory scale fixed bed reactors at constant conditions (mean temperature ca. 900°C, 1 bar, residence time 0.3 s). Sample gases from the updraft gasifier and from the PDU fluid bed gasifier were used as feeds. These tests indicated that carbonate rocks and nickel catalysts were efficient catalysts for tar decomposition [1,2]. Ammonia decomposition in turn was facilitated also with nickel catalysts and in addition with iron containing materials in updraft gasification gas [3,4]. The main results of these tests are collected in Table 1 and Table 2. Similar results have been obtained elsewhere with carbonate rocks [9–11] and nickel catalysts [12–14].

Tar from the updraft gasifier was thermally quite unstable containing phenolic and aliphatic compounds that decomposed readily also with the inert reference material (SiC) and with alumina silicate and iron sinter. Tar from the fluid bed gasifier on the other hand consisted of thermally quite stable aromatic compounds like benzene and

Table 2
Conversion of tar and ammonia with the tested materials. Laboratory scale fixed bed tube reactor, mean temperature 900–910°C, residence time 0.2–0.3 s, pressure 1 bar. Feed from updraft and fluid bed gasifiers, peat as feedstock.

Catalyst	Conversion (%), updraft		Conversion (%), fluid bed	
	Tar	NH_3	Tar	NH_3
SiC	77	0	4	44
Alumina-silicate	88	NA	NA	NA
Iron sinter	91	87	NA	NA
Dolomite	100	0	99	53
Iron containing dolomite	100	75	99	53
Nickel catalyst (Ni/Al_2O_3)	100	100	100	100

NA = not analysed.

naphthalene resulting to low tar conversion with SiC at 900°C, (Table 2).

The high ammonia decomposing activity of iron materials with the updraft gasifier gas (Table 2) can be due to the reduction of iron oxides present in these materials to active metallic iron. On the other hand the reduction potential of the fluid bed gasifier gas was lower and less metallic iron should have been present with this gas. This could thus be the explanation to the observed inactivity of the iron dolomite in fluid bed gasifier gas. The relatively high ammonia conversions obtained with the inert materials can possibly be attributed to thermal reactions and to some extent also to reactor wall effects at the applied conditions.

With the most active catalysts almost equilibrium gas composition was achieved (Table 1) [1,2]. The formation of CO and H_2 and the reaction of oxidating components (H_2O, CO_2) as well as literature data [15,16] suggested that hydrocarbons were decomposed via steam (Eq. (1)) or CO_2-reforming (dry reforming) (Eq. (2)) reactions producing CO and H_2. Ammonia was most likely decomposed with the metal catalysts (nickel catalysts and iron materials) via the reverse of ammonia synthesis reaction (Eq. (3)) taking place on metal surfaces [17]. According to the literature [15,16] nickel catalysts and dolomite catalysed also water-gas shift reaction (Eq. (4)).

Laboratory experiments performed later with the fixed bed pressurised reactor with CO_2/N_2 and H_2O/N_2 gas mixtures confirmed that hydrocarbons can decompose in gasification gas at 900°C by reactions (Eq. (1)) and (Eq. (2)) with nickel catalysts and dolomites [8]. Furthermore, these reactions took place very rapidly at equally high conversions with these materials at the applied conditions [8]. However, available literature data [18–20] suggests that the main hydrocarbon decomposition reaction with nickel catalysts can be different than with dolomites. Methane reforming with CO_2 has been observed to be slower than reforming with steam with nickel catalyst (Ni/MgO) at 600°C indicating that steam reforming could be the main reaction with nickel catalysts [18]. On the other hand with basic oxides (MnO, MgO) adsorption and subsequent activation of CO_2 has been reported to take place quite readily [19,20]. Dolomite in calcined state obviously behave similarly implementing that reaction (2) can be more important with it than with nickel catalysts.

$$C_nH_m + nH_2O \rightarrow nCO + (n+m/2)H_2 \qquad (1)$$

$$\Delta H^0\ (900°C) = -928\ \mathrm{kJ\ mol^{-1}}\ \text{(for toluene)}$$

$$C_nH_m + nCO_2 \rightarrow 2nCO + m/2H_2 \qquad (2)$$

$$\Delta H^0\ (900°C) = -1163\ \mathrm{kJ\ mol^{-1}}\ \text{(for toluene)}$$

$$2NH_3 \leftrightarrow N_2 + 3H_2 \qquad (3)$$

$$\Delta H^0\ (900°C) = -112\ \mathrm{kJ\ mol^{-1}}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (4)$$

$$\Delta H^0\ (900°C) = 33\ \mathrm{kJ\ mol^{-1}}.$$

The highly endothermic hydrocarbon reforming reactions caused quite high axial temperature gradient in the catalyst bed. Thus the temperature of the upper part of the catalyst bed was with the most active materials lower than in the middle part of the bed. Hence, with nickel catalyst fed with the fluidised bed gasifier product gas, this temperature difference was 50–70°C and with less active materials the difference was consequently lower.

In gasification conditions carbon deposition that can cause rapid catalyst deactivation is possible by hydrocarbon decomposition reactions (5) and (6) or by Boudouard reaction (7). Carbon deposition can occur if gas does not contain enough oxidising components (H_2O, CO_2) or the catalyst temperature is too low [15]. Thermodynamic calculations made for the gas compositions presented in Table 1 indicated that carbon will be present in equilibrium at temperatures lower than 600–640°C at 1 bar pressure and 750–780°C at 25 bar pressure.

$$C_nH_m \rightarrow \text{'carbon'} + xH_2 \qquad (5)$$

$$CH_4 \leftrightarrow C + 2H_2 \qquad (6)$$

$$\Delta H^0\ (900°C) = -91\ \mathrm{kJ\ mol^{-1}}.$$

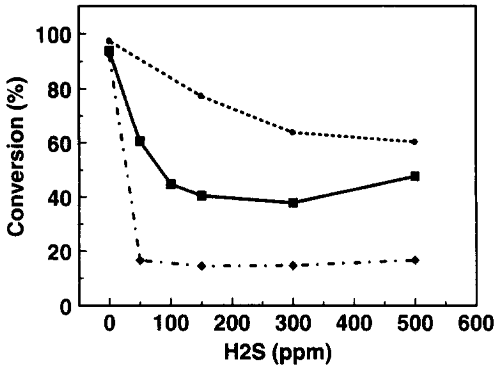

Fig. 2. Effect of H_2S at different temperatures on the conversion of ammonia. Laboratory scale pressurised fixed bed reactor, nickel catalyst (Ni/Al_2O_3), residence time 0.5 s, 20 bar and 800–950°C. Simulated gasification gas. – ● – 950°C, -□- 900°C, · - □ - · 800°C.

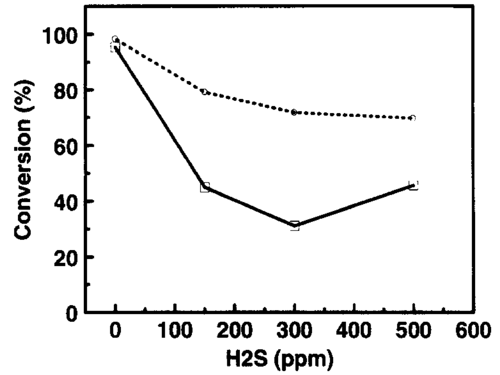

Fig. 3. Effect of H_2S at different temperatures on the conversion of ammonia. Laboratory scale pressurised fixed bed reactor, nickel catalyst (Ni/Al_2O_3), residence time 0.5 s, 900°C (mean value) and 5 (· · ·) and 20 (—) bar. Simulated gasification gas.

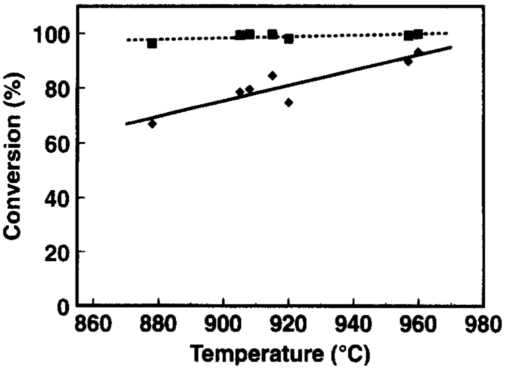

Fig. 4. Effect of temperature on tar (· · ·) and ammonia (—) conversion with the monolith catalyst (Ni/Al_2O_3). Dust containing gas from the PDU fluidised bed gasifier, several biomass feedstocks, 5 bar.

$$2CO \leftrightarrow C + CO_2 \qquad (7)$$

$$\Delta H^0\ (900°C) = 168\ \mathrm{kJ\ mol^{-1}}.$$

Later experiments with the pressurised fixed bed laboratory scale reactor indicated that dolomites and limestones were efficient tar decomposing catalysts only if they were calcined [5,6]. At atmospheric gasification conditions calcination takes place at about 800°C thus enabling their use above this temperature for example in the gasifier-engine applications. However, at the IGCC process conditions (pressure 20–25 bar) the partial pressure of CO_2 in the gas is sufficiently high (ca. 3 bar) to prevent calcination even at 900°C. Consequently experiments at these conditions (900°C, 20 bar, 0.5 s residence time, $N_2/CO_2/H_2O$ atmosphere) with limestones and dolomites resulted to almost complete deactivation of these materials. Temperatures in the range of 950–1000°C were required to keep them in activated state in gasification gas at 20 bar pressure [6].

Biomass derived gasification gas contains about 100 ppm H_2S, which is a known catalyst poison. Work with nickel catalysts with the pressurised laboratory scale equipment showed that high pressure and low temperature enhanced deactivation by H_2S. Studies made with simulated gasification gas covered H_2S range 0–500 ppmv, temperature range 800–950°C and 5 and 20 bar pressures (Fig. 2 and Fig. 3). These studies showed also that it was possible to compensate deactivation at high pressure by using high temperatures (900–950°C). Ammonia decomposing function of the catalyst was more susceptible to poisoning by H_2S than the tar decomposing function [7]. These results agree well with those obtained by Krishnan et al. [12].

The most recent tests with the monolith catalyst fed with dusty fluid bed gasification gas indicated that complete tar decomposition and about 80% ammonia conversion were achieved at 900°C temperature, 1 s residence time (SV 2500 1/h) and at 5 bar pressure. Changes in operation conditions affected more to ammonia conversion than to tar conversion at the applied condition range, Fig. 4 and Fig. 5. At the highest temperatures about 95% ammonia conversion was measured. The yields of H_2 and CO were increased with increasing temperature whereas the yield of CO_2 was decreased

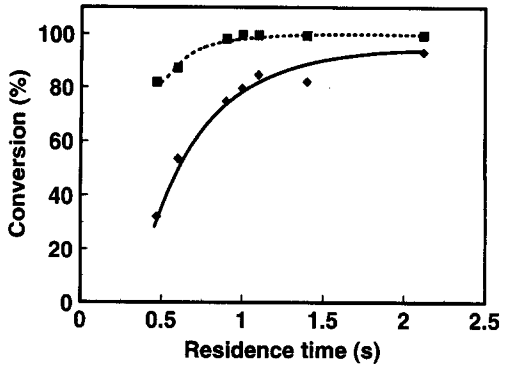

Fig. 5. Effect of residence time on tar (· · ·) and ammonia (—) conversion with the monolith catalyst (Ni/Al_2O_3). Dust containing gas from the PDU fluidised bed gasifier, several biomass feedstocks, 5 bar.

Table 3
Yields of the gas main components in the studied temperature range. Monolith catalyst residence time 0.9–1.1 s, pressure bar. Gasifier feedstock was a mixture of forest waste wood and peat

Temperature, °C	Tar conversion, %	NH_3 conversion, %	Gas yields, mol out/mol in				
			H_2	H_2O	CO	CO_2	CH_4
880	96	67	1.9	0.7	1.7	0.8	0.2
905	99	79	2.5	0.7	2.1	0.8	0.2
960	100	93	2.7	0.8	2.1	0.7	<0.1

(Table 3). Almost equilibrium gas composition was achieved at the applied conditions (Table 4). However, the residual content of ammonia was larger than the equilibrium value even at the highest temperature unlike in the tests with the fixed bed reactors (Table 1). Possible reason can be partial deactivation of the catalyst surface by H_2S enhanced by pressure, differences in catalyst formulation and lower surface temperature of the monolith catalyst compared to that of the fixed catalyst bed.

Residence times over 1 s were required for high tar and ammonia conversion. At lower values conversions decreased markedly. However, with the fixed bed reactors equally high tar and ammonia conversions were achieved at shorter (about 0.3 s) residence times at the same mean temperature. The reason for this can be differences in actual catalyst surface temperatures with the monolith and fixed bed as well as differences in mass transfer to catalyst surface. According to literature [21] heat and mass transfer between bulk of the fluid and catalyst surface are poorer in monolith than in fixed bed in otherwise comparable conditions. Furthermore, the conversion in steam reformers is reported [15,22] to be limited mainly by the heat flux supplied by unit weight of catalysts. Hence the highly endothermic reforming reactions can lower catalyst surface temperatures considerably inside the channels leading to lowering of reaction rates.

However, in these tests the measured monolith temperature gradient was about 20°C which was lower than in the fixed beds. The reason for this can be the fact that the measured monolith temperature in these tests indicated rather the gas- than the channel wall- or monolith temperature,

Table 4
Gas composition and the calculated equilibrium composition in the studied temperature range. Monolith catalyst, residence time 0.9–1.1 s, pressure 5 bar. Gasifier feedstock was a mixture of forest waste wood and peat.

Component	880°C		905°C		960°C	
	measured	equilibrium	measured	equilibrium	measured	equilibrium
CO, vol.-%	18	17.9	18.6	17.2	18.8	17.7
CO_2, vol.-%	9.4	8.6	9.2	9	8	8.4
CH_4, vol.-%	0.6	<0.1	0.6	<0.1	0.1	<0.1
H_2, vol.-%	20.5	19.7	20.3	20.1	20.4	19.5
H_2O^a, vol.-%	8.8	10.9	11.1	13.1	12	13.4
N_2, vol.-%	42.5	42.8	40.3	40.6	40.6	41
NH_3, ppm	820	70	610	60	190	50
tar, ppm	50	0	19	0	5	0

[a] calculated from material balance

Table 5
Gas composition at the monolith catalyst reactor inlet and outlet with the tested fuels. Pressure 5 bar, temperature 910–920°C and residence time 0.9–1.2 s

Component	Glassifier fuel and content of gas component, vol.-%									
	wood chips		eucalyptus chips		forest waste wood		bark		peat	
	in	out	in	out	in	out	in	out	in	out
CO	12.6	18.1	13.5	19.2	11	16	11.4	16.4	8.6	13
CO_2	10.8	7.9	12.5	8.5	12.3	9.5	12.4	9.6	12.8	10.3
CH_4	3.4	0.2	3.8	0.3	3.2	0.6	3	0.5	2.3	0.4
H_2	8.9	17.1	10.1	17.2	8.5	14.7	8.8	14.3	9.1	15.2
H_2O[a]	19.3	15.5	11.6	10.1	12.7	10.6	11.4	9.6	17.5	14.5
N_2	44.7	41.3	48.3	44.7	51.9	48.6	52.8	49.7	49.4	46.6
NH_3, ppm	560	140	510	140	1900	290	1200	230	2700	170
tar, ppm	1500	< 10	1600	< 10	1200	< 10	1000	< 10	880	< 10
H_2S, ppm	30	30[a]	30	20[a]	80	70[a]	90	80[a]	170	160[a]

[a] Calculated from material balance.

because it was not possible to place thermocouples so that only channel surface temperature could have been measured. Moreover, with the fixed catalyst beds the measured bed temperature was presumably closer to the actual catalyst surface temperature, because of the better thermal conductivity of the bed and because it was obtained with thermocouples placed inside the bed.

Composition of gasification gas was dependent on feedstock. The greatest differences were found in the contents of tar, ammonia, H_2S and water (Table 5). However, catalytically treated gas was almost equilibrated at the conditions applied and hence the residual amounts of ammonia and tar at the outlet gas were quite the same regardless of the feedstock.

Catalyst activation (reduction) process seemed not to affect the catalyst performance. Within measuring accuracy ammonia and tar conversions were the same regardless the catalyst was reduced with H_2 or directly with gasification gas.

The use of a monolith type of reactor seems to be the most promising way of avoiding plugging problems typical for fixed or moving bed reactors with high particulate loadings. No catalyst blocking, carbon deposition or catalyst deactivation was observed during the longest test run with the applied catalysts. At this test tar and ammonia conversion remained practically constant, being about 80% for ammonia and 100% for tar. During this test H_2S content of gas varied in the range 30–90 ppmv, dust content in the range 0.8–3.7 $g/m^3{}_n$. However, tests in the range of thousands of operating hours are needed to demonstrate the applicability of this type of gas cleaning process for gasification applications.

4. Conclusions

Gasification gas derived from biomass feedstocks can be purified efficiently from tar and ammonia with nickel catalysts. To avoid deactivation caused by H_2S temperatures over 900°C should be used specially in pressurised (IGCC) conditions. Plugging problems caused by dust can be avoided by using monolith type of catalysts, which are thus particularly suitable for clean up of fluidised bed gasifier product gas. Dolomites and limestones can be used as tar decomposing catalysts if they are calcined, which means that near atmospheric pressure and temperatures around 900°C should be applied in gasification processes. Ammonia decomposition can, in addition to nickel catalysts, be enhanced with iron containing materials over 900°C temperatures.

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