THE ROLE OF FUEL VOLATILES FOR THE EMISSION OF NITROGEN OXIDES FROM FLUIDIZED BED BOILERS— A COMPARISON BETWEEN DESIGNS

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The nitrogen oxides formed during fluidized bed combustion of solid fuels originate from fuel nitrogen in both char and volatiles. In the course of combustion these fuel constituents not only contribute to the production but also take part in the reduction of the emission.

In order to study the role of the nitrogen-containing volatiles for the production and reduction of nitrogen oxides in fluidized bed boilers a series of tests has been carried out with fuels having different contents of volatiles in a range from anthracite to wood in two types of boiler, a circulating and a stationary fluidized bed boiler.

It was found that the different designs of boilers result in different behaviours of the nitrogen-containing volatiles. In stationary fluidized bed boilers the volatiles tend to reduce the emissions of NO comparable to what takes place in a pulverized coal flame, whereas in circulating fluidized bed boilers the volatiles do not have the same beneficial effect. In circulating fluidized bed boilers the emission of NO tends to increase with an increasing content of volatiles in the fuel, whereas the emission decreases from the stationarry fluidized bed type of boiler burning fuels with a larger amount of volatiles.

Introduction

Solid fuel combustion is characterized by the evolution and combustion of fuel volatiles and by combustion of the char residue. The nitrogen oxides formed during combustion in a fluidized bed originate from fuel nitrogen in both char and volatiles. In the course of combustion the nitrogen-containing volatiles may contribute to the reduction of nitrogen oxides. The volatiles not containing nitrogen and combustion products from char in the form of carbon monoxide and hydrogen may also take part in the reduction of nitric oxide by reactions catalyzed by char and other surfaces which are available, especially in the particle bed of a fluidized bed combustor. Furthermore, char itself reacts with nitric oxide to form nitrogen. In summary, char as well as volatiles play decisive roles for the formation and destruction of nitrogen oxides in solid fuel combustors.

This very simplified picture of the origin of the emissions of nitrogen oxides will be used as a starting point for the explanation of differences in the character of nitrogen oxide emissions from commercial combustors of various designs. The interest is concentrated on circulating fluidized bed (CFB) boilers compared with stationary fluidized bed (SFB) boilers. In addition, the influence of volatiles on the emissions from pulverized fuel (PC) combustion is discussed.

The purpose of the paper is thus to give a picture of the role of fuel volatiles in different combustors. A set of experiments has been conducted in two fluidized bed boilers with different fluidization properties, one SFB and one CFB. The boilers have been fed with fuels having a wide variation in the content of volatiles, from anthracite to wood, and the emissions have been measured. The observations made have been supported by a comparison with literature data. In order to further illustrate the role of volatiles, examples are given from NO_x reducing measures, where the characteristic properties of the combustors with respect to emissions are employed.

Experimental

The Boilers:

The CFB boiler used has a thermal power of 8 MW and was built by Götaverken Energy in 1981, Fig. 1a. The height of the combustion chamber is 8.5 m and the cross-section about 1.8 m². The fluidizing velocity is normally in the range of 3 to 6 m/s. The fuel is fed with a screw feeder in the
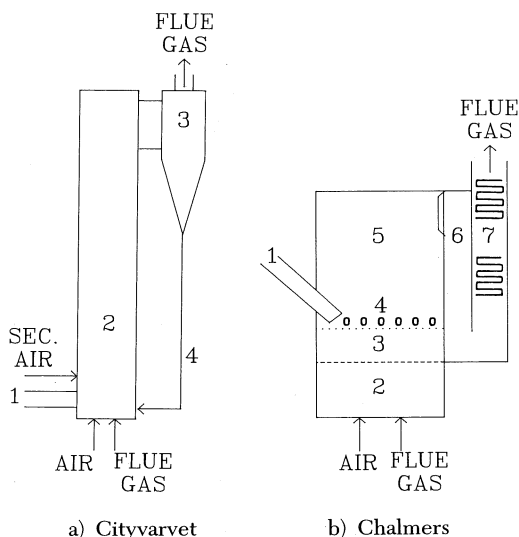
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a) Cityvarvet   b) Chalmers

FIG. 1. Schematic picture of the boilers

a) Cityvarvet. 1—Fuel feed screw, 2—Combustion chamber with fluidized bed, 3—Cyclone, 4—Particle return leg

b) Chalmers. 1—Fuel feed chute, 2—Air plenum, 3—Fluidized bed, 4—Secondary air nozzles, 5—Freeboard, 6—Empty gas pass, 7—Convection gas pass

lower part of the combustion chamber close to the bottom. Secondary air is introduced through an air register as shown in Fig. 1a. The bed particles are recirculated to the combustion chamber by a hot cyclone. External recirculation of particles from a secondary fly-ash collector is possible, but is not normally employed. Silica sand and ashes were used as a bed material and no limestone was added during the experiments.

The SFB boiler is a 16 MW boiler built in 1982 at Chalmers University. The features of this boiler are shown in Fig. 1b. The characteristic data are: cross-section 10 m^2, bed depth 1 m, height of freeboard 4 m, fluidizing velocity during the present tests 1.5 m/s. The fuel is fed on to the surface of the bed. Secondary air can be supplied through a number of nozzles as indicated in the figure. The bed material was of the same type as that of the CFB.

The Fuels:

A range of fuels has been selected, from anthracite with 11% of volatiles to wood chips with 86% of volatiles. The properties of the fuels are presented in Table I.

The wood chips were delivered in the form of non-uniform pieces about 20 mm in length and 5

mm thick. The peat consisted of cylinders, diameter 70 mm, length 100 to 150 mm. Some of the cylinders were broken into pieces, producing a fine fraction corresponding to about 10% of the fuel fed. The brown coal was also supplied in the form of cylinders with a diameter of 60 mm and a length of 35 mm.

Special care has been given to the analysis of the nitrogen content of the fuel since the results are presented as conversion of fuel nitrogen to NO. The calculation of the nitrogen conversion is based on the amount of fuel nitrogen that is released in the combustion chamber and converted to NO. A conversion of 1% of the fuel nitrogen to NO corresponds (in the case of bituminous coal) to a concentration in the order of 20 ppm NO at 6% O_2 (dry).

The Tests:

During the tests the boilers were run at constant operating conditions equal to the ones normally employed for boiler operation, with one exception, that the excess air ratio of the CFB boiler was 1.1 instead of 1.25. The deviation from the desired value was caused by an error in the excess air measurement for boiler operation, which was discovered after the tests and corrected for. Tables II and III give the principal data. It can be deduced from the tables that not only the CFB boiler but also the SFB boiler was run with some secondary air. Flue gas recirculation was employed in order to maintain a constant bed temperature when using fuels with different moisture content and heating values. For the same reason some coal had to be added with the wood. The duration of each test was one to two hours, starting when the boilers had attained stationary conditions.

The gas analyses were taken with conventional, calibrated gas analysers after the convection pass in the SFB and after the cyclone just before the convection pass in the CFB. The flue gas flow was calcualted by means of the oxygen concentration at the location of the gas sampling. The results are presented in the form of a conversion to NO since the emission of NO_2 is negligible and N_2O has been considered separately (Åmand & Andersson[10]).

Results

The conversion of fuel nitrogen to NO in the SFB boiler is shown in Fig. 2. It is evident that the volatile content of the fuel has a positive effect on the reduction of the emission of NO.

The corresponding results for the CFB boiler are presented in Fig. 3. The influence of volatiles, although leading to a more complicated relationship, does not on the whole have the same trend as in

TABLE I
The fuels

Type	Wood[a] chips	Peat[b]	Brown coal	Bituminous coal	Petroleum coke	Anth-[a] racite
Size, mm, mass mean		—see text—		6.5	7	1.9
% < 1 mm	0	10	0	11	14	50
Volatiles, % maf	86.0	72	53.1	35.5	14.3	11.1
Prox. anal, % as delivered:						
Combustibles	64.7	48.6	80	87	91	74.0
Ash	0.04	3.2	5	7	2	6.4
Moisture	35.3	48.2	15	6	7	19.6
Ultimate anal., % maf:						
C	51.1	56.3	67.5	82.7	89.8	92.1
H	6.3	4.6	4.9	5.2	4.1	1.6
O	42.3	36.5	25.9	8.8	2.7	2.6
S	0.03	0.5	0.8	1.6	2.0	2.3
N	0.3	2.0	0.9	1.7	1.4	1.4
Heating value, lower, MJ/kg maf	18.8	21.8	25.7	33.1	35.4	32.0

[a]CFB (Cityvarvet only).
[b]SFB (Chalmers only).

the SFB. The trend is rather reversed—a high volatile content leads to a high NO emission. It is also noted that there is a minimum of conversion for fuels with properties like bituminous coals.

The NO emission is susceptible to a variety of design and operating parameters which are not easily controlled or even identified. For that reason, a confirmation of the results with independent tests is desirable. A number of tests comprising different fuels can be found in the literature. The principal data from these tests are given in Tables II and III and the corresponding comparison with the data of the present investigation is made in Fig. 4 and Fig. 5.

TABLE II
Key to Fig. 4. Comparison of the influence of fuel volatiles on the fuel nitrogen conversion to NO between different SFBs

	Hampartsoumian[1] B *__*__*	Furusawa[2] E ○--○--○	Wittler[3] D +--+--+	Asai[4,5] C ●—●—●	This work A *. . .*. . .*
Bed temp.°C	<800–850	1000	850	830	845
Excess air ratio	1.25	1.30	1.25	1.25	1.25
Prim. air stoich.	1.25	1.30	1.25	1.25	1.10
Bed area m²	0.3	0.002–0.005	0.3	0.3	10
Height, furnace, m	2	0.5–0.85	1.3	4	5
Ca/S	0	0	0	unknown	0
Fuels used	Anthracite (7.64)	Char (3.99)	Anthracite (9.15)	Semianthr (12.4)	Pet. coke (14.4)
(Volatiles within brackets given on maf basis)	Bituminous coal (37.8)	Char (19.2)	Engl. coal (36.7)	Bit. coal (44.5)	Bit. coal (35.5)
	Peat (67.9)	Bit. coal (52.6)	Pol. coal (34.4)	Ind. waste (84.5)	Brown coal (53.1)
			Ruhr coal (37.2)		Peat (72.1)

TABLE III

Key to Fig. 5. Comparison of the influence of fuel volatiles on the fuel nitrogen conversion to NO between different CFBs

	Asai[5] C O--O--O	Suzuki[6] B ×--×--×	Shimuzu[7] E O—O—O	Lee[8] D +—+—+	Legros[9] F ●—●—●	This work A *…*…*
Bed temp. °C	830	850–870	850	850–920	850–880	845–850
Excess air ratio	1.25	1.2	1.2	1.15–1.25	1.15–1.25	1.05–1.08
Prim. air stoich	1.25	unknown	0.7–0.8	0.7–0.8	0.5–0.8	0.7–0.8
Bed area m^2	0.03	0.009	0.002	unknown	0.15	1.82
Height, furnace, m	7.6	5	4.3	unknown	7.13	7.8
Ca/S	unknown	2	0	unknown	0	0
Fuel used	Semianthr. (12.4)	Coke (2.56)	Coke (14.0)	Proc. culm. (9.53)	Anthracite (8.37)	Anthracite (11.1)
(Volatiles within brackets given on maf basis)	Bit. coal (44.5)	Semianthr. (14.2)	Semianthr. (13.8)	Pet. coke (11.2)	Minto coal (41.3)	Pet. coke (14.4)
	Ind. waste (84.5)	Low-vol. coal (21.4)	Bit. coal (43.8)	Sub-bit. coal (36.4)	Highvale coal (42.9)	Bit. coal (35.5)
		Medium-vol coal (28.5)	Brown coal (47.1)	Sub-bit. coal (36.5)	Lignite (47.8)	Brown coal (53.1)
		High-vol. coal (38.2)		Appalachian coal (38.4)	Hog fuel (71.8)	Woodchips/ coal (74.7)
		Brown coal (48.2)		Brown coal (57.9)		
				Diatomite (90.9)		

All the sets of data in Fig. 4 show that an increasing amount of fuel volatiles leads to reduced emissions of NO. The explanation has been given, e.g. by Hampartsoumian and Gibbs,[1] that nitrogen-containing volatile compounds, mostly consisting of ammonia, react in the splash zone and in the lower part of the freeboard where the particle concentration is low. They then contribute to the reduction
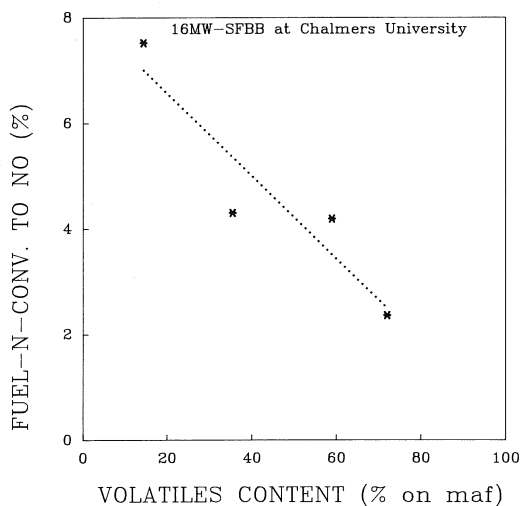
FIG. 2. The conversion of fuel nitrogen to NO in the stationary fluidized bed boiler during the combustion of fuels with different contents of volatiles.
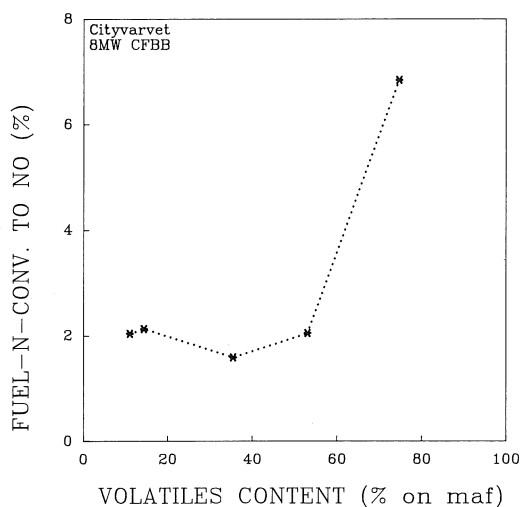
FIG. 3. The conversion of fuel nitrogen to NO in the circulating fluidized bed boiler during the combustion of fuels with different contents of volatiles.
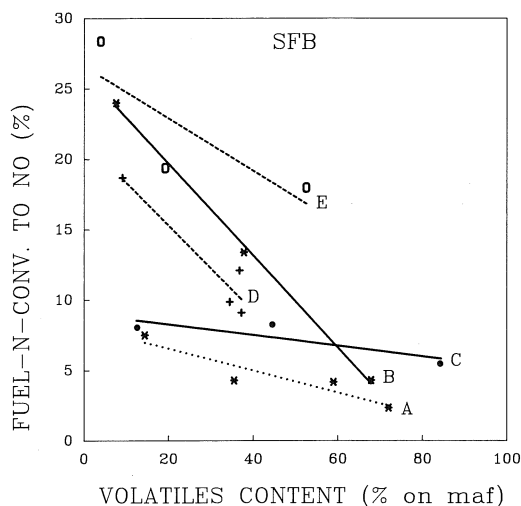
FIG. 4. Influence of fuel volatiles on the conversion ratio of fuel nitrogen to NO. Combustion in stationary fluidized beds. Key: See Table II.

of NO in the case that secondary air is not supplied close to the reaction zone. This has been demonstrated by Hirama et al.[11] and by Tatebayashi et al.[12]

The sets of data from CFB combustors, Fig. 5, do show the opposite trend compared to the SFB combustors in Fig. 4. The general concept of an explanation for this opposite trend is based on the dominance of char as a reducing agent of NO in CFBs. The char may consume NO by direct re-
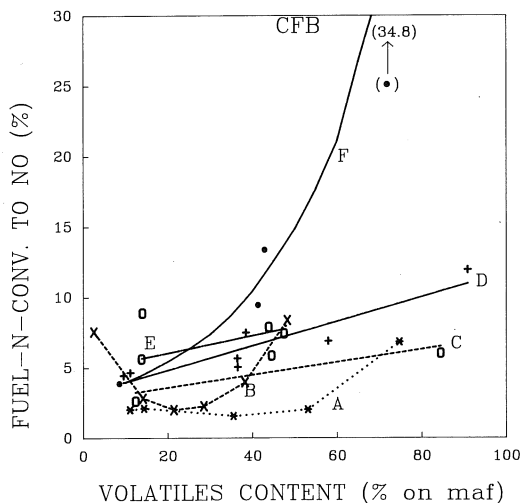

FIG. 5. Influence of fuel volatiles on the conversion ratio of fuel nitrogen to NO. Combustion in circulating fluidized beds. Key: See Table III.

action or by acting as a catalyst for the reaction between NO and CO or H$_2$. The role of nitrogen-containing volatiles in the reduction of NO, on the other hand, is less important since they tend to be broken down by the surfaces of particles (Hirama et al.[11]). This decomposition takes place particularly on char particles but also on sand, CaSO$_4$ and ashes which are found in concentrations ranging from 1000 kg/m^3 in the bottom to 1–5 kg/m^3 in the top of the furnace.

A fuel containing less fixed carbon results in a lower content of char in the combustion chamber (at constant power), which leads to less char surface for reduction of NO. If the contribution from the volatiles were small there would be an increase in the NO emission with increasingg content of volatiles in the fuel, as in the case of the CFB. On the other hand, based on the above reasoning, in the SFB there must be a positive contribution to NO reduction by the volatiles.

However, this cannot be the whole truth. If the curve for CFB obtained in the present investigation is compared with that of Suzuki et al.,[6] it is found that they both display a minimum. Actually, the data points of Shimuzu[7] also, if plotted in the same way, would agree with such a behaviour. The explanation of the increase in the conversion of fuel nitrogen to NO at low volatile fuels is only tentative for the moment:

1. Low-reactive fuels burn in a different way compared to bituminous coals and tend to have more reactions in the pores of the particles, which leads to different NO reduction characteristics (Shimuzu[7]).
2. Low volatile fuels produce less volatile-CO. It is however unclear how this influences the reduction of NO on the surfaces of the char, since CO may be produced in sufficient quantities by the combustion of char itself.

Finally, the difference in the level of conversion between the different investigations should be noted. There are several influencing factors outside of the present subject which may have contributed. Important to the present study is the inclination of the curves and the difference between emissions from fuels with different volatile contents.

Discussion

It is instructive to compare the well-known emission properties of pulverized coal combustion with fluidized bed combustion. Except for the possibility of thermal NO$_x$ production in a PC flame, there are two major differences related to fuel volatiles. The first difference concerns the quantity of volatile nitrogen released during devolatilization. It is known, e.g. from the results of Pohl and Sarofim,[13] that

under fluidized bed conditions (i.e. low tempera-
ture) the fractional yield of fuel-N upon devolatili-
zation is directly proportional to the volatile frac-
tion, but at the higher temperature of PC
combustion the fractional fuel-N exceeds that of the
volatile and can reach 70–80% for a 35% ASTM
volatile coal. The second characteristic property of
PC combustion is that these large amounts of vol-
atile nitrogen compounds either tend to be oxidized
to NO or contribute to the reduction of previously
produced NO in a complicated network of gas phase
reactions depending on the local conditions (oxygen
concentration and temperature). As a result, un-
staged flames from fuels with high volatile content
tend to have a larger conversion to NO than those
from fuels with a low volatile content, whereas the
order is reversed when air staging is used to take
advantage of the volatile nitrogen compounds to re-
duce the NO emission. This is illustrated by Fig.
6 which is based on the work of Kremer and
Schulz.[14,15]

Considering the differences in amount of vola-
tiles released and temperature, this information can
be translated to the freeboard of an SFB boiler, and
it supports the description just given of the role of
volatiles in an SFB. The arrangement of the air
supply to the bed becomes important not only to
produce volatile nitrogen which can react in the
freeboard but also to increase the concentration of
char in the bed. The importance of secondary air
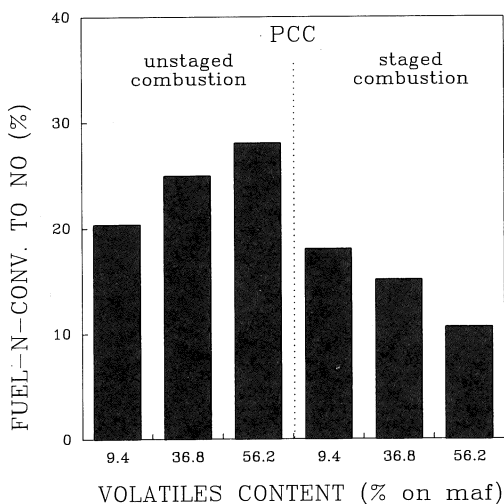in stationary fluidized bed combustors was investi-

gated already in 1977.[16] In addition, specially for
high volatile fuels, the contact between air and vol-
atiles in the freeboard becomes decisive for the for-
mation or destruction of NO.

The situation in a CFB is different. Due to the
high particle loading in the furnace, the reactions
producing or reducing NO from volatile nitrogen
compounds are greatly influenced by particle sur-
faces. The present results do not give definite in-
formation about the influence of volatiles, but it is
quite obvious that the positive effects noticed in the
SFB are absent or of small importance. Instead, it
seems that in the CFB the influence of char dom-
inates the reduction of NO. This would explain why
high volatile fuels are less effective in the CFB. For
this reason, air-staging may not be as efficient in
reducing NO as it is the SFB. In fact, in some CFB
designs air staging has no effect at all [Åmand &
Leckner[17]]. More efficient ways to increase the char
reaction surface for NO reduction would be to in-
crease the presence of very fine char particles by
fly-ash recirculation. The result from such an ex-
periment in the present boiler is shown in Fig. 7.

The judgement of the role of nitrogen-containing
volatiles in CFBs or SFBs is further supported by
experiments with ammonia injection. Ammonia can
be taken as a representative substance for the ni-
trogen-containing volatiles. Injection of ammonia in
the dense bed of an SFB or in the combustion
chamber of a CFB boiler is known to have a small
and even negative effect on the emissions of NO
[Hampartsoumian & Gibbs,[18] Åmand & Leckner[19]].
The ammonia is broken down by the char and other
bed particles. Injection into the splash zone or the
lower part of the freeboard of an SFB boiler, on
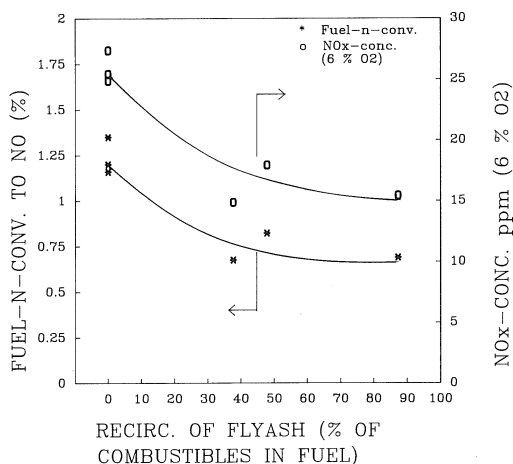the other hand, yields a substantial reduction of NO.

FIG 6. Influence of fuel volatiles on the conver-
sion ratio of fuel nitrogen to NO. Pulverized coal
combustion. Fuels: Anthracite, bituminous coal and
brown coal. Excess air ratio = 1.35. Primary air
stoichiometry at staged air supply = 0.90. Re-writ-
ten from data in ref.14 and 15.

FIG. 7. Reduction of the NO emission by fly ash
reinjection in the Cityvarvet CFB boiler.

Conclusions

The NO emissions from fluidized bed combustors are less dominated by the properties of volatile fuel nitrogen compounds than pulverized coal combustion.

The NO emissions from the stationary type of fluidized bed boiler are decreased by the volatile fuel nitrogen, whereas in the circulating type of fluidized bed boiler the NO emissions tend to increase with high volatile fuels.

The measures to reduce the NO emissions should take advantage of these tendencies: where the volatiles are important, the air supply becomes important; where the char is important, factors which increase the char reaction surface become important (for instance fly ash recirculation, total excess air ratio, etc).

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