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Reactivity of sewage sludge, RDF, and straw chars towards NO

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The figures are presented in greyscale, making color imaging unnecessary

1 **Abstract:** The reaction of NO with chars of sewage sludge, refuse derived fuel (RDF), and straw was
2 investigated in a fixed bed reactor at temperatures from 800 to 900°C and NO inlet concentrations from
3 400 to 1500 ppmv. The effect of ash forming elements in the chars was examined by comparing the
4 reactivity of raw and demineralized chars. Compared to straw char, the reaction rates of sewage sludge
5 and RDF char, at 800°C and 400 ppmv inlet NO, was an order of magnitude and a factor of six higher,
6 respectively. The very high reactivity of the two waste chars was attributed to the catalytic effect of their
7 large content of calcium and iron. A simple first order globalized rate expression was employed to describe
8 the reactivity of waste chars toward NO, which predicted reasonably well the the conversion of char
9 nitrogen to NO during char combustion at 800°C in 10% O₂. A comparison with literature data revealed
10 a higher reactivity of the waste chars towards NO compared to that of coal and biomass chars. The results
11 in this work provide a simple and validated rate expression to simulate waste char-NO reaction in boilers,
12 and moreover facilitate a potential utilization of waste chars as primary or secondary measures for NO
13 reduction.

14 **Keywords:** NO reduction; char reactivity; waste combustion; sewage sludge; refuse derived fuel

15 **1 Introduction**

16 Waste fuels are increasingly used in utility and industrial boilers to reduce fuel costs and avoid
 17 landfilling [1]. Minimizing NO_x emissions from waste combustion is important due to the harmful
 18 environmental impact and strict emission limits. Two widely used waste combustion technologies are
 19 fluidized bed combustion and grate-firing. In both processes, the NO primarily stems from the fuel bound
 20 nitrogen, either through volatile or char nitrogen oxidation [2], while the contribution of thermal and
 21 prompt NO is small or negligible [3–5]. Once formed, NO may be reduced through homogeneous
 22 reactions or by heterogeneous reduction over char [6]. While the gaseous chemistry of NO is fairly well
 23 established [2,7], the reaction between char and NO is less understood. Studies show that in comparison
 24 to coal, biomass chars generally exhibit a higher reactivity towards NO reduction, partly due to higher
 25 contents of potassium [8], sodium [9], calcium, and iron [10], and possibly due to more favorable surface
 26 properties, e.g., surface area and pore size distribution [11]. The simultaneous formation and reduction of
 27 NO during char combustion is summarized in R1-R9 [12,13]. The sequence of NO adsorption and
 28 subsequent reduction over char catalysed by ash forming element, M, is illustrated by R3-R9. Here, (-CX)
 29 denotes a carbon surface complex of either nitrogen or oxygen, while (-C) is a free carbon active site. The
 30 presence of CO has been shown to promote the reduction of NO, presumably by homogeneous reaction
 31 with NO catalysed by char, demonstrated by the non-elementary R6.

32

33 The reaction mechanism involves both catalytic and non-catalytic reaction steps. It indicates that larger
 34 contents of surface nitrogen and catalytic inorganic element would lead to a higher NO reduction
 35 reactivity. Waste fuels often have both high nitrogen and inorganic element content in the unreacted char.
 36 Consequently, these chars could be expected to be very reactive towards NO reduction; however, this has
 37 to the knowledge of the authors not been examined.

38 The objective of the present work is to investigate the reduction of NO over sewage sludge, refuse
 39 derived fuel (RDF), and straw chars. The chars of raw and demineralized fuels were prepared in a
 40 horizontal oven and subsequently subjected to surface property and chemical composition
 41 characterization. NO reduction experiments were performed in a fixed bed reactor to investigate the
 42 reactivity of different chars towards NO. Based on the experiments, simple rate expressions that are
 43 applicable in large-scale simulations were provided for modelling the NO-char reduction reaction in
 44 combustion. Apart from providing an improved fundamental understanding of the char nitrogen to NO
 45 conversion and char-NO reduction reaction, the outcome of this study may facilitate the use of chars in
 46 NO reduction from boilers.

47

48 **2 Experimental**

49 2.1 Fuels and their demineralization

50 Two waste based fuels, sewage sludge (SSL) and RDF, and one biomass, straw (S), were investigated.
 51 A previously reported demineralization method [13,14] was adopted in this study. The fuels were ground
 52 and sieved to a size fraction of 212-1000 μm and subsequently suspended in 500 mL HNO_3 (Sigma
 53 Aldrich, CAS number: 7697-37-2) solution at a pH value of 2 and heated to 60°C. In the sewage sludge
 54 extraction, the pH increased significantly, wherefore HNO_3 was intermittently added to maintain a pH of

55 2. The leaching was performed for one hour at 60°C under stirring at 750 rpm. After one hour, the liquid
56 was removed, and the process repeated. Then, the demineralized fuels were filtered with 250 mL deionized
57 water until the permeate pH was approximately 6.0. The obtained demineralized fuels were dried at 105°C
58 for one day. Notably, RDF was not demineralized due to the limited amount of available sample.

59 2.2 Char preparation

60 Chars from raw and demineralized fuels were produced in a horizontal oven at 800°C under a N₂ flow
61 of 2.5 NL/min. The oven was preheated to 800°C, after which approximately 15 g of sample was rapidly
62 pushed into the oven and pyrolyzed for 10 minutes. Following this, the sample was quickly moved to a
63 water cooled section to ensure prompt cooling to a temperature of ~150°C. Then, the sample was
64 withdrawn from the reactor and collected. The char yield was determined from the initial and final sample
65 mass.

66 2.3 Fixed bed reactor combustion and NO reduction

67 Figure 1 presents the quartz fixed bed reactor used for combustion and NO reduction experiments. Three
68 independent heating elements ensured a uniform temperature in the reactor. A thermocouple, located 0.5
69 cm below the porous plate, measured the reaction temperature. A solid feeding device allowed the
70 admission of samples at the desired temperature and gas phase composition in the reactor. In the
71 experiments, 1.75 g quartz sand pre-treated at 800°C with a size of 250-355 µm was added together with
72 the char samples to ensure plug flow through the bed and facilitate the sample admission. Blank tests
73 revealed that the thermally treated sand exhibited no reactivity towards NO reduction. Reduction
74 experiments were carried out at three NO inlet concentrations [400,800,1500 ppmv] and temperatures
75 [800,850,900°C] using 20-50 mg char with a size of 125-180 µm to minimize mass transfer limitations
76 and avoid issues in feeding fine particles. To extract kinetic information, the mass of sewage sludge and
77 RDF char was reduced to avoid complete conversion of NO to N₂. Additional combustion experiments
78 using 20 mg, 125-180 µm char were carried out at 800°C in 10% O₂. The total volumetric flow rate was
79 1 NL/min in both combustion and NO reduction experiments, with the balance being made up by N₂.

80 Moreover, the composition of the dry flue gas was continuously monitored by a series of on-line gas
 81 analysers (NGA2000, Fischer-Rosemount); CO and CO₂ were measured by infrared-absorption, O₂ by a
 82 paramagnetic detector, and NO by an ultraviolet analyser. In addition, the nitrogen combustion product
 83 distribution was determined by a Fourier Transform Infrared Spectrometer (FTIR) (Multigas 2030 FTIR,
 84 MKS instruments).

85
 86 **Figure 1:** Schematic illustration of the fixed bed reactor.

87 A typical plot of the NO concentration versus time, depicting the complete steps in the reduction
 88 experiments, is shown in Figure 2. Each experiment involved four steps (S1-S4), NO signal stabilization
 89 (S1), char introduction and NO reduction (S2), NO cutoff and residual char combustion in 10vol% O₂
 90 forming a NO concentration peak (S3), and NO signal stabilization (S4). The experiment was stopped

91 when the NO concentration in S4 equaled that in S1. Little to no reduction of NO was observed over pure
92 fuel ash.

93
94 **Figure 2:** Example of a NO versus time curve, illustrating the steps during a reduction experiment. S1:
95 stabilization of the NO signal, S2: introduction of char and NO reduction commences, S3: NO feeding is
96 stopped, and 10vol% O₂ is introduced to burn residual char, and S4: stabilization of NO signal. The
97 reduction was carried out at 800°C with an inlet concentration of 400 ppm NO using straw char.

98 The influence of external and internal mass transfer limitations were assessed based on the Maer and
99 Weisz-Prater criteria [15], respectively. The results are provided in the supplemental material (Table S1)
100 for the most reactive chars, sewage sludge and RDF. These indicate that the kinetics play a dominant role;
101 hence, mass transport limitations were neglected in the estimation of kinetic parameters.

102 2.4 Physiochemical fuel and char properties

103 The specific BET surface area and the mesoporosity (BJH) of the chars were determined from N₂
104 adsorption at its boiling point (77 K) in the p/p₀ range of 0.01-0.99. The carbon, hydrogen, nitrogen, and
105 sulphur content, and inorganic element concentration of the raw fuels and chars were determined by
106 standard CHNS and inductively coupled plasma emission spectroscopy (ICP-OES), respectively.

107 Table 1 displays selected properties of the raw fuels. The complete ICP-OES results for the raw fuels
108 and chars can be found in the supplemental material (Table S2).

Table 1: Properties of the raw fuels.

	[wt% d.b.]					[mg/kg d.b.]					
Fuel	C	H	N	S	Ash	K	P	Mg	Ca	Fe	Na
S	46.9	6.0	0.56	0.12	4.2	14000	910	960	2300	41	230
SSL	29.0	3.8	3.80	0.96	50.2	6300	34000	4300	37000	85000	2400
RDF	48.7	6.6	1.16	0.28	16.4	1600	760	4440	37300	454	2000

110

111 Table 2 summarizes the ultimate analysis, char yield, and selected ash composition of the chars. The
 112 char yields of the demineralized fuels were lower than those of the raw fuels, as expected. Due to the large
 113 ash content, the waste chars contained a significantly lower carbon content in comparison with that of the
 114 biomass chars. Demineralization halved the ash content of the straw char, while only a small decrease was
 115 observed for sewage sludge char. Demineralization of sewage sludge removed a significant amount of
 116 calcium and to a lesser extent potassium and iron. Although dependent on the chemical association,
 117 previous studies have elucidated the catalytic importance of these elements and additionally that of sodium
 118 and magnesium in the NO-char reaction [16]. In this study, the major catalytic elements are expected to
 119 be potassium, calcium and iron.

120

Table 2: Elemental and proximate analysis of the chars

	[wt% d.b.]						[mg/kg d.b.]					
Char	C	H	N	S	Ash	Char Yield	K	P	Mg	Ca	Fe	Na
S	72.38	1.42	0.45	0.029	18.7	25.8	43642	2789	2329	4459	<3	740
SSL	17.91	0.52	1.37	0.188	79.4	56.7	5803	16708	6745	61579	39697	1485
RDF	39.91	1.21	1.21	0.728	56.7	31.2	4314	1673	9778	95688	9675	5880
DM S	82.15	1.53	0.83	0.032	8.4	16.9	530	727	<0.2	283	<3	<120

DM SSL	22.28	0.56	1.99	0.107	76.8	56.5	3090	10614	4175	5698	33059	603
-----------	-------	------	------	-------	------	------	------	-------	------	------	-------	-----

Table 3 shows the BET surface area, pore volume, and mean pore diameter of the chars. The demineralized and raw sewage sludge char surface areas were similar, while the RDF and straw chars displayed lower values. In comparison, demineralized straw char exhibited a high surface area and consequently pore volume; however, the volume and surface area mainly stem from micro- and some mesopores, leading to small pore diameters. Although some disagreement exists, it is widely accepted that surface area and pore structure play an important role in the NO reduction reaction [11]. While it has been difficult to correlate the NO-char reaction rate with BET areas, incorporating the surface area associated with macro- and some mesopores (<20nm by mercury porosimetry) yielded a better basis [6].

Table 3: BET surface area (SA), pore volume (V_p), and mean pore diameter ($d_{p,mean}$) of the chars. Note, demineralized straw char contained both micro- and mesopores.

Char	SA [m ² /g]	V_p [cm ³ /g]	$d_{p,mean}$ [nm]
S	25.1	$2.4 \cdot 10^{-2}$	3.404
SSL	66.0	$9.0 \cdot 10^{-2}$	4.856
RDF	43.2	$7.1 \cdot 10^{-2}$	3.385
DM S	429.5	0.18	1.932/3.382
DM SSL	55.8	$7.2 \cdot 10^{-2}$	4.852

3 Kinetics of NO reduction

The reactivity of solid fuel chars towards NO is commonly evaluated from globalized first order rate expressions [17–20], where the reaction rate is frequently based on the mass of carbon in the char. Globalized rates are useful in Computational Fluid Dynamic (CFD) simulations [21], since more detailed schemes require extensive computational requirements. The kinetic data for the NO-char reaction can be

138 obtained from fixed bed reactor experiments under the assumption of plug flow in quasi steady state. The
 139 integral form of the design equation is shown in Eq. 1 for a first order rate expression.

$$140 \quad -\ln(1 - X_{\text{NO}}) = k_{\text{NO}} \cdot W/V_g \quad \text{Eq. 1}$$

141 Here, X_{NO} (-) is the conversion of NO, k_{NO} ($\text{m}^3_{\text{gas}} \text{s}^{-1} \text{kg-C}^{-1}$) is the carbon mass based first order rate
 142 constant, W (kg-C) is the instantaneous carbon mass in the bed, and V_g ($\text{m}^3_{\text{gas}}/\text{s}$) is the volumetric gas
 143 flowrate. The instantaneous carbon mass was determined from the CO and CO₂ measurements during NO
 144 reduction experiments.

145 The conversion of char nitrogen to NO in fixed bed char combustion was investigated using a one-
 146 dimensional, transient, heterogeneous reactor model followed by a one-parameter description of the flue
 147 gas mixing in the downstream process using n stirred tank reactors in series. The residence time
 148 distribution methodology and results are demonstrated in the supplemental material (Figure S1 and Table
 149 S3). The main nitrogen products of char nitrogen oxidation are NO, N₂, HCN, and N₂O [6]. Based on
 150 FTIR measurements, the nitrogen combustion products by direct char oxidation were assumed to be NO
 151 with a fraction f_{NO} and N₂O with a fraction $f_{\text{N}_2\text{O}}$, while N₂ was formed by the reduction of NO over char.
 152 The reduction of N₂O to N₂ over char was not examined in this work. The conservation equation for the
 153 gas and solid phase in the packed bed reactor are shown in Eq. 2 and 3, respectively [22], along with the
 154 initial and boundary conditions.

$$155 \quad \frac{dC_{\text{char}}}{dt} = -\epsilon R_C \quad \text{Eq. 2}$$

$$156 \quad \frac{\delta C_i}{\delta t} = D_{\text{ax}} \frac{\delta^2 C_i}{\delta x^2} - u_{\text{int}} \frac{\delta C_i}{\delta x} - R_C \quad \text{Eq. 3}$$

$$157 \quad C(t = 0) = C_0 \text{ where } C_0 = \begin{bmatrix} C_{\text{O}_2,0} = 1.11 \frac{\text{mol}}{\text{m}^3_{\text{gas}}} \\ C_{\text{CO}_2,0} = 0 \frac{\text{mol}}{\text{m}^3_{\text{gas}}} \\ C_{\text{CO},0} = 0 \frac{\text{mol}}{\text{m}^3_{\text{gas}}} \\ C_{\text{NO},0} = 0 \frac{\text{mol}}{\text{m}^3_{\text{gas}}} \end{bmatrix}$$

$$158 \quad C(x = 0) = C_0$$

$$dC(x = h_{\text{react}}) = 0$$

Here, C_{char} (mol/m³_{reactor}) is the molar concentration of carbon in the reactor, C_i (mol/m³_{gas}) is the concentration of gas component i ($i=\text{CO}, \text{CO}_2, \text{O}_2, \text{NO}$), t (s) is the time, x (m) is the coordinate along the bed, ϵ (-) is the bed porosity, D_{ax} (m²/s) is the axial dispersion coefficient, determined from the Gunn correlation [23], u_{int} (m/s) is the interstitial gas velocity, and R_C (mol/m³_{gas}/s) is the char oxidation rate.

The energy conservation equation and initial conditions for the solid phase is shown in Eq. 4. As the char constitutes 1% of the bed material, the energy equation was based on the silica sand. Hence, it is assumed that the temperature of the char equals that of the sand at any given time. Moreover, due to the heating elements around the reactor, the temperature of the gas phase was assumed to be constant. This assumption was validated by the thermocouple below the bed, showing a discrepancy of $\pm 7^\circ\text{C}$. The energy equation includes effects from conductivity, convection, and char combustion. Radiation was neglected as the influence of this on the overall heat transfer was estimated to be around 10%.

$$C_{\text{sand}} C_{p,\text{sand}} \frac{\delta T_{\text{sand}}}{\delta t} = k_{\text{eff}} \frac{\delta T_{\text{sand}}^2}{\delta x^2} + h S (T_{\text{gas}} - T_{\text{sand}}) + \epsilon \Delta H_R R_C \quad \text{Eq. 4}$$

$$T_{\text{sand}}(t = 0) = T_0 \text{ where } T_0 = 298 \text{ K}$$

$$T_{\text{sand}}(x = 0) = T_{f0} \text{ where } T_{f0} = 1073 \text{ K}$$

$$dT_{\text{sand}}(x = h_{\text{react}}) = 0$$

Here, C_{sand} (mol/m³_{reactor}) is the molar concentration of sand in the reactor, C_p (kJ/mol/K) is the specific heat capacity of sand, T_{sand} (K) is the sand temperature, k_{eff} (kJ/m/s/K) is the effective thermal conductivity determined from [24], h (kJ/m²/s/K) is the gas-solid heat transfer coefficient, S (m²/m³) is the volumetric solid surface area, and ΔH_R is the enthalpy of reaction between O_2 and char to form CO (-110.5 kJ/mol) and CO_2 (-396.6 kJ/mol). The fraction of CO_2 formed from char combustion was determined from the experimentally obtained concentration profiles. For straw, sewage sludge, and RDF chars, this parameter was set at 0.99, 0.95, and 0.97, respectively.

The char combustion rate was simplified to an expression first order in oxygen and char concentration, Eq. 5. The formation of NO was assumed proportional to the char combustion rate, Eq. 6, while the

184 reduction was determined from the experimentally obtained rate constant, Eq. 7. The net formation of NO
 185 was thereby calculated by the difference in formation and reduction, Eq. 8.

$$186 \quad R_C = k \cdot C_{\text{Char}} \cdot C_{\text{O}_2}, \text{ where } k = A_C \cdot \exp(-E_{a,C}/R/T) [=] \frac{\text{m}^3_{\text{reactor}}}{\text{mol s}} \quad \text{Eq. 5}$$

$$187 \quad R_{\text{NO,formed}} = f_{\text{NO}} \frac{x_{\text{N}}}{x_{\text{C}}} R_C [=] \frac{\text{mol}}{\text{m}^3_{\text{gas}} \text{ s}} \quad \text{Eq. 6}$$

$$188 \quad R_{\text{NO,reduced}} = k_{\text{R,NO}} C_{\text{Char}} C_{\text{NO}} [=] \frac{\text{mol}}{\text{m}^3_{\text{gas}} \text{ s}} \quad \text{Eq. 7}$$

$$189 \quad R_{\text{NO.net}} = R_{\text{NO,formed}} - R_{\text{NO,reduced}} \quad \text{Eq. 8}$$

190 To describe the dispersion downstream to the reactor, n stirred tank reactors in series were assumed.
 191 The number of reactors in series was determined from residence time distribution measurements. For each
 192 tank, the mass conservation equation assuming no reaction is shown in Eq. 9.

$$193 \quad \frac{dC_i}{dt} = \frac{1}{\tau} (C_{i,\text{in}} - C_{i,\text{out}}) \quad \text{Eq. 9}$$

194 Here, τ denotes the residence time in one tank. The coupled differential equations were solved by
 195 discretizing in space using a central finite difference approximation followed by the solution of the
 196 coupled ordinary differential equations using a stiff ODE solver in MatLab. Figure 3 illustrates the steps
 197 in the combustion model. The values of the combustion parameters A_C and $E_{a,C}$ were fitted the
 198 experimentally obtained CO_2 and O_2 curves using a Maximum Likelihood Estimate (MLE) function
 199 following the previous work of Sin and Gernaey [25]. Subsequently, the NO and CO profiles were
 200 calculated based on the char combustion kinetics. The experimentally obtained reduction rate constant
 201 was used to describe the reduction of NO over char.

202
 203 **Figure 3:** Schematic representation of the combustion model.

204 Since the optimization problem is non-convex, the MLE function depends on the starting values of the
 205 parameters to be optimized. The initial guess of the parameters were based on the previous study of
 206 Karlström et al. [26]. In the case of sewage sludge char combustion, a strong correlation was noted
 207 between the two kinetic parameters. This resulted in a large standard deviation, causing the lower limit of
 208 the pre-exponential factor to be negative, i.e. non-unique estimate of this parameters. Consequently, the
 209 activation energy was specified as a parameter and only the pre-exponential factor was fit to the data. To
 210 get a unique estimate of the activation energy and pre-exponential factor, additional experiments must be
 211 planned, e.g. combustion at different temperatures. An example of concentration plots from combustion
 212 modelling is illustrated in the supplemental material (Figure S2).

$$\begin{array}{ll}
 213 & A_{\text{initial}} = 100 \frac{\text{m}^3_{\text{react}}}{\text{mol s}} \qquad E_{\text{a,initial}} = 50\text{-}60 \text{ kJ/mol}
 \end{array}$$

4 Results and Discussion

4.1 Reduction of NO over char

Figure 4a illustrates the conversion of 400 ppmv NO over 50 mg char at 800°C, while Figure 4b depicts the corresponding transient first order rate constant of the chars. The results in Figure 4a demonstrate that an almost complete reduction of NO was achieved for the raw sewage sludge and RDF chars, while the straw char showed a somewhat lower reduction of NO. The NO reduction was lower for the demineralized fuel chars as compared to the raw fuel chars. The results of Figure 4b indicate that the reactivities of the waste chars were significantly higher than those of the straw char. The NO reduction rate of the sewage sludge char was approximately 12 times that of the straw char, while the RDF char exhibited half the reactivity of the sewage sludge char and six times that of the straw char. From Table 2, it is observed that the straw char contained the highest amount of potassium, which is likely to be the most active element in catalyzing NO reduction [8]. In comparison, the waste based chars exhibited a larger content of iron, calcium, and sodium, all of which may catalyze the NO reduction and thereby compensate for the lower potassium content compared to straw char. In addition, although the conversion of NO of the demineralized sewage sludge char was lower than that of straw char in Figure 4a, it is suggested based on Figure 4b that the carbon in the former is more reactive than the latter, probably due to the larger content of iron. The demineralized straw char, showing the highest surface area and pore volume among the chars, displayed the lowest reactivity, as very small amounts of catalytic elements were present in the structure. Moreover, this char exhibited the lowest average pore diameter, which could be an additional contributing factor for the low reactivity. In several chars, a transient kinetic behavior followed by a steady state reduction rate was observed, similar to the observations of Garijo et al. [27,28] and Zhao et al. [29]. This behavior is further discussed in the following sections. The repeatability of the experimental results was examined, showing a relative standard error of maximum 4%, as seen in the supplemental material (Figure S3).

Figure 4: Conversion of NO (X_{NO}) (50 mg char) (a) and first order carbon mass based reaction rate constant (k_{NO}) for the NO reduction (b) versus reaction time for the five different chars at 800°C using an inlet NO concentration of 400 ppmv NO.

4.2 Effect of ash forming elements on reactivity

Figure 5 presents the maximum rate constant at 800°C and 400 ppmv NO as a function of the molar ratio of (Fe+Ca+K)/C (a) and the BET surface area (b) in the unreacted chars. Iron, calcium, and potassium may influence the catalytic activity through different pathways. However, for simplicity, the catalytic term was defined as the molar ratio (Fe+Ca+K)/C. The maximum rate constant was chosen to describe the initial reactivity, since the preliminary increase in reactivity was attributed to particle heating and NO accumulation, and therefore negligible deactivation was assumed prior to this point. The initial rate constant has typically been used in modelling of NO in fast char combustion [6]. The results indicate that the initial reactivity is proportional to the molar ratio of (Fe+Ca+K)/C in the unreacted chars. A higher content of calcium, iron, and potassium would conceivably enhance R7 and R8, thereby facilitating the NO reduction. Given the variable chemical and physical properties of the waste based fuels, this observation provides a method of classifying the fuel chars in terms of their reactivity towards NO. Although the mass ratio could be used as a basis to describe the reactivity prior to deactivation of the chars, the long-term reactivity cannot purely be based on this due to the complicated transient char

structure change and ash transformation. Moreover, there appears to be no direct correlation between the surface area and reactivity even when neglecting DM straw, presumably due to the significant effect of ash forming elements and narrow surface area sample size [11].

Figure 5: Maximum first order reaction rate constant ($k_{NO,max}$) of the examined chars against the initial concentration of iron, calcium, and potassium expressed in mol element per mol carbon (a) and the BET surface area. (b) The rate constant was determined from reduction experimentation at 800°C and 400 ppmv NO.

4.3 Influence of temperature and NO inlet concentration

Figure 6 depicts $k_{NO,max}$ against $1/T$ at varying NO inlet concentrations for sewage sludge and RDF chars. In agreement with previous studies, the reactivity increased with temperature [30]. The results show that the rate constant depends on the NO inlet concentration, thereby indicating a fractional dependence on the NO concentration. However, a reliable estimate of the reaction order and rate constant could not be made using a global fractional order rate expression, as the reaction order was strongly dependent on the temperature and carbon conversion. More complex models are necessary to fully describe the char reactivity, as discussed further in the following sections. However, for simplicity and as a first attempt to provide a rate expression for NO reaction with sewage sludge/RDF char in large-scale simulations, e.g. in CFD modelling [21], concentration averaged rate constants were derived using the results shown in Figure

274 6. For the averaged $k_{\text{NO,max}}$, the recommended kinetic parameters to be used for modelling purposes are
 275 summarized in Table 4.

276
 277 **Figure 6:** Arrhenius plot of the maximum carbon mass based reaction rate constant ($k_{\text{NO,max}}$) for NO
 278 reduction over RDF and sewage sludge chars at varying NO inlet concentrations. The symbols in black
 279 and grey refer to sewage sludge and RDF chars, respectively, while the dotted lines represent the averaged
 280 rate constants.

281 **Table 4:** Pre-exponential factor A ($\text{m}^3 \text{kgC}^{-1} \text{s}^{-1}$) and activation energy E_a (kJ/mol) for reduction of NO
 282 over char.

Char	A	E_a
Straw	$3.91 \cdot 10^7$	145
Sewage sludge	$1.39 \cdot 10^8$	133
Refuse derived fuel	$1.35 \cdot 10^8$	141

283
 284 4.4 Formation and reduction of NO in char combustion

285 The form of the char nitrogen combustion product distribution, determined by FTIR, is illustrated in
 286 Figure 7. As it was not possible to measure N_2 and HCN, these were calculated as a rest fraction based on
 287 the material balance. The presence of HCN during char combustion has previously been reported [31,32].

288 However, unless radical quenching compounds such as iodine are added, the amount is often small in a
 289 combustion atmosphere [33]. Consequently, the rest fraction was presumed to consist mainly of N₂. The
 290 results show that the majority of the emitted nitrogen was in the form of NO and N₂ with a smaller quantity
 291 of N₂O. In addition, no significant amounts of NH₃, HNCO, and NO₂ were detected. It has previously
 292 been suggested that the fractional conversion of char nitrogen to N₂O increased with the char nitrogen
 293 content or the NO concentration [34]. In agreement with this, the straw, RDF, and sewage sludge chars
 294 exhibited a fractional conversion to N₂O of 1%, 2%, and 7%, respectively. The formation mechanisms of
 295 N₂O during char combustion were suggested to be by direct char nitrogen oxidation (R1 and R10),
 296 reaction between char nitrogen and NO (R11, reverse R2 and R10, or direct reaction between NO and (-
 297 CN) [35]), or release and subsequent homogeneous oxidation of HCN. In general, the reaction between (-
 298 CN) and NO can be disregarded [6], since no N₂O was detected without the presence of oxygen [36–38].
 299 This was additionally verified in this study, where the products of NO reduction over char were
 300 investigated using FTIR, showing that no significant amounts of N₂O, HNCO, NH₃, and NO₂ were
 301 formed. The relative importance of the homogeneous and heterogeneous mechanisms of N₂O formation
 302 is as of yet unknown [32]. In the combustion model, N₂O was presumed to form primarily by direct
 303 oxidation of char nitrogen, with a fractional conversion f_{N_2O} equal to that measured by FTIR. This would
 304 lead to an overestimation of the actual NO fractional conversion f_{NO} , as N₂O is believed to decompose
 305 over the char at an even faster rate than NO reduction [39].

306

Figure 7: Nitrogen product distribution from char combustion at 800°C in 10% O₂. NH₃, HNCO, and NO₂ were not detected in significant quantities and therefore not shown here.

Figure 8 presents the experimental and modelled NO combustion selectivity (a) and concentration profiles (b) from fixed bed char combustion at 800°C in 10 vol% O₂. Although the nitrogen content in the RDF and sewage sludge chars were higher than in straw char, the experimental selectivity to form NO was lower. The concentration averaged $k_{NO,max}$ were used in the computations since the time for complete combustion of the chars was short, i.e., 20-30 s. A reasonable prediction of the conversion of char nitrogen to NO was achieved for the straw and RDF chars, while the conversion of sewage sludge char nitrogen to NO was slightly overestimated. This was additionally reflected in the concentration plots, wherein the qualitative trend of the data was well described with minor quantitative differences. In the case of sewage sludge and RDF, a slight overestimation of the NO release near the maximum was observed. As the formation of by-products were not the cause between model and experiment, the discrepancies were apparently a consequence of NO reduction by CO over char and ash (R4) [40] or reactivity enhancement by the presence of O₂ [29]. In addition to this, the experimental release of NO in RDF char was higher than predicted at later stages in the combustion. This could be caused by the assumption that the NO formation is proportional to the carbon burnout. Although, this is a common simplification in several char-NO modelling studies [30,41,42], the proportionality between the rates for coal chars is not always

325 prominent [6], especially at temperatures around 600°C [32]. For the purposes of this study, the simplified
 326 combustion model provided reasonable predictions of the NO concentration profile and the conversion of
 327 char nitrogen to NO during combustion of straw and RDF chars. For the sewage sludge chars, the
 328 reduction rate constant was two times lower in an inert atmosphere, as compared to the combustion
 329 atmosphere. The results here indicate that the averaged rate constants could be useful in predicting the
 330 reactivity of the raw chars towards NO, and therefore potentially be implemented in large-scale
 331 simulations. However, it should be taken into consideration that the results provided here are based on a
 332 limited range of operating conditions as well as on several assumptions, which would require further
 333 evaluation. Some of these are discussed in the following section.

334
 335 **Figure 8:** Experimental and predicted NO selectivity (a) and concentration profiles (b) from the
 336 combustion raw chars at 800°C in 10vol% O₂. The error bars depict the repeatability of the experiments.
 337 The predictions were made using a concentration averaged first order reaction rate in the combustion
 338 model presented in Eq. 2-9.

339 4.5 Assessment of the rate expression

340 Figure 9 illustrates the first order rate constant against the reaction time (a) and carbon conversion (b)
 341 for sewage sludge, RDF, and straw chars. Unless otherwise stated in the legend, the data are extracted
 342 from the 900°C and 1500 ppmv NO experiments. In Figure 9a, all chars exhibited a maximum reactivity

343 followed by a steady decline, the slope of which differed depending on temperature and NO inlet
 344 concentration. It became obvious that the reactivity decrease was not caused by carbon depletion, as
 345 illustrated in Figure 9b. Possible explanations for the declining reactivity are deactivation due to a long
 346 char residence time, formation of thermally stable oxides, and change in carbon active sites [6,27]. As
 347 thermal annealing is expectedly of smaller importance at the investigated temperatures, the dominating
 348 deactivation mechanism from long char residence times may be caused by transformation of catalytic ash
 349 species, e.g. evaporation of potassium or formation of possibly less-catalytic silicates of calcium and iron.
 350 Additionally, the production of surface complexes could lead to a blockage of the pores or active sites,
 351 thereby inhibiting reactions R8 and R9, wherein the catalytic site is regenerated and a new carbon site is
 352 formed. Further, the internal surface area may increase or decrease during carbon conversion, thus
 353 influencing the availability and number of active sites for NO reduction. To capture the effects of NO
 354 concentration and carbon conversion, fractional order and Random Pore Model (RPM) [43] rate
 355 expressions were employed; however, none of these yielded obvious advantages in comparison with the
 356 simple first order equation, as seen in the supplemental material (Figure S4). In future work, a more
 357 thorough understanding of the deactivation mechanism, i.e. change in surface structure and ash forming
 358 element content, as a function of time and carbon conversion is needed to describe the reduction reactivity
 359 of waste chars.

360

361 **Figure 9:** First order carbon mass based rate constant (k_{NO}) versus time on stream (a) and carbon
 362 conversion (b) at 900°C and 1500 ppmv NO. Additional data for sewage sludge from 900°C and 800
 363 ppmv NO, and 800°C and 1500 ppmv NO.

364 4.6 Comparison of reactivity with literature data

365 Figure 10 compares the obtained reaction rates with selected literature values. The results indicate that
 366 the waste chars in general exhibited a higher reactivity than biomass chars and significantly higher than
 367 the rate constant recommended by Levy et al. [17] for coal char, the default choice for char + NO in
 368 ANSYS Fluent 18.0. Although the chars employed in this study were to some extent deactivated by the
 369 pyrolysis in the horizontal oven, the obtained rate of sewage sludge char was higher than and the RDF
 370 char comparable to that of bark and straw char reported by Zhao et al. [29], wherein the pyrolysis time
 371 was minimized and oxygen was introduced to enhance the kinetics. Similarly, the reactivity of the waste
 372 chars exceeded the rates reported by Garijo et al. [27], who performed in-situ pyrolysis to minimize the
 373 thermal deactivation.

374 The results of the present study provide an indication of the potential utilization of waste char in the
 375 reduction of NO in thermal conversion processes. This could possibly be by primary measures if the fuel
 376 and air feeding is controlled in such a way that the more reactive chars are present at reducing conditions
 377 within the boiler or through secondary techniques, if the char is employed subsequent to the combustion
 378 chamber, e.g. char bed or direct injection to the cyclone.

379

Figure 10: Comparison of carbon mass based reaction rates (R_{NO}) obtained in this work with that from other studies. The assumed properties and conditions were 100 m²/g, 1.2 atm and NO inlet concentration of 500 ppmv.

Additionally, the obtained averaged first order kinetic data can be used in modelling studies to evaluate pollutant formation from waste combustion, where interaction between waste char and NO is expected to be prominent, i.e. in fluidized bed combustors.

5 Conclusions

The reactivities of sewage sludge, refuse derived fuel (RDF), and straw chars towards NO were investigated in a fixed bed reactor at temperatures between 800 and 900°C using NO inlet concentrations from 400 to 1500 ppmv. On a carbon mass basis, the reactivities of sewage sludge and RDF chars were one order of magnitude and six-fold higher than that of straw char, respectively. A demineralization study indicated that the high reactivity could be attributed primarily to the high content of calcium and iron in the waste chars. The initial reactivities correlated well with the (Ca+K+Fe)/C ratio of the unreacted chars, implying that calcium, potassium, and iron played an important role in char reactivity towards NO.

During combustion of straw, RDF, and sewage sludge chars at 800°C in 10% O₂ in the fixed bed reactor, the char nitrogen was primarily converted to NO and N₂, and to a lesser extent N₂O (<7%). A mathematical model based on a first order reaction rate expression for NO reduction over char was able to provide a reasonable prediction of the conversion of char nitrogen to NO in the combustion experiments.

The high reactivity of waste chars towards NO indicates a potential utilization of the chars in the reduction of NO emission from combustion systems. Moreover, the simplified, concentration averaged, first order rate expression for NO reduction over straw, RDF, and sewage sludge chars can be implemented in large scale simulations of combustion plants.

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408 **Supplemental material:** Supplemental material – Reactivity of sewage sludge, RDF, and straw chars
409 towards NO.docx

410 **Table S1:** Investigation of the influence of external and internal mass transfer limitations regarding the
411 NO reduction reactions. $-r_{obs} = \frac{1}{W} F_{NO,in} X_{NO}$, Maer's criterion $\phi_{Maer} = \frac{-r_{obs} \rho_C R_C}{k_g C_{NO,0}} < 0.15$, relative
412 mass transfer resistance $Rel_{ext} = \frac{d_C/(6k_g)}{1/(k_{obs}\rho_C)}$, Weisz Prater modulus and criterion $\phi_{WP} = \frac{-r_{obs} \rho_C R_C^2}{k_g C_{NO,0}} \ll 1$,
413 Thiele modulus: $\phi = \frac{d_C}{6} \cdot \left(\frac{k \cdot \rho_C}{D_{eff}} \right)^{\frac{1}{2}}$, and effectiveness factor: $\eta = \frac{3 \cdot \phi \cdot \coth(3 \cdot \phi) - 1}{3 \cdot \phi^2}$ [S1,S3] Symbols: W is the
414 instantaneous mass of carbon, $F_{NO,in}$ inlet molar flow of NO, X_{NO} conversion of NO at given W, ρ_C is
415 the char density, d_C and R_C are char diameter and radius, respectively, k_g gas film mass transfer constant,
416 k is the first order reaction rate constant, D_{eff} is the effective diffusivity.

417 **Table S2:** Complete ICP-OES of fuels and chars

418 **Table S3.** Mean residence time (t_m) and number of ideal reactors n_{CSTR} for each compound.

419 **Figure S1:** Schematic showing the input of tracer to determine the dispersion subsequent to the packed
420 bed reactor (a), residence time distribution plots for CO, CO₂, O₂ (b), and NO (c). Repetitions are shown
421 in the distribution plot of NO.

422 **Figure S2:** O₂, CO₂, CO, and NO concentration profiles from combustion of 20 mg RDF char at 800°C
423 in 10 vol% O₂. The combustion kinetic parameters were fit to the CO₂ and O₂ profiles, while the CO was
424 calculated based on a CO₂ fraction of 0.97 based on experimental data. The NO concentration plot was
425 calculated from the combustion kinetic parameters and the experimentally obtained reduction rate
426 constant.

427 **Figure S3:** Repeatability investigation of the NO reduction over char at 800°C using an NO inlet
428 concentration of 400 ppmv NO. The subscripts denote the repetition number.

429 **Figure S4:** Comparison of the predicted NO versus observed NO conversion for sewage sludge and RDF
430 chars at 900°C at varying NO inlet concentrations using first order ($n=1$), fractional order ($n=[0;1]$), and

431 random pore model (RPM) rate expressions. For the first order expression the concentration average of
432 the maximum first order rate constant ($k_{\max}$) was used. For the fractional order and RPM expressions, a
433 Maximum Likelihood function was used to minimize the squared sum error between model and
434 experiment at three different concentrations simultaneously.

435 **References**

- 436 [1] Seeker WR. Waste Combustion. *Proc Combust Inst* 1990;23:867–85.
- 437 [2] Hupa M, Karlström O, Vainio E. Biomass combustion technology development - It is all about
438 chemical details. *Proc Combust Inst* 2017;36:113–34. doi:10.1016/j.proci.2016.06.152.
- 439 [3] Frank A, Castaldi MJ. CFD analysis of municipal solid waste combustion using detailed chemical
440 kinetic modelling. *Waste Manag Res* 2014;32:745–54. doi:10.1177/0734242X14538305.
- 441 [4] Rogaume T, Auzanneau M, Jabouille F, Goudeau JC, Torero JL. The effects of different airflows
442 on the formation of pollutants during waste incineration. *Fuel* 2002;81:2277–88.
443 doi:10.1016/S0016-2361(02)00151-5.
- 444 [5] Rogaume T, Jabouille F, Torero JL. Effect of excess air on grate combustion of solid wastes and
445 on gaseous products. *Int J Therm Sci* 2009;48:165–73. doi:10.1016/j.ijthermalsci.2008.02.003.
- 446 [6] Glarborg P, Jensen AD, Johnsson JE. Fuel nitrogen conversion in solid fuel fired systems. *Prog*
447 *Energy Combust Sci* 29 2003;29:89–113. doi:10.1016/S0360-1285(02)00031-X.
- 448 [7] Glarborg P, Miller JA, Ruscic B, Klippenstein SJ. Modelling nitrogen chemistry in combustion.
449 *Prog Energy Combust Sci* 2018;67:31–68.
- 450 [8] Wu X, Song Q, Zhao H, Yao Q. Catalytic Mechanism of Inherent Potassium on the Char-NO
451 Reaction. *Energy and Fuels* 2015;29:7566–71. doi:10.1021/acs.energyfuels.5b01550.
- 452 [9] Zhong BJ, Tang H. Catalytic NO reduction at high temperature by de-ashed chars with catalysts.
453 *Combust Flame* 2007;149:234–43. doi:10.1016/j.combustflame.2006.04.004.
- 454 [10] Zhao Z, Li W, Li B. Catalytic reduction of NO by coal chars loaded with Ca and Fe in various
455 atmospheres. *Fuel* 2002;81:1559–64. doi:10.1016/S0016-2361(02)00077-7.

- 456 [11] Calo JM, Suuberg EM, Aarna I. The Role of Surface Area in the NO-Carbon Reaction. *Energy &*
457 *Fuels* 1999;13:761–2.
- 458 [12] Chambrion P, Kyotani T, Tomita A. Role of N-containing surface species on NO reduction by
459 carbon. *Energy & Fuels* 1998;12:416–21.
- 460 [13] Karlström O, Perander M, DeMartini N, Brink A, Hupa M. Role of ash on the NO formation during
461 char oxidation of biomass. *Fuel* 2017;190:274–80. doi:10.1016/j.fuel.2016.11.013.
- 462 [14] Aho A, DeMartini N, Pranovich A, Krogell J, Kumar N, Eränen K, et al. Pyrolysis of pine and
463 gasification of pine chars - Influence of organically bound metals. *Bioresour Technol* 2013;128:22–
464 9. doi:10.1016/j.biortech.2012.10.093.
- 465 [15] Wu SL, Iisa K. Kinetics of NO Reduction by Black Liquor Char. *Energy & Fuels* 1998;12:457–63.
- 466 [16] Wu X, Song Q, Zhao H, Zhang Z, Zhang L, Yao Q. Influence of mineral transformation on the
467 reactivity evolution during rice straw char-NO reaction. *Fuel* 2013;113:553–9.
468 doi:10.1016/j.fuel.2013.05.102.
- 469 [17] Levy JM, Chan LK, Sarofim AF, Beér JM. NO/char reactions at pulverized coal flame conditions.
470 *Symp Combust* 1981;18:111–20. doi:10.1016/S0082-0784(81)80016-1.
- 471 [18] Guo F, Hecker WC. Effects of CaO and burnout on the kinetics of NO reduction by Beulah Zap
472 char. *Symp Combust* 1996;26:2251–7.
- 473 [19] Guo F, Hecker WC. Kinetics of NO reduction by char: Effects of coal rank. *Symp Combust*
474 1998;27:3085–92. doi:10.1016/S0082-0784(98)80170-7.
- 475 [20] Schönenbeck C, Gadiou R, Schwartz D. A kinetic study of the high temperature NO-char reaction.
476 *Fuel* 2004;83:443–50. doi:10.1016/j.fuel.2003.08.007.

- 477 [21] Nikolopoulos A, Malgarinos I, Nikolopoulos N, Grammelis P, Karrelas S, Kakaras E. A decoupled
478 approach for NO_x-N₂O 3-D CFD modeling in CFB plants. Fuel 2014;115:401–15.
479 doi:10.1016/j.fuel.2013.06.036.
- 480 [22] Zhou H, Jensen AD, Glarborg P, Jensen PA, Kavaliauskas A. Numerical modeling of straw
481 combustion in a fixed bed. Fuel 2005;84:389–403. doi:10.1016/j.fuel.2004.09.020.
- 482 [23] Gunn DJ. On axial dispersion in fixed beds. Chem Eng Process 1993;32:333–8. doi:10.1016/0255-
483 2701(93)80020-H.
- 484 [24] Fjellerup J, Henriksen U, Jensen AD, Jensen PA, Glarborg P. Heat transfer in a fixed bed of straw
485 char. Energy and Fuels 2003;17:1251–8. doi:10.1021/ef030036n.
- 486 [25] Sin G, Gernaey K. Data handling and parameter estimation. In: Van Loosdrecht MCM, Nielsen
487 PH, Lopez-Vazquez DM, Brdjanovic D, editors. Exp. Methods Wastewater Treat., London: IWA
488 Publishing; 2016, p. 201–34.
- 489 [26] Karlström O, Brink A, Hupa M, Tognotti L. Multivariable optimization of reaction order and
490 kinetic parameters for high temperature oxidation of 10 bituminous coal chars. Combust Flame
491 2011;158:2056–63. doi:10.1016/j.combustflame.2011.03.003.
- 492 [27] Garijo EG, Jensen AD, Glarborg P. Kinetic Study of NO Reduction over Biomass Char under
493 Dynamic Conditions. Energy & Fuels 2003;17:1429–36.
- 494 [28] Garijo EG, Jensen AD, Glarborg P. Reactivity of coal char in reducing NO. Combust Flame
495 2004;136:249–53. doi:10.1016/j.combustflame.2003.09.007.
- 496 [29] Zhao K, Glarborg P, Jensen AD. NO Reduction over Biomass and Coal Char during Simultaneous
497 Combustion. Energy & Fuels 2013;27:7817–26.
- 498 [30] Karlström O, Brink A, Hupa M. Time dependent production of NO from combustion of large

- 499 biomass char particles. *Fuel* 2013;103:524–32. doi:10.1016/j.fuel.2012.06.030.
- 500 [31] Winter F, Wartha C, Löffler G, Hofbauer H. The NO and N₂O formation mechanism during
 501 devolatilization and char combustion under fluidized-bed conditions. *Symp Combust*
 502 1996;26:3325–34. doi:10.1016/S0082-0784(96)80180-9.
- 503 [32] Molina A, Eddings EG, Pershing DW, Sarofim AF. Char nitrogen conversion: implications to
 504 emissions from coal-fired utility boilers. *Prog Energy Combust Sci* 2000;26:507–31.
- 505 [33] Molina A, Sarofim AF, Ren W, Lu J, Yue G, Beér JM, et al. Effect of boundary layer reactions on
 506 the conversion of CHAR-N to NO, N₂O, and HCN at fluidized-bed combustion conditions.
 507 *Combust Sci Technol* 2002;174:43–71. doi:10.1080/713712945.
- 508 [34] Johnsson JE. Formation and reduction of nitrogen oxides in fluidized-bed combustion. *Fuel*
 509 1994;73:1398–415.
- 510 [35] Chambrion P, Kyotani T, Tomita A. C-NO reaction in the presence of O₂. *Symp Combust*
 511 1998;27:3053–9.
- 512 [36] Sørensen CO, Johnsson JE, Jensen A. Reduction of NO over wheat straw char. *Energy and Fuels*
 513 2001;15:1359–68. doi:10.1021/ef000223a.
- 514 [37] Dong L, Gao S, Song W, Xu G. Experimental study of NO reduction over biomass char. *Fuel*
 515 *Process Technol* 2007;88:707–15. doi:10.1016/j.fuproc.2007.02.005.
- 516 [38] Guerrero M, Millera Á, Alzueta MU, Bilbao R. Experimental and Kinetic Study at High
 517 Temperatures of the NO Reduction over Eucalyptus Char Produced at Different Heating Rates.
 518 *Energy & Fuels* 2011;25:1024–33.
- 519 [39] Johnsson JE, Jensen A. Effective diffusion coefficients in coal chars. *Proc Combust Inst*
 520 2000;28:2353–9. doi:10.1016/S0082-0784(00)80647-5.

- 521 [40] Barišić V, Kilpinen P, Hupa M. Comparison of the catalytic activity of bed materials from the
522 combustion of biomass and waste fuels in a circulating fluidized bed boiler toward NO reduction
523 by CO. *Energy and Fuels* 2006;20:1925–32. doi:10.1021/ef060094j.
- 524 [41] De Soete GG. Heterogeneous N₂O and NO formation from bound nitrogen atoms during coal char
525 combustion. *Symp Combust* 1991;23:1257–64. doi:10.1016/S0082-0784(06)80388-7.
- 526 [42] Jones JM, Patterson PM, Pourkashanian M, Williams a. Approaches to Modelling Heterogenous
527 Char NO Formation/Destruction during Pulverised Coal Combustion. *Carbon N Y* 1999;37:1545–
528 52.
- 529 [43] Bhatia SK, Perlmutter DD. A Rondon Pore Model for Fluid-Solid Reactions:1. Isothermal, Kinetic
530 Control. *AIChE J* 1980;26:379–86.

531