

Experimental comparison of biomass chars with other catalysts for tar reduction

Z. Abu El-Rub^{a,*}, E.A. Bramer^{a,1}, G. Brem^{a,b,2}

^a *University of Twente, Laboratory of Thermal Engineering, P.O. Box 217, 7500 AE Enschede, The Netherlands*

^b *TNO, P.O. Box 342, 7300 AH Apeldoorn, The Netherlands*

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Abstract

In this paper the potential of using biomass char as a catalyst for tar reduction is discussed. Biomass char is compared with other known catalysts used for tar conversion. Model tar compounds, phenol and naphthalene, were used to test char and other catalysts. Tests were carried out in a fixed bed tubular reactor at a temperature range of 700–900 °C under atmospheric pressure and a gas residence time in the empty catalyst bed of 0.3 s. Biomass chars are compared with calcined dolomite, olivine, used fluid catalytic cracking (FCC) catalyst, biomass ash and commercial nickel catalyst. The conversion of naphthalene and phenol over these catalysts was carried out in the atmosphere of CO₂ and steam. At 900 °C, the conversion of phenol was dominated by thermal cracking whereas naphthalene conversion was dominated by catalytic conversion. Biomass chars gave the highest naphthalene conversion among the low cost catalysts used for tar removal. Further, biomass char is produced continuously during the gasification process, while the other catalysts undergo deactivation. A simple first order kinetic model is used to describe the naphthalene conversion with biomass char.

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1. Introduction

In a previous paper [1], a review of catalysts for tar elimination in biomass gasification processes was made. It was concluded that the biomass char can be a material of high potential for tar reduction in the biomass gasification process. Therefore, it is important to compare the performance of biomass char for tar reduction with other types of active catalysts. The properties that determine the technical suitability of a catalyst for the tar removal in a gasification process are [2]: (1) activity; how fast one or more reactions (e.g., tar conversion reactions) proceed in the presence of the catalyst, (2) selectivity; the fraction of the starting mate-

rial (tar) that is converted to the desired product (light gases), and (3) stability; the chemical, thermal, and mechanical stability of a catalyst determines its lifetime in industrial reactors. Activity and stability are the most important for tar conversion in the gasification process and to a less extent the selectivity as long as the tar is converted to light gases.

The attractiveness of char as a catalyst originates from its low cost and its natural production inside the gasifier. However, it will be consumed by gasification reactions with steam or CO₂ in the producer gas. The need for a continuous external char supply or withdrawal depends on the balance of char consumption and production in the gasification system. Char was noticed to have a good catalytic activity for tar removal [3–6]. In the downdraft gasifier, both the fuel and the gas flow downwards through the reactor enabling the pyrolysis gases to pass through a throated hot bed of char. This results in the cracking of most of the tars into non-condensable gases and water.

* Corresponding author. Tel.: +31 534891091; fax: +31 534893663.

E-mail addresses: zabuelrub@yahoo.com (Z. Abu El-Rub), e.a.bramer@ctw.utwente.nl (E.A. Bramer), g.brem@mep.tno.nl (G. Brem).

¹ Tel.: +31 53 4892530; fax: +31 53 4893663.

² Tel.: +31 555493290; fax: +31 555493287.

The two stage gasifier developed by the Technical University of Denmark (DTU) gives almost complete tar conversion ($<15 \text{ mg/N m}^3$) [4]. The high tar removal of this gasifier is related to passing the volatiles through a partial oxidation zone followed by a char bed. They found that the char bed has some selectivity in reducing the higher tar compounds. However, the total tar reduction factor is close to the naphthalene reduction as naphthalene is the dominating compound in the tar. Chembukulam et al. [3] found that the conversion of tar and pyrolygneous liquor over semicoke/charcoal at $950 \text{ }^\circ\text{C}$ resulted in almost complete decomposition into gas. Ekstorm et al. [6] reduced the primary tar content from 50 g to 3 g after passing the tar over carbon black at $750 \text{ }^\circ\text{C}$.

The tar mixture is classified into five classes by Padban [7]: Undetectable, heterocyclic, light aromatic hydrocarbons (LAH), light polyaromatic hydrocarbons (LPAH) and heavy polyaromatic hydrocarbons (HPAH). The LAH tars are not considered as problematic because they do not condense at typical application temperatures. Therefore, they are not studied in the present comparison. The HPAH are also not studied because of low concentrations in the tar mixture. Finally, the GC-undetectable tars are not studied because they simply cannot be determined. Table 1 characterizes the commonly used model tar compounds in literature [8–12]. It shows that naphthalene and phenol are the best model tar compounds that represent LPAH and heterocyclic tars, respectively.

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The objective of this paper is to compare the tar reduction performance of biomass char with other catalysts. This comparison was carried out in a fixed bed tubular reactor using model tar compounds reduction. Biomass char was compared with calcined dolomite, olivine, used fluid catalytic cracking (FCC) catalyst, biomass ash and commercial nickel catalyst. Two reference experiments were carried out, one with an inert bed material (silica sand) and another in an empty reactor in a steam and CO_2 atmosphere.

2. Experimental

Testing of biomass chars and the other catalysts was carried out using two model tar compounds phenol and naphthalene. The experimental conditions are given in Table 2. The following experiments were performed:

- Measuring the reactor temperature profile.
- Comparison of catalysts using phenol as a model tar compound.
- Comparison of catalysts using naphthalene as a model tar compound.
- Determining the apparent kinetic constant of the biomass char using naphthalene model tar compound.

Table 1
Characteristics of the common model tar compounds used in literature [8–12]

Model tar compound	Remarks
Naphthalene	The order of thermal reactivity is [8]: toluene \gg naphthalene $>$ benzene Represents the LPAHs tars or tertiary tars At $900 \text{ }^\circ\text{C}$, Naphthalene is the major single compound in the tars [9]
Phenol	Represents heterocyclic tars Major tar compound with process temperature lower than $800 \text{ }^\circ\text{C}$ [10]
Benzene	It represents a stable aromatic structure apparent in tars formed with high-temperature processes [11] It is not considered as a problematic tar
Toluene	It represents a stable aromatic structure apparent in tars formed with high-temperature processes [12] It is not considered as a problematic tar Less harmful than most of the other tar compounds [12] High-temperature chemistry of toluene is fairly well-known [12] High-temperature tar is more unsaturated than toluene. Thus, with toluene catalyst deactivation due to charring can be less severe and the hydrocarbon conversion to gases is too high in comparison with real tar [12] Gives higher conversion than real tar would, and based on toluene conversion, results would be unrealistic with respect to the decomposition of the gasifier product tar [12]
Cyclohexane	It is not considered as a problematic tar
<i>n</i> -Heptane	It is not considered as a problematic tar

Table 2
Experimental conditions of catalysts screening

	Phenol	Naphthalene
Temperature ($^\circ\text{C}$)	700, 900	900
Initial tar compound concentration (g/N m^3)	8–13	40, 90
Pressure (atm)	1	1
Gas residence time ^a (s)	0.3	0.3
Catalyst bed volume (cm^3)	25	25
Catalyst bed height (cm)	2	2
Feed gas composition		
CO_2 (Vol.%)	6	6
H_2O (Vol.%)	10	10
N_2 (Vol.%)	Balance	Balance

^a See Eq. (2).

The operating conditions that are commonly used for comparing the catalysts activity for tar conversion are, mostly, $800\text{--}900 \text{ }^\circ\text{C}$ and around $0.2\text{--}0.4 \text{ s}$ gas residence time in the empty catalyst bed in the atmosphere of steam and CO_2 [12–14].

In the thermal approach for tar removal, high temperatures are used ($>1000 \text{ }^\circ\text{C}$). This approach has the disadvantage of high energy cost. On the other hand, the catalytic approach uses lower temperatures, but uses a catalyst. The economics of the gasification process is improved because of the lower energy cost. A temperature of

900 °C was selected for the comparison to insure that the selected catalyst can give complete tar conversion as can be got in research and industry using low cost catalysts such as dolomite. Moreover, it can be better compared with other research works. Performing the comparison at higher temperature can lead to thermal cracking of the tars which does not give an accurate measure for the activity of the catalyst.

The tar conversion reaction is not fast. Thus, we have to insure that the tar has enough residence time in the catalyst bed to be converted. Several definitions for residence time have been used in literature. The residence time (τ) in the catalyst bed with respect to the empty catalyst bed volume is selected. The value of 0.3 s residence time is a good selection for comparison looking at the results of other research works in literature. In addition, the value of the residence time with respect to the catalyst weight ($\hat{\tau}$) with the unit (kg h m^{-3}) is given in Table 6 for the sake of comparison. Both residence times were calculated based on the gas flow rate at the inlet of the bed including the steam content in the gas at the bed temperature.

The major components found in the producer gas are H_2O , CO_2 , H_2 , CO and CH_4 . The most important components responsible for tar conversion are H_2O and CO_2 because of the dry and the steam reforming reactions. That is the reason they were used in the feed gas with tar.

2.1. Setup

The fixed bed reactor is made of a quartz tube, which is 75 cm in length and 4 cm internal diameter. The bed is supported by a porous quartz disc and heating is done by a tubular electrical furnace. The longitudinal temperature

profile is measured by a K-type thermocouple which is fitted in a small quartz pipe placed in the centre of the reactor. Steam and model tar compound are introduced in the gas stream by means of two separate saturation units. The concentrations of steam and model tar compound can be altered by changing the saturation temperature. The feeding line as well as the product line is externally heated (250 °C) to prevent tar compound condensation. The flow of the feed gases is regulated by critical nozzles and mass flow controllers. Fig. 1 shows the experimental setup.

Catalysts screening experiments using naphthalene were performed at a high temperature (900 °C) in order to get a high naphthalene conversion. Catalysts screening experiments using phenol were performed at 700 °C because phenol is thermally unstable at 900 °C. Fig. 2 illustrates the temperature profile inside the reactor. The temperature along the catalyst bed is constant, i.e., model tar compound removal occurs at isothermal conditions. Insulation around the reactor especially around the inlet and outlet were made so that the temperature along the reactor was always above the dew point of model tar compounds to prevent condensation.

2.2. Tar sampling method

There is not yet an international standard method for measuring tar in producer gas from biomass gasifiers. However, in the beginning of the year 2003 a European project named “Tar Measurement standard” started to focus on the standardization at a European level (CEN) of a Guideline for the measurement of the tar [15,16]. In this comparison study the tar content in the gas was determined using solid phase adsorption method (SPA) [17].

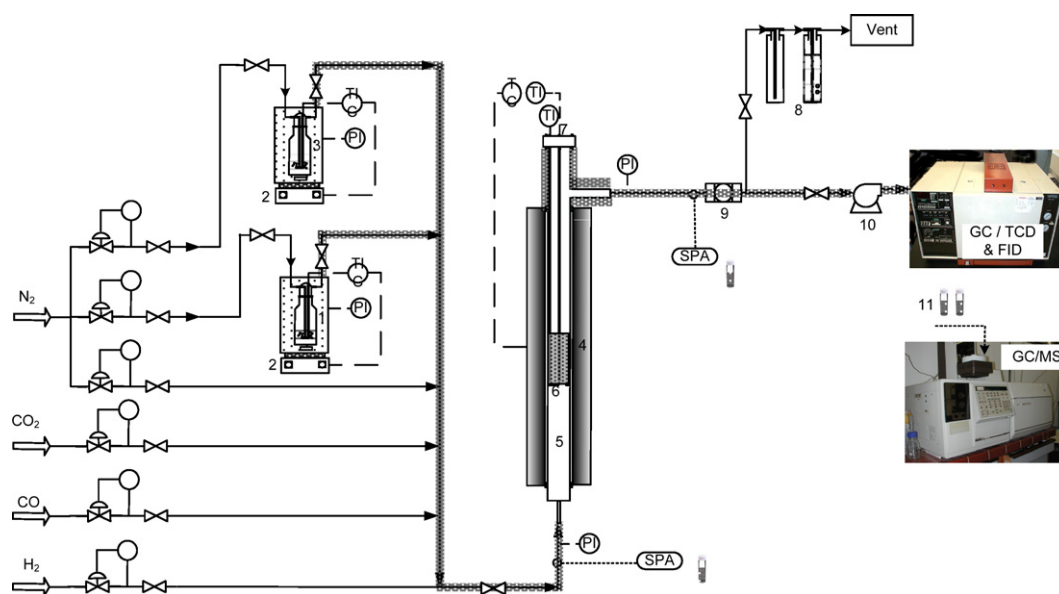


Fig. 1. Experimental setup for catalysts comparison (1. water saturator; 2. heater; 3. model tar compound saturator; 4. tubular furnace; 5. quartz tubular reactor; 6. catalyst bed; 7. quartz tubes for thermocouples; 8. water condenser; 9. filter; 10. heated pump; 11. SPA sample vials; GC: gas chromatography; FID: flame ionization detector; TCD: thermal conductivity detector; MS: mass spectrometry; SPA: solid phase adsorption).

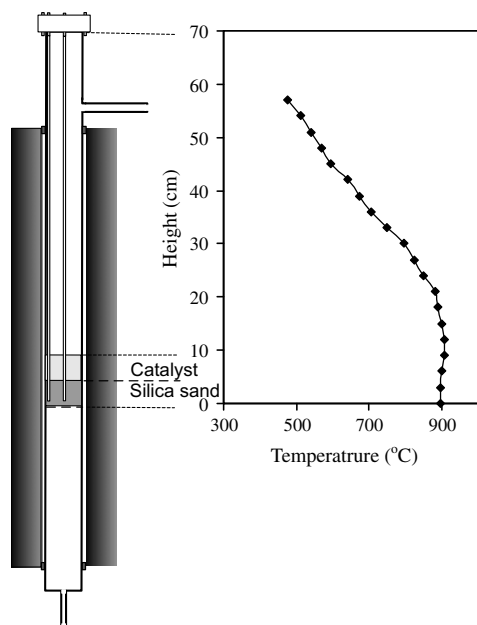


Fig. 2. Reactor temperature profile.

The advantages of the SPA method compared to the conventional cold trapping method used by the Guideline [18], include sampling speed (one sample per min compared to one sample per hour), simplicity, less solvent consumption, faster workup, accuracy and repeatability. The SPA method is reliable to measure class 2–5 tars: from xylenes up to tar compounds with a molecular weight of 300 kg/kmol (coronene) [7].

2.3. Gas analysis

The tar containing sample from the SPA method was analyzed in a gas chromatograph in combination with a mass spectrometer (GC/MS). When samples from the feed and the product gas are taken, tar conversion can be determined. Measurements on volumetric concentration of H_2 , N_2 , CH_4 , CO can be done online by gas chromatography in combination with a thermal conductivity detector (GC/TCD). CO_2 concentration could only be measured offline using an infrared Maihak Multor 610 detector.

2.4. Test procedure

The experimental runs were started by pouring a weighed sample of the bed material (catalyst) on top of a silica bed. The feed gas flow rate was regulated to give the desired space time of 0.3 s. The reactor is preheated to the required temperature with an oven. Calcination required for some catalysts was carried out in situ at the reactor temperature and atmospheric pressure for 1 h at constant nitrogen flow. After calcination, all the gaseous reagents were fed and the catalysts were then stabilized for at least 15 min before the feed and product gas were sampled.

2.5. Tested catalysts

Char is a general word and it is not enough to be used when comparing its performance with other research works. The source material of char and method of production affect its physical and chemical properties. Therefore, it should be always accompanied with the ultimate analysis, proximate analysis, mineral content, BET internal surface area, pore size distribution and porosity. This allows a better comparison and repeatability of the results.

Commercial biomass char (C.B. Char), calcined dolomite, olivine, and “in-equilibrium” (once used) fluid catalytic cracking (FCC) catalyst were obtained from commercial suppliers. Biomass ash and another biomass char were produced from pinewood biomass in our laboratory. The biomass char was produced by pyrolyzing the pinewood at 500 °C and the biomass ash was produced by burning the produced pinewood char at 600 °C. FCC catalyst was obtained at an average particle size of 57 μm . Silica sand (inert material) and commercial nickel catalyst (highly active catalyst) were used as extremes for comparing the activity of the selected catalysts. The particles of dolomite, olivine and biomass chars were sieved to a particle size range of 1.4–1.7 mm. Nickel catalyst particles were crushed and sieved to a particle size range of 1.4–1.7 mm. The produced biomass ash was very fine with a particle size less than 0.3 mm. Tables 3–5 provide some chemical characteristics of the catalysts.

2.6. Experimental data evaluation

The main property selected for determining the suitability of a catalyst for the gasification process is the activity. For catalysts comparison, the following activity measures can be used [2].

Conversion of the tar model compounds naphthalene and phenol were calculated from their inlet and outlet concentrations as shown in Eq. (1). This equation is often used in literature [11,19–21] for ease of results comparison with other research works. Further, the analysis of output tar from the tar cracker show no other formed tar molecules under the carried experimental conditions. The data points that represent the model tar compound conversion were

Table 3
The chemical composition of the compared catalysts (wt.%)

Element	Olivine	Dolomite	Nickel	Biomass ash
MgO	48.5–50.0	21.5	–	15
CaO	0.05–0.10	30.5	–	44.3
SiO ₂	41.5–42.5	0.15	7	–
Fe ₂ O ₃	6.8–7.3	0.20	–	–
Al ₂ O ₃	0.4–0.5	0.061	12	–
NiO	0.3–0.35	–	70	–
MnO	0.05–0.10	–	–	–
Cr ₂ O ₃	0.2–0.3	–	–	–
NiCO ₃	–	–	5	–
K ₂ O	–	–	–	14.5

Table 4
Chemical characteristics of the spent FCC catalyst

APS (μ)	SA (m^2/g)	MSA (m^2/g)	ABD (g/cc)	Fe (wt.%)	Na (wt.%)	C (wt.%)	Ti (wt.%)	ReO (wt.%)	SiO ₂ (wt.%)	Mg (wt.%)	Al ₂ O ₃ (wt.%)
57	172	79	0.86	0.3	0.15	0.08	0.97	3.73	50.58	0.21	44.3

APS, average particle size; MSA, matrix surface area; SA, surface area; ABD, apparent bulk density.

Table 5
The ultimate analysis of used biomass char produced by pyrolyzing pinewood at 500 °C and commercial biomass char (wt.%)

Element	Pinewood char	Commercial biomass char (C.B. char)
C	87.9	89.03
N	0.3	0.24
H	0.6	0.12
Ash	4.7	9.55
O (by difference)	6.5	1.06

Table 6
Bed properties of tested catalysts

Bed material ^a	Catalyst bed density (g/cm^3)	Particle size (mm)	Weight time ($\text{kg}_{\text{cat}} \text{h}/\text{m}^3$)
Olivine	1.97	1.4–1.7	0.27
Raw dolomite	1.93	1.4–1.7	0.27
Silica sand	1.73	1.4–1.7	0.24
FCC (spent)	1.13	0.057	0.16
Nickel	1.03	1.4–1.7	0.14
Commercial biomass char (C.B. char)	0.52	1.4–1.7	0.04
Biomass char	0.26	1.4–1.7	0.03
Biomass ash	0.09	<0.25	0.01

^a The catalyst bed is added on the top of a silica sand bed of the same volume.

average points. For every point 5 samples, on average, were taken

$$X = \frac{(C_{\text{in}} - C_{\text{out}})}{C_{\text{in}}} \quad (1)$$

where X is the model tar compound conversion, C_{in} is the inlet model tar compound concentration and C_{out} is the outlet model tar compound concentration.

Several definitions for the gas residence time have been used in literature. The residence time (τ) in the catalyst bed with respect to the empty catalyst bed volume was selected and defined as

$$\tau = \frac{V_{\text{R,cat}}}{Q_{\text{in}}(T, P_{\text{tot}})} \quad (2)$$

where $V_{\text{R,cat}}$ is the volume of catalyst bed with respect to the volume of empty reactor, m^3 and $Q_{\text{in}}(T, P_{\text{tot}})$ is the inlet volume flow rate, $\text{m}^3 \text{s}^{-1}$.

The activity of the catalyst is defined in terms of kinetics. The reaction rate is calculated as the rate of change of the amount of tars with time relative to the reaction volume (used in this study) or mass of the catalyst. A first order

kinetic model was used for making a kinetic study for naphthalene conversion. This model is easy for data evaluation and comparison of results with literature. The reaction rates were measured in the temperature and concentration ranges that are common in the industrial gasification processes

$$-r_{\text{tar}} = k_{\text{app}} C_{\text{tar}} \quad (3)$$

where r_{tar} is the rate of model tar conversion, $\text{kmol}/\text{m}^3 \text{s}$, k_{app} is the apparent kinetic constant, s^{-1} and C_{tar} is the tar concentration, kmol/m^3 .

To verify plug flow conditions in the fixed bed we need to calculate the longitudinal or axial dispersion coefficient (D_l) which characterizes the degree of backmixing during the flow. This coefficient is used in the dimensionless Peclet number (Pe) to determine the type of flow

$$Pe = \frac{\langle v \rangle L}{D_l} \quad (4)$$

$Pe \rightarrow 0$ large dispersion, hence mixed flow

$Pe \rightarrow \infty$ negligible dispersion, hence plug flow

where L is the length of the bed, m and $\langle v \rangle$ is the average actual fluid velocity, m/s.

Peclet number was found to be very high, hence plug flow conditions can be assumed. Under plug flow conditions, the apparent kinetic constant can be integrated as

$$k_{\text{app}} = \frac{-\ln(1 - X)}{\tau} \quad (5)$$

where τ is the gas residence time in the empty bed volume based on inlet gas velocity and reactor temperature, s.

The apparent rate constant of naphthalene conversion over biomass char was estimated according to Arrhenius' law. The estimated apparent activation energy of char was assumed to be constant in the studied temperature range (700–900 °C)

$$k_{\text{app}} = k_{\text{o,app}} e^{(-E_{\text{app}}/RT)} \quad (6)$$

where $k_{\text{app,o}}$ is the apparent frequency factor, s^{-1} and E_{app} is the apparent activation energy, kJ/kmol .

3. Results and discussion

3.1. Phenol conversion

Two types of experiments were performed; thermal and catalytic phenol elimination. The thermal experiments were performed in an empty reactor to study the stability of phe-

Table 7
Dry gas composition at the reactor outlet, inlet and outlet phenol concentrations, and thermal and catalytic conversion of phenol; average feed gas composition: 6 vol.% CO₂, 10 vol.% H₂O and balance N₂, $\tau = 0.3$ s

Catalyst	T (°C)	Dry gas composition (vol.%)				Phenol		
		H ₂	CO	CO ₂	N ₂	Out (g/N m ³)	In (g/N m ³)	Conversion(wt.%)
Empty reactor	700	0.14	8.9×10^{-4}	6.0	93.8	10.9	11.6	6.0
	800	1.16	2.6×10^{-3}	5.7	93.1	0.2	11.4	98.2
	900	1.60	2.5×10^{-3}	5.8	92.6	0.2	12.4	98.4
Silica sand	700	0.23	9.1×10^{-4}	6.4	93.4	7.8	11.9	34.5
	900	1.0	2.6×10^{-3}	6.0	93.0	0.0	9.1	100
Olivine	700	0.27	7.4×10^{-4}	6.1	93.7	6.3	11.0	42.7
	900	1.0	2.5×10^{-3}	4.0	95.0	0.0	10.9	100
C.B. Char	700	2.18	1.5	7.2	89.1	1.6	8.7	81.6
	900	5.09	9.2	3.2	82.6	0.0	7.9	100
FCC	700	0.19	9.3×10^{-4}	5.7	94.1	1.1	8.5	87.1
	900	0.89	2.6×10^{-3}	5.7	93.4	0.0	9.8	100
Dolomite	700	0.85	2.6×10^{-3}	5.8	93.3	1.0	10	90.0
	900	0.40	2.6×10^{-3}	6.5	93.1	0.0	13.5	100
Nickel	700	1.90	1.9	6.2	90.0	1.0	11.1	91.0
	900	0.08	1.2×10^{-3}	6.5	93.5	0.0	10.0	100

nol at 700 and 900 °C. The activity of six different catalytic bed materials for phenol conversion was tested. For both types of experiments, dry gas and phenol analysis were performed. The summary of these experimental results is given in Table 7.

Carbon mass balance was based on dry gas analysis that includes phenol content and excludes steam content. Further, nitrogen inlet mole (mass) flow rate should equal nitrogen output mole (mass) flow rate. For all catalysts experiments except char experiments, the closing error of carbon was less than 20% based on the carbon input (see Fig. 3).

Carbon mass balance was not verified for experiments with char as a catalyst. The carbon mass balance was not made because the biomass char catalyst is not an inert material as it reacts with steam and CO₂ in the feed gas. At the time of these experiments, it was difficult to measure

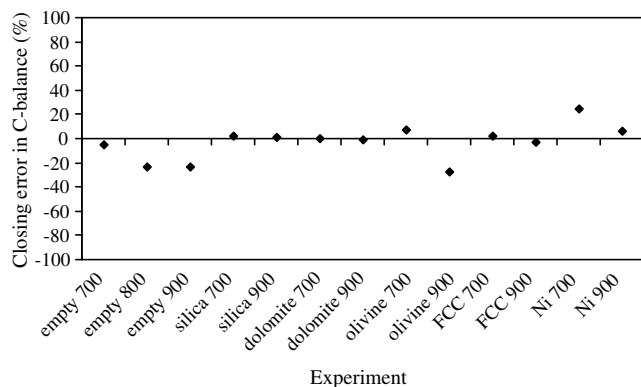


Fig. 3. Carbon mass balance closing error (%) of the thermal and catalytic conversion of phenol conversion experiments.

the carbon loss of the char. Later, the setup was further developed and converted to a sort of a macro reactor where it is connected to a balance. Thus, for upcoming char experiments the weight of the char could be measured with time and thus the carbon balance could be verified.

It is expected that at equilibrium H₂ and CO are produced while CO₂ and H₂O are consumed. Moreover, the amount of H₂ produced is higher than that of CO. Even though, the dry reforming reaction produces more CO than H₂ produced by the steam reforming reaction, it seems that the steam reforming reaction is thermodynamically more favorable. The produced amounts of H₂ and CO increased with increasing temperature for all catalysts expect dolomite and nickel where they show opposite trend.

The steam and dry reforming reactions convert the phenol to CO and H₂ when reacted with H₂O and CO₂. Phenol is stable at a temperature of 700 °C with only 6.3 wt.% conversion. However, it loses its stability as temperature increases. The conversion is more than 97 wt.% at 800 °C and more than 98 wt.% at 900 °C. No significant amounts of other tars in the outlet gas were detected.

The catalytic experiments were performed at two temperatures: 700 and 900 °C. The following results were obtained:

3.1.1. At 900 °C

All catalysts gave 100 wt.% phenol conversion. It was noted that more than 98 wt.% of phenol was already thermally eliminated.

3.1.2. At 700 °C

The sequence of the catalysts with respect to decreasing activity is: nickel > dolomite > FCC > char > olivine > sand, see Fig. 4.

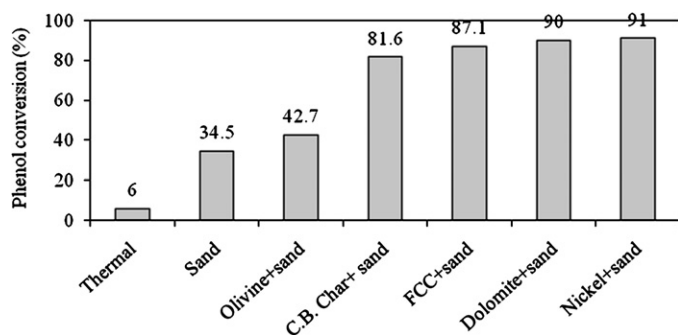


Fig. 4. Effect of catalysts on phenol conversion. $T = 700\text{ }^{\circ}\text{C}$, $\tau = 0.3\text{ s}$, feed gas composition: 6 vol.% CO_2 , 10 vol.% H_2O and balance N_2 , inlet phenol concentration: 8–12 $\text{g}/\text{N m}^3$.

Dolomite and nickel catalyst gave the highest phenol conversion (90 and 91 wt. %, respectively). They are known to be reforming catalysts and thus catalyze steam and dry reforming reactions of phenol while H_2 and CO are produced. As temperature increased, the produced amount of H_2 decreased for both these catalysts, whereas for other catalysts increases. This confirms that these two catalysts have the same mechanism of tar removal which is expected to be reforming and not cracking.

C.B. char gave moderate phenol conversion (82 wt.%). This is a reasonable result because heterocyclic tars (e.g., phenol) at a gasification temperature of $800\text{ }^{\circ}\text{C}$ or above are thermally cracked. Thus, only a small amount of the heterocyclic tars (phenol) remains in the producer gas to be removed catalytically. The gas analysis in Table 7 shows that the biomass char reacts with the reactive gases in the feed gas (steam and CO_2). Therefore, the concentration of both CO and H_2 were higher the amounts produced with other catalysts. Although, the other catalyst were not consumed (inert), but they have limited life time because of the deactivation. On the other hand, even though the biomass char has limited lifetime, it is continuously activated by the gasification reactions with steam and CO_2 . Further, the char consumption by the gasification reactions can be balanced by the gasification process where some char is produced. The char production inside the gasifier can be influenced by manipulating the gasification process parameters, such as, temperature, particle size, moisture content, ..., etc. The continuous biomass char activation and the continuous supply of the char to the tar cracker make the biomass char more stable than the other catalysts. For a self-sustained gasification process with a biomass char as a tar catalyst, a model is required to balance the amount of char consumed in the tar cracker with the amount of char produced in the biomass gasifier.

Olivine gave a poor phenol conversion (43 wt.%). The H_2 and CO concentrations in the output gas of the olivine experiments are close to that of FCC and silica sand experiments. This gives an indication that olivine probably has a mechanism of phenol cracking closer to that of FCC and silica sand. This remark is confirmed with the H_2 concentrations that have the same trend of increase with increas-

ing the temperature for the three catalysts. FCC gave a moderate phenol conversion (87 wt.%). The dry gas analysis showed that FCC mechanism is not a reforming catalyst, but as known to be a cracking catalyst. Obviously, silica sand showed significant catalytic activity for phenol conversion, about 34 wt.%.

No significant amounts of tars other than phenol were detected in the outlet gas. However, phenol could be converted to heavier compounds that are not detected by SPA.

3.2. Naphthalene conversion

Naphthalene is considered as a major tar compound at $900\text{ }^{\circ}\text{C}$ [9]. This compound is thermally stable at such high temperature as only 2% was converted over silica sand bed. Therefore, naphthalene needs to be catalytically converted. The activity of the different catalysts for naphthalene conversion is presented in Fig. 5.

Two inlet naphthalene concentrations were used to see the performance of the catalyst at high naphthalene loadings, such as in updraft fixed bed gasifiers. The ranking of reactivity obtained at $40\text{ g}/\text{N m}^3$ is: commercial nickel > dolomite > olivine > silica sand. The relative low activity of the used type of dolomite can be related to the low iron content as it has been reported that the activity of dolomite increases with increasing the iron metal content [22]. The activity of olivine can be increased by a pre-treatment of olivine in order to make the iron active and present on the surface of olivine [23]. Devi et al. [24] could increase the activity of olivine after pre-treatment from 46% to 80% naphthalene conversion at comparable experimental conditions. In addition, the large particle size used in the experiments may cause some internal mass transfer limitations. Commercial nickel based catalyst is, as expected, very active, but nickel catalysts are very expensive and more sensitive to deactivation by H_2S and high tar content in the feed.

FCC, biomass char, C.B. char and biomass ash were tested at a bed temperature of $900\text{ }^{\circ}\text{C}$, $90\text{ g}/\text{N m}^3$ initial

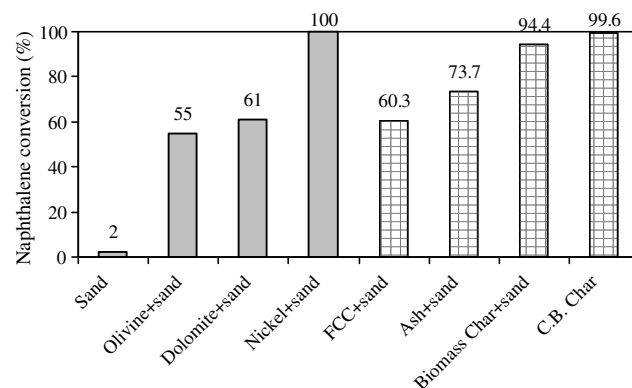


Fig. 5. Effect of catalyst bed material on naphthalene conversion, $T = 900\text{ }^{\circ}\text{C}$, $\tau = 0.3\text{ s}$, feed gas composition: 6 vol.% CO_2 , 10 vol.% H_2O and balance N_2 , initial naphthalene concentration: $40\text{ g}/\text{N m}^3$ (■) and $90\text{ g}/\text{N m}^3$ (▤).

naphthalene concentration and 0.3 s residence time. The ranking of reactivity obtained is: C.B. char > biomass char > ash > FCC.

The above results agree with the expectations expressed in the previous paper [1], where nickel catalyst, dolomite and char were expected to have the best performance. Nickel catalyst had the highest activity for naphthalene removal. Dolomite gave lower naphthalene conversion than expected because of the low iron content of the tested type. However, other types with higher content are expected to give better performance. The biomass chars gave the highest activity among the tested catalysts excluding nickel catalyst. The latter is rather expensive catalyst and sensitive to deactivation.

3.3. Reaction rate for naphthalene removal over char

From the previous sections it was found that both biomass chars gave the highest naphthalene conversion excluding the commercial nickel catalyst. The temperature effect on naphthalene conversion was studied for C.B. char (1.4–1.7 mm and 0.5–0.8 mm) in the temperature range of 700–900 °C as shown in Fig. 6. It is possible that the tar in the producer gas is adsorbed on the active sites of the char particles and undergoes gasification and polymerization reactions. The char catalyzes the gasification reactions of the adsorbed tars with steam and CO₂. Moreover, the char catalyzes the formation of tar radicals that take part in heavy hydrocarbon polymerization reactions, while the reaction products are deposited as coke on the surface of the char. Experiments show that naphthalene removal increased with increasing bed temperature. This can be related, besides the increased kinetic rate of naphthalene conversion, to reduction of the rate of coke formation. The coke covers the catalyst active sites and blocks the pores, which lead to deactivation of the catalyst. The tar mechanism for tar removal will be extensively investigated in an upcoming publication.

A reactivity study was done for C.B. char (0.5–0.8 mm) at a temperature range of 700–900 °C. The estimated apparent activation energy of char was assumed to be constant in the studied temperature range. The apparent rate

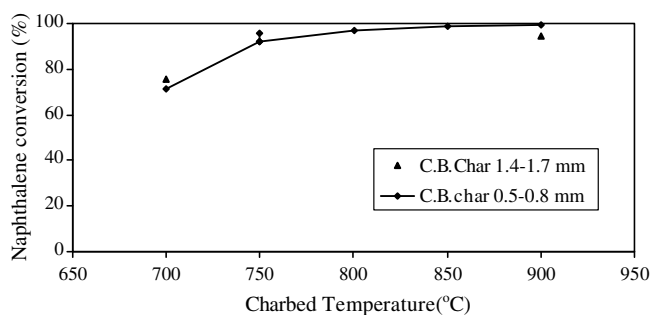


Fig. 6. Effect of temperature on naphthalene conversion with commercial biomass char, $\tau = 0.3$ s, $C_{o,n} = 20$ g/N m³, feed gas composition: 7% H₂O, 4% H₂, 6% CO, 10% CO₂, 2.4% CH₄, balance N₂.

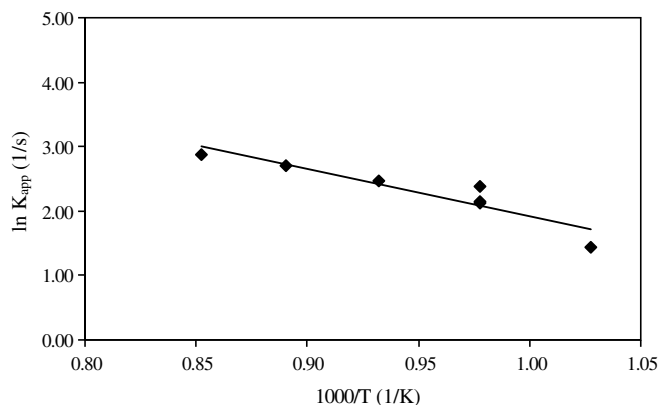


Fig. 7. Temperature dependency of the apparent reaction rate constant according to Arrhenius' law, $\tau = 0.3$ s, $C_{o,n} = 20$ g/N m³, feed gas composition: 7% H₂O, 4% H₂, 6% CO, 10% CO₂, 2.4% CH₄, balance N₂.

Table 8

Apparent activation energy (E_{app}) and the apparent pre-exponential factor ($k_{o,app}$) of C.B. char, $\tau = 0.3$ s; p.s.: 0.5–0.8 mm

Property	Value
E_{app} (kJ/mol)	61
$k_{o,app}$ (s ⁻¹)	1.10 ⁴
$k_{o,app}$ (m ³ kg ⁻¹ h ⁻¹)	7.6 × 10 ⁴

constant was varied with temperature by an Arrhenius-type relationship, as shown in Fig. 7. The apparent activation energy (E_{app}) and the apparent pre-exponential factor ($k_{o,app}$) are listed in Table 8. The effect of particle size on the naphthalene conversion was found to be low as shown in Fig. 6, i.e. the naphthalene conversion is kinetically controlled.

The measured apparent kinetic parameters for naphthalene conversion over biomass char might include some internal mass transfer limitations because the tested particle size is not relatively small (1.4–1.7 mm). On the other hand, it would be interesting to compare these results with results of other researchers. However, no comparative research could be found on tar conversion kinetic parameters for biomass char. In Tables 9 and 10 a comparison was made with other catalysts usually used in tar reduction. However, the comparison is not simple for the following reasons: (a) different representations of the space time (τ) in terms of catalyst volume/weight and volumetric feed flow rate at normal/reactor temperature, (b) many reported values for the kinetic constant were evaluated under variety of mass transfer limitations, and (c) treatment of different tars compositions originated from different gasification conditions or model tar components.

For ease of comparison, the first order rate constants results of C.B. Char were calculated in two different units. For a temperature of 900 °C, the C.B. Char gives a high rate constant value higher than several different dolomites but less than that of BASF G1-25 S CPRD. Therefore, biomass char can be considered as a catalyst of high potential for tar removal.

Table 9
Comparison of first order kinetic parameters for different catalysts used for tar elimination

Gasification conditions		Catalyst bed		Kinetic parameters				Ref.
Temperature (°C)	Agent	Type	Temperature (°C)	E_{app} (kJ mol ⁻¹)	$K_{o,app}$			K^f (900 °C)
					N m ³ kg ⁻¹ h ⁻¹	m ³ _{Tb,wet} kg ⁻¹ h ⁻¹	s ⁻¹	
	Air	Norte dolom. ^g	780–920	100 ± 20		(1.51 ± 0.8) × 10 ⁶		53 [25] ^a
	Air	Chilches dolom.	780–920	100 ± 21		(1.45 ± 0.76) × 10 ⁶		51 [25] ^a
	Air	Malagan dolom.	780–920	100 ± 22		(1.30 ± 0.54) × 10 ⁶		46 [25] ^a
	Air	Sevilla dolom.	780–920	100 ± 23		(1.24 ± 0.77) × 10 ⁶		44 [25] ^a
750–780	Steam	Dolomite	780–910	42	1.96 × 10 ³			26 [26] ^a
750–780	Steam	Magnecite	780–911	42	1.46 × 10 ³			20 [26] ^a
750–780	Steam	Calcite	780–912	42	1.28 × 10 ³			17 [26] ^a
800–860	Steam	BASF G1-25 S		58 ± 30		1.56 × 10 ⁵		408 [27] ^a
850	Air	Olivine	800–900	114		3.60 × 10 ⁶		30 [23] ^b
Heavy fraction of mild gasification coal liquids		SiC	500–750	96.9			3.83 × 10 ⁴	1.9 [28]
		SFCC ^c	500–750	85.8			1.59 × 10 ⁴	2.4 [28]
		FWC ^d	500–750	81.2			1.30 × 10 ⁴	3.1 [28]
		CPRD ^e	500–750	76.3			9.26 × 10 ⁴	37 [28]

^a Internal diffusion controls.

^b Catalyst mixed with sand.

^c SFCC (sorbent-free coal char).

^d FWC (foster wheeler char).

^e CPRD (calcined plum run dolomite).

^f Takes the unit of $K_{o,app}$.

^g dolom.: dolomite.

Table 10
Comparison of first order kinetic parameters for different catalysts used for naphthalene elimination

Model tar	Agent	Catalyst bed		Kinetic parameters			Ref.
		Type	Temperature	E_{app} kJ mol ⁻¹	$K_{o,app}$		
					m ³ _{Tb,wet} kg ⁻¹ h ⁻¹	s ⁻¹	
Naphthalene	H ₂ O + CO ₂ + CO + H ₂	Olivine	825–900	141	1.7.10 ⁷		9 [24]
Naphthalene	H ₂ O + CO ₂	Char	700–900	61	7.6 × 10 ⁴	1.0 × 10 ⁴	199 ^b This work

^a Takes the unit of $K_{o,app}$.

^b The unit is m³_{Tb,wet} kg⁻¹ h⁻¹.

3.4. Concluding remarks

From the experimental comparison of phenol conversion, the following conclusions can be drawn:

- At 900 °C the conversion of phenol is dominated by thermal cracking.
- At 700 °C the ranking of the different catalysts activity for phenol conversion is nickel > dolomite > FCC > char > olivine > sand.
- The output gas analysis of phenol conversion at 700 °C suggests that the dolomite and nickel share a phenol conversion mechanism which is probably reforming. On the other hand, FCC, olivine and silica sand share a different phenol conversion mechanism which can be cracking.

From the experimental comparison of naphthalene conversion, the following remarks can be concluded:

- At 900 °C, the naphthalene is thermally stable.
- The ranking of the different catalysts activity for naphthalene conversion at 900 °C is: nickel > C.B. char >

biomass char > biomass ash > FCC > dolomite > olivine > silica sand.

- The first order kinetic rate constant of biomass char for naphthalene conversion in the temperature range 700–900 °C was found to have an apparent activation energy (E_{app}) of 61 kJ/mol and pre-exponential factor ($k_{o,app}$) of 1.10⁴ s⁻¹ (equivalent 7.6 × 10⁴ m³ kg⁻¹ h⁻¹).
- Among the low cost material catalysts used for naphthalene conversion, biomass char shows the highest activity.

The continuous activation of the biomass char by the steam and CO₂ content in the producer gas and the continuous external supply of the biomass char from the gasifier to the cracker make the biomass char more stable than the other catalysts.

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References

- [1] Abu El-Rub Z, Bramer EA, Brem G. A review of catalysts for tar elimination in biomass gasification processes. *Ind Eng Chem Res* 2004;43:6911–9.
- [2] Hagen J. *Industrial catalysis: a practical approach*. Weinheim: Wiley-VCH; 1999.
- [3] Chembukulam SK et al. Smokeless fuel from carbonized sawdust. *Ind Eng Chem Prod Res Dev* 1981;20:714–9.
- [4] Brandt P, Larsen E, Henriksen U. High tar reduction in a two-stage gasifier. *Energy Fuel* 2000;14:816–9.
- [5] Zanzi R, Sjoström K, Bjornbom E. Rapid high-temperature pyrolysis of biomass in a free-fall reactor. *Fuel* 1996;75(5):545–50.
- [6] Ekström C, Lindman N, Pettersson R. *Fundamentals of thermochemical biomass conversion*. London and New York: Elsevier Applied Science; 1982. p. 601–18.
- [7] Kiel JHA et al. *Primary measures to reduce tar formation in fluidized-bed biomass gasifiers*. The Netherlands; 2004.
- [8] Jess A. Mechanics and kinetics of thermal reactions of aromatic hydrocarbons from pyrolysis of solid fuels. *Fuel* 1996;75(12):1441–8.
- [9] Milne TA, Abatzoglou N, Evan RJ. *Biomass gasifier “Tars”: their nature, formation and conversion*. National Renewable Energy Laboratory (NREL); 1998.
- [10] Spliethoff H. Status of biomass gasification for power production. *IFRF Combust J* 2001. Article No. 200109.
- [11] Simell PA, Hiirvensalo EK, Smolander V. Kinetics, catalysts, and reaction engineering: steam reforming of gasification gas tar over dolomite with benzene as a model compound. *Ind Eng Chem Res* 1999;38:1250–7.
- [12] Simell P, Leppalahti JK, Kurkela E. Tar-decomposing activity of carbonate rocks under high CO₂ partial pressure. *Fuel* 1995;74(6):938–45.
- [13] Simell P, Bredenberg JB-S. Catalytic purification of tarry fuel gas. *Fuel* 1990;69(10):1219–25.
- [14] Delgado J, Aznar PM, Corella J. Calcined dolomite, magnesite, and calcite for cleaning hot gas from a fluidized bed gasifier with steam: life and usefulness. *Ind Eng Chem Res* 1996;35:3637–43.
- [15] Coda B et al. Standardization of the ‘Guideline’ method for measurement of tars and particles in biomass producer gases. *Science in thermal and chemical biomass conversion*. Canada: Vancouver; 2005.
- [16] <<http://www.tarweb.net/>>.
- [17] Brage C et al. Use of amino phase adsorbent for biomass tar sampling and separation. *Fuel* 1997;76(2):1237–42.
- [18] Simell P et al. Provisional protocol for the sampling and analysis of tar and particulates in the gas from large-scale biomass gasifiers. Version 1998. *Biomass Bioenergy* 2000;18(3):19–38.
- [19] PeAñez P et al. Hot gas cleaning and upgrading with a calcined dolomite located downstream a biomass fluidized bed gasifier operating with steam–oxygen mixtures. *Energy Fuel* 1997;11:1194–203.
- [20] Duo B et al. High-temperature removal of NH₃, organic sulfur, HCl, and tar component from coal-derived gas. *Ind Eng Chem Res* 2002;41:4195–200.
- [21] Zhao H, Draelants DJ, Baron GV. Performance of a nickel-activated candle filter for naphthalene cracking in synthetic biomass gasification gas. *Ind Eng Chem Res* 2000;39:3195–201.
- [22] Simell PA, Leppalahti JK, Bredenberg JB-S. Catalytic purification of tarry fuel gas with carbonate rocks and ferrous materials. *Fuel* 1992;71:211–8.
- [23] Devi L et al. Catalytic decomposition of biomass tars: use of dolomite and untreated olivine. *Renew Energy* 2005;30:565–87.
- [24] Devi L. Catalytic removal of biomass tars; olivine as prospective in-bed catalyst for fluidized-bed biomass gasifiers. Eindhoven, The Netherlands: Technical University of Eindhoven; 2005.
- [25] Orio A, Corella J, Narvaez I. New developments on the effectiveness of dolomites of different origin for hot raw gas cleaning in biomass gasification with air. *Ind Eng Chem Res* 1997;36:3800–8.
- [26] Delgado J, Aznar PM, Corella J. Biomass gasification with steam in fluidized bed: effectiveness of CaO, MgO and CaO–MgO for hot raw gas cleaning. *Ind Eng Chem Res* 1997;36(5):1535–43.
- [27] Aznar PM et al. Commercial steam reforming catalysts to improve biomass gasification with steam–oxygen mixtures. 2. Catalytic tar removal. *Ind Eng Chem Res* 1998;37(7):2668–80.
- [28] Shamsi A. Catalytic and thermal cracking of coal-derived liquid in a fixed-bed reactor. *Ind Eng Chem Res* 1996;35(4):1251–6.