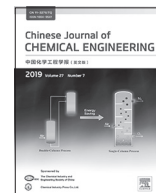




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Article

Synergetic NO reduction by biomass pyrolysis products simulating their reburning in circulating fluidized bed decoupling combustion[☆]Hai-Sam Do^{1,2}, Tuyet-Suong Tran^{1,2}, Zhennan Han³, Xi Zeng¹, Shiqiu Gao¹, Guangwen Xu^{1,3,*}¹ State Key Laboratory of Multi-phase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China² University of Chinese Academy of Sciences, Beijing 100049, China³ Institute of Industrial Chemistry and Energy Technology, Shenyang University of Chemical Technology, Shenyang 110142, China

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ABSTRACT

The present work investigated the synergetic effect of pyrolysis-derived char, tar and gas (py-gas) on NO reduction, which may occur in circulating fluidized-bed decoupling combustion (CFBDC) system treating N-rich fuel. Experiments were carried out in a lab-scale drop-tube reactor for NO reduction by some binary mixtures of reagents including char/py-gas, tar/py-gas and tar/char. At a specified total mass rate of 0.15 g·min⁻¹ for NO-reduction reagent, the char/py-gas (binary reagent) enabled the best synergetic NO reduction in comparison with the others. There existed effective interactions between char and some species in py-gas (i.e., H₂, C_xH_y) during NO reduction by pyrolysis products, meanwhile the tar/py-gas or tar/char mixture only caused a positive effect when tar proportion was necessarily lowered to about 26%. On the other hand, the synergetic effects were not improved for all tested binary reagents by increasing the reaction temperature and residence time.

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1. Introduction

Nitrogen oxides (NO_x), one of the main gas-phase pollutants released in fuel combustion, not only injures human health but also forms acid rain and photochemical smog [1, 2]. Various technological in-combustion and post-combustion approaches are available to reduce NO_x emission from actual combustion systems. In this regard, we have developed an efficient low-NO_x combustion technology, the so-called circulating fluidized bed decoupling combustion (CFBDC), which has been well proven by an industrial system treating distilled spirits lees (DSL) that is a massive high-N biomass waste generated from the production process of distilled spirit in China. The actual running data show that the NO_x emission was lowered by about 70% comparing to the traditional CFB combustion [3–5], making the NO content in its flue gas be 120–170 mg·m⁻³ for the DSL containing N of about 4.0 wt%. The CFBDC technology, as illustrated in Fig. 1, is based on the reaction decoupling concept which separates the combustion process into drying/pyrolysis of fuel and combustion of pyrolysis-generated char and volatile. Thus, the system is composed of a fluidized-bed pyrolysis

reactor and a riser combustor, the pyrolysis-generated volatile consisting of non-condensable pyrolysis gas (py-gas) and condensable tar is sent to an intermediate position of the riser combustor to allow its co-burning with char. The co-burning of fuel pyrolysis products in such an intermediate position can be considered as a reburning way that effectively reduces the NO_x formed by burning char in the bottom zone.

Fuel reburning is a well-known low-NO_x combustion technique. Many studies have been performed on reburning of different fuels including gas (e.g., natural gas and other hydrocarbon fuels), liquid (e.g., residual fuel oil) and solid (e.g., coal and biomass) [6]. Considering NO as the main component of NO_x in most practical flue gas, the mechanisms of lowering NO_x in reburning were almost studied through considering NO reduction reactions in terms of gas-phase homogeneous reactions between volatiles (gaseous fuel, tar and py-gas) and NO and gas–solid heterogeneous reactions between char and NO. For the CFBDC technology, the results from earlier studies [5, 7–9] indicated that both such mechanisms were involved to form a combined action of char, tar, and py-gas in reducing NO (in Fig. 1).

Many studies have been conducted regarding the homogeneous NO reduction reaction using gaseous reactants. Fan *et al.* [10] reported that hydrocarbon gases such as CH₄ and C₃H₆ have great impact on NO reduction, whereas CO or H₂ is hard to reduce NO efficiently. The simulation conducted by Glarborg *et al.* [11] indi-

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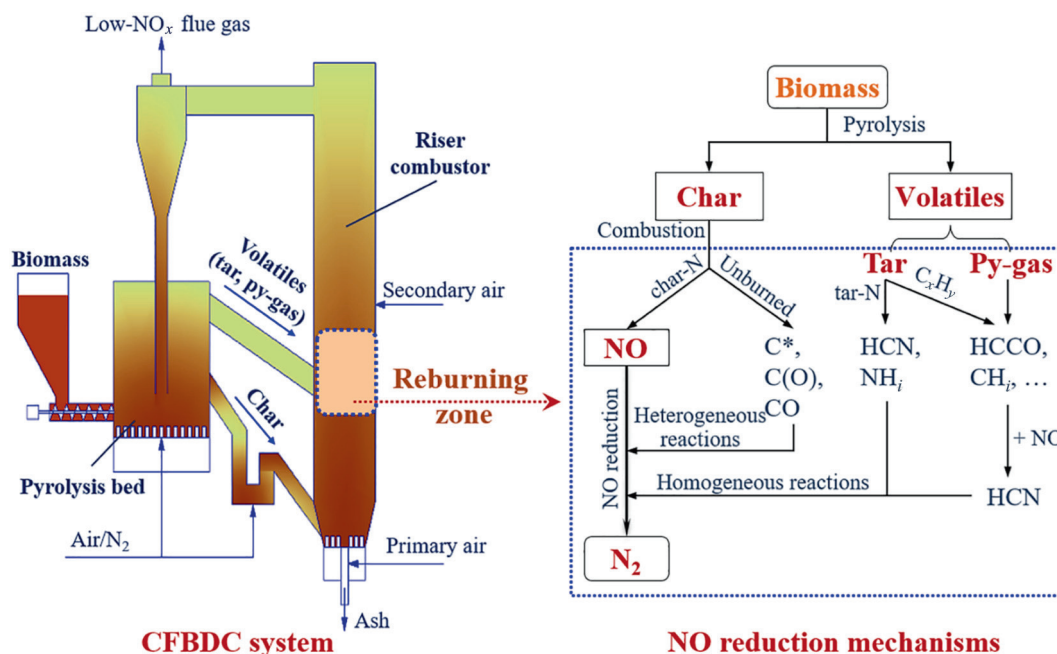


Fig. 1. A schematic diagram of CFBDC system and possible mechanisms for NO reduction inside the reburning zone.

cated that the gas mixture of CO and H₂ removed 20%–30% of the NO entering the reburning zone and the NO conversion increased with rising the CH₄ content in such a mixture. Concerning the interactions among gas components during NO reduction by biomass volatile, Wu *et al.* [12] reported that CO had no contribution to NO reduction and there was a synergetic effect for H₂ and CH₄. Most of literatures have revealed in general that the reduction ability of NO is evident for hydrocarbon gases, even though arguments exist on whether non-hydrocarbon gases have effective reduction capability for NO or not.

The pyrolysis tar, which is gaseous product at high temperature, also take part in the homogeneous NO reduction reactions as described above. Many hydrocarbons and other compounds containing in tar such as phenols, aromatics, aliphatics, carboxylic acid, and ester groups [13] should cause high effect in reducing NO but there were very few studies on the NO reduction by tar. Luo *et al.* [14–17] revealed that tar is highly helpful in increasing the NO reduction efficiency by biogas, while the effectiveness of NO reduction by model tar compounds was also observed.

Regarding the heterogeneous reaction mechanism, the char derived from pyrolysis (coal and biomass) has been widely tested as an effective reagent for NO reduction. The influential factors of heterogeneous NO reduction by char in the above mechanism include the char types, structure of char particles and presence of gas species on char surface. Dong *et al.* [18, 19] reported that biomass char was more active in reducing NO than coal char did, and the NO reduction over biomass char can be enhanced with the gas components CO, O₂ and SO₂ present in the reaction atmosphere. The NO reduction activity of char was correlated with the specific surface area and porosity of char particles [20, 21]. Shu *et al.* [22] and Lu *et al.* [21, 23] have studied the contribution of char to the total NO reduction during reburning biomass and coal. Results indicated that the contribution of char to the total NO reduction was higher for higher-volatile fuel. However, it is difficult to distinguish the effects of the heterogeneous and homogenous reactions when they simultaneously occurred in the reburning zone. The synergetic reduction of NO by char and volatile matters has not been well understood.

Following our previous findings about the characteristics of NO reduction using char, tar and py-gas from DSL pyrolysis as reagents [8], this study further investigates the interactions between two

reagents among char, tar and py-gas in reducing NO to reveal their synergetic NO reduction occurring in the CFBDC process. The effects of reagent proportion, reburning stoichiometric ratio (SR), reaction temperature and residence time on the synergetic NO reduction by some binary reagents such as char/py-gas, tar/py-gas, tar/char mixtures were systematically carried out in an experimental drop-tube reactor. In addition, the influences of some reducing gases (*i.e.*, CO, H₂, and CH₄) on the NO reduction by char/py-gas mixture were evaluated to understand the combined homogeneous–heterogeneous reaction mechanism for NO reduction.

2. Experimental

2.1. Facility and reagents

An experimental drop-tube reactor (DTR) system, which was described in other publications [8, 9] studying the NO reduction by different reagents including pyrolysis char, tar, and py-gas of biomass/coal, was also adopted in this study testing the synergetic NO reduction among such reagents. The experiments were carried out with simultaneous feeding of more than one NO reduction reagent, thus simulating the conditions for reburning of multi-reactants involved in CFBDC to the possible greatest extent. Fig. 2 shows that the testing apparatus consists of a reaction zone, a simulated flue gas supplying system, a NO reductant feeding system and a flue gas analysis system. The reaction zone of the DTR was made with a corundum tube of 100 mm in inner diameter and 1680 mm in length, which was heated by an external electric furnace to allow reaction temperatures of up to 1550 °C. The concentrations of gaseous products (NO, CO, and O₂) in the inlet and outlet flue gas were continually monitored using an SDL M3080 online gas analyzer (Beijing SDL Technology, China).

Similar to our previous studies [8], the NO reduction reagents tested in this study include char, tar and py-gas derived from pyrolysis of DSL. Char and tar were prepared by pyrolysis of DSL in N₂ at 500 °C in a fixed-bed reactor for 30 min, which is quite close to the condition adopted for fuel pyrolysis in CFBDC [4]. The py-gas was a model gas made according to the composition of pyrolysis-generated non-condensable gas. Table 1 shows the

Table 2

Correspondence of specified mass rate (SMr) and feeding mass rate (FMr) of reagents

Level	Char		Tar		Py-gas (STP)	
	SMr/g.min ⁻¹	FMr/g.min ⁻¹	SMr/g.min ⁻¹	FMr/g.min ⁻¹	SMr/g.min ⁻¹	FMr/L.min ⁻¹
1	0.034	0.055	0.040	0.040	0.038	0.085
2	–	–	0.056	0.056	–	–
3	0.072	0.115	0.078	0.078	0.075	0.171
4	0.115	0.186	0.114	0.114	0.113	0.256
5	0.153	0.246	0.149	0.149	0.151	0.342
6	0.196	0.316	0.190	0.190	0.188	0.427
7	–	–	–	–	0.226	0.512
8	0.240	0.386	–	–	–	–

sequently, the feeding rates of reagents specified in this paper are all defined on basis of reagent mass rate (g.min⁻¹) excluding amount of ash or inert gas. Table 2 summarizes the feeding mass rate (FMr) of reagents adopted in experiments of this study.

The synergetic NO reduction was investigated between a pair of reagents among char, tar and py-gas. Thus, two of such three reagents were simultaneously fed into the DTR reactor for each test. The combined reagents were also called the binary reagents or reagent mixtures, and the contents of individual reagents were determined according to experimental conditions as summarized in Table 3. There, the different mass proportion of a binary reagent shows the variation of its mass ratio between the flowrates of two individual reagents, but the work maintained the total mass rate of the binary reagent to be about 0.15 g.min⁻¹.

The NO reduction efficiency by a reagent was generally defined as

$$\eta = \left(1 - \frac{[\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}}\right) \times 100\%, \quad (1)$$

where η is the NO reduction efficiency (%), $[\text{NO}]_{\text{in}}$ is the NO concentration (ppmv) at the inlet of reburning zone (included the dilution effect by adding carrier gas), and $[\text{NO}]_{\text{out}}$ is the NO concentration (ppmv) measured at the reactor outlet. The definition means that the gas volume variation through the reactor was neglected in esti-

imating the NO reduction efficiency according to the measured NO concentrations.

In order to effectively compare the overall NO reduction efficiencies realized by different mixtures of reagents at a similar total mass rate, all data of NO reduction efficiency were normalized to 0.15 g.min⁻¹ of the binary reagent feeding rate. It was assumed that the NO reduction efficiency is proportional to the amount of reagent fed into the reactor. As a result, the NO reduction efficiency in Eq. (1), η_e (%), was modified to the normalized value, η_e (%), via the following equation:

$$\eta_e = \left(1 - \frac{[\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}}\right) \times \frac{0.15}{m} \times 100\%, \quad (2)$$

where m (g.min⁻¹) is the total mass rate of reagents (binary reagent) fed into the reactor, as listed in Table 3.

Two parallel experiments have been carried out to demonstrate the repeatability. The data presented throughout this paper are the average values of two similar tests. The results showed that the deviation of the realized NO reduction efficiency was in $\pm 3\%$, as also indicated by error bars in plots.

3. Results and Discussion

3.1. NO reduction by individual reagents

To enable evaluation of synergetic NO reduction by binary reagents in the lab-scale DTR, the NO reduction by individual reagents were first determined to obtain the baseline of comparison. The NO reduction characteristics of char, tar and py-gas were primarily tested at the same normalized mass feeding rate of 0.15 g.min⁻¹ in earlier work [8]. In this study, a series of experiments with different amounts of fed reagent were performed to clarify the influence of reductant concentration on NO reduction. For all tests, the amounts of oxygen and reagent were simultaneously varied to maintain the stoichiometric ratio (SR) in 0.6–1.0, showing the reburning conditions from a moderate fuel-rich combustion to a stoichiometric combustion of the fed reagent. The initial concentration of NO in the simulated flue gas was kept at 800 ppmv.

Fig. 3 shows the NO reduction efficiencies (η) varying with mass feeding rate of reagents defined in Table 2. The tests are for all reagents of char, tar and py-gas but at a reaction temperature of 900 °C, the typical condition for the riser combustor in a CFBDC system. At the same SR, the achieved NO reduction increased with increasing the feeding rate of all reagents. As shown previously [8], the actual NO reductants in fuel reburning are C*, CH₄, H, and many others generated from the C and H elements containing in the reagent. Thus, the molar ratios of total C and H elements in reagent to fed NO, which is denoted as CH/NO ratio, corresponding to the specified mass rates of char, tar and py-gas are further mentioned in Fig. 3. The presented values of CH/NO ratio were calculated based on the ultimate analysis data shown in Table 1. From

Table 3

Specified mass rates of reagents in testing NO reduction by binary reagents

No.	Reagent mass rate/g.min ⁻¹		Total rate/g.min ⁻¹	Proportion/wt%	CH/NO ratio
	Char	Py-gas		char	
1	0.034	0.113	0.147	23	9.15
2	0.072	0.075	0.147	49	8.56
3	0.115	0.038	0.153	75	8.29
	Tar	Py-gas		tar	
4	0.040	0.113	0.153	26	10.62
5	0.078	0.075	0.153	51	11.21
6	0.114	0.038	0.152	75	11.68
	Tar	Char		tar	
7	0.115	0.040	0.155	26	9.02
8	0.072	0.078	0.150	52	9.88
9	0.034	0.114	0.148	77	10.94
	Char	CO		char	
10	–	0.150	0.150	0	3.32
11	0.034	0.115	0.150	23	4.28
12	0.072	0.079	0.151	48	5.36
13	0.115	0.035	0.150	77	6.59
	Char	H ₂		char	
14	–	0.150	0.150	0	92.58
15	0.034	0.115	0.150	23	73.13
16	0.072	0.078	0.150	48	52.14
17	0.115	0.034	0.149	77	27.01
	Char	CH ₄		char	
18	–	0.152	0.152	0	29.37
19	0.034	0.116	0.151	23	24.25
20	0.072	0.076	0.148	48	18.30
21	0.115	0.035	0.151	77	12.67

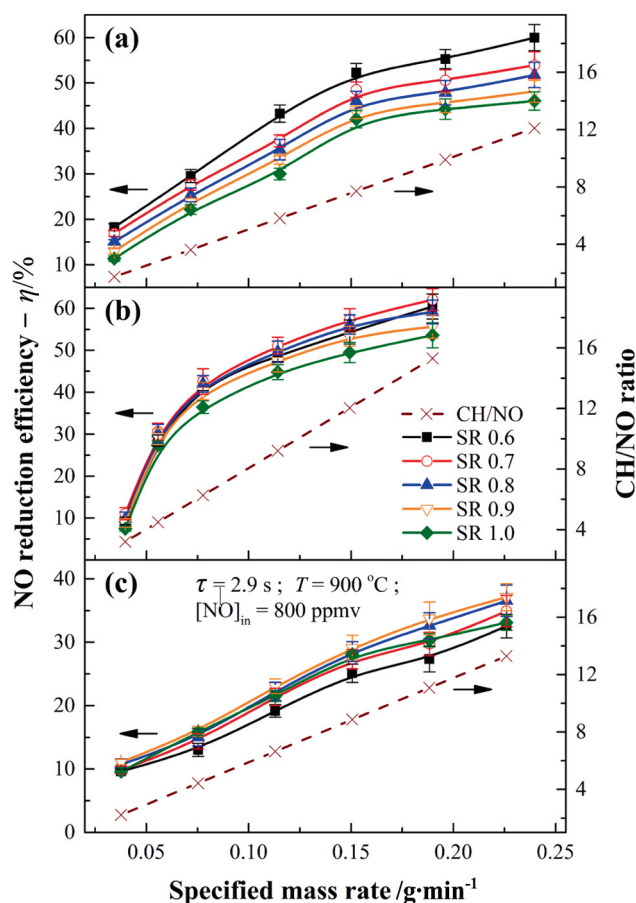


Fig. 3. Variation of NO reduction efficiency with specified mass rate at different SR values for individual reagents: (a) Char, (b) Tar, (c) Py-gas.

Fig. 3 one can see that the significant elevation of NO reduction efficiency by increasing reagent feeding rate are well correlative with the increase in the CH/NO ratio. The higher CH/NO ratio obtained by adding more reagent apparently provided more available reductants consisting of C and H. Exposure of NO to reducing radicals or char-active surface area was thus increased for both the gas-phase homogeneous reactions or heterogeneous reactions (see Fig. 1), respectively. In addition, quick consumption of oxygen by the high amounts of reagent fed into reaction zone must also enhance the formation of low-oxygen atmosphere, which is more effective for reducing NO [24, 25].

On the other hand, the panels (a)–(c) of Fig. 3 show that the realized NO reduction efficiency η by individual reagent increases rapidly with raising the reagent mass rate only to a determined value, which is called the dilution limit. From that limit, the improvement on NO reduction becomes slower against the increase in the reagent mass rate due to the less efficient mixing between reagent and flue gas [24]. Bilbao *et al.* [26] stated that the dilution effect was more significant in the systems with higher concentrations of reactants. Therefore, determining the dilution limit should be an important issue for effectively operating the practical systems.

The dilution limit is different for different reagents. In Fig. 3(a) and (b) it is respectively $0.153 \text{ g}\cdot\text{min}^{-1}$ and $0.078 \text{ g}\cdot\text{min}^{-1}$ for char and tar reagents, and the corresponding CH/NO ratios are 7.70 and 6.26. The dilution limit for tar is obviously shifted to a lower reagent mass rate than that of char does. This is in agreement with the fact that the reagent tar is easier to decompose into many active species or radicals, as compared to the active sites on char surface [7, 15, 16]. Therefore, there was an effective NO reduction

for tar, even though its concentration is highly diluted in the reaction zone. Their corresponding CH/NO ratios are nearly equivalent, suggesting the suitable CH/NO ratio of 6.0–8.0 and it can be used to determine the dilution limits of individual reagents including char and tar.

However, in a CFBDC system the generated tar exists in the gas phase and it is transferred from the pyrolysis bed to the reburning zone of the combustor with the flow of py-gas at high temperature. Thus, the dilution of tar should be better than that in our experiments. For py-gas reagent in Fig. 3(c), the obtained limit value seems to be $0.15 \text{ g}\cdot\text{min}^{-1}$, but the phenomenon is not as distinct as that for the char, tar reagents. It is well known that the gas-phase reagent is easier to diffuse into the simulated flue gas than the solid- or liquid-phase reagents does. Py-gas should be well diluted even in experiments. As a result, the dilution limit is negligible for py-gas reagent, and this would be much close to the actual operation in a CFBDC system.

Concerning the synergetic NO reduction presented in the following sections, where at least two kinds of reagents are fed together into the reaction zone, the dilution issue becomes more important because a bad mixing of multi-reagents with flue gas may obviously inhibit the NO reduction capability of the reagents so that the identification of the synergetic effect becomes difficult. In order to minimize the effect of dilution, the conditions for all experiments were fixed at $0.15 \text{ g}\cdot\text{min}^{-1}$ of the total mass rate of reagents (see Experimental Section). Consequently, the amount of char injected into reaction zone was below its limit value of $0.153 \text{ g}\cdot\text{min}^{-1}$, while the influence from dilution limit is ignorable for py-gas and tar.

3.2. Synergetic effect of binary reagent

The synergetic NO reduction was tested for several binary reagents specified in Table 3. In order to effectively identify the synergetic effect on NO reduction by such binary reagents, we defined the synergetic difference, $\Delta\eta_e$ (%), to be

$$\Delta\eta_e = \eta_e - \sum \eta_i \quad (3)$$

where η_e (%) is the measured NO reduction efficiency of a binary reagent at the specified mass rate of $0.15 \text{ g}\cdot\text{min}^{-1}$, and η_i (%) is the absolute NO reduction efficiency of the related single reagent “i” (char, tar, or py-gas) fed at the similar mass rate of reagent “i” as in the binary case (from the Section 3.1). This synergetic difference measures the improved or diminished NO reduction efficiency through the combining reagents.

Figs. 4–6 show respectively the results from testing the binary reagents of char/py-gas, tar/py-gas and tar/char with different reagent proportions (normalized to mass percentage). The plotted data are the actual efficiencies (η_e) and synergetic differences ($\Delta\eta_e$) in NO reduction estimated according to Eq. (3) under different SRs. For an effective comparison, the NO reductions for individual reagents of char, tar and py-gas derived from similar fuel [8] were also presented in Figs. 4–6.

For the char/py-gas binary reagent, the realized η_e sharply decreased with the rise in SR, and the decrease was more apparent than that obtained for individual reagents of char and py-gas at a similar specified mass rate (Fig. 4(a)). Moreover, increasing the percentage of char in the binary mixture, the realized NO reduction diminished but was still higher than that achieved by 100% char, especially under the fuel-rich conditions of $\text{SR} < 1$. Generally, increasing SR decreases the synergetic interaction on promoting NO reduction between char and py-gas reagents. Thus, the synergetic difference ($\Delta\eta_e$) decreased with raising SR in Fig. 4(b). For example, $\Delta\eta_e$ for a binary mixture of 23% char at SR of 0.6 and 1.0 were respectively 30.4% and 7.4%, but those for a mixture of

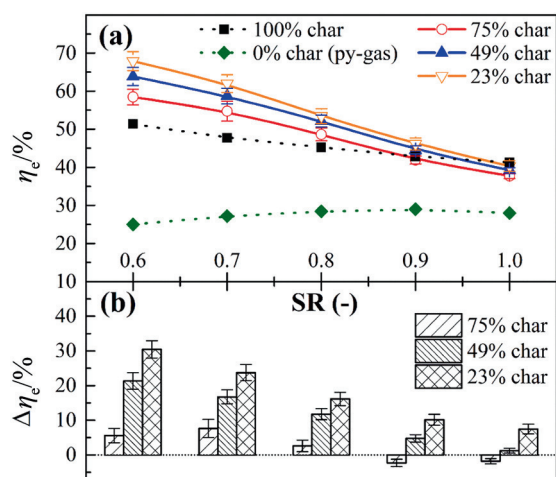


Fig. 4. Synergetic NO reduction by binary reagent of char/py-gas at varied SRs but a typical reaction temperature of 900 °C: (a) NO reduction, (b) Synergetic difference: “Sets 1–3” in Table 3.

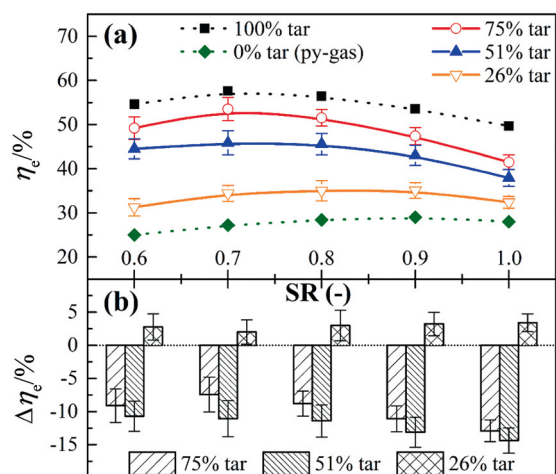


Fig. 5. Synergetic NO reduction by binary reagent of tar/py-gas at varied SRs but a typical reaction temperature of 900 °C: (a) NO reduction, (b) Synergetic difference: “Sets 4–6” in Table 3.

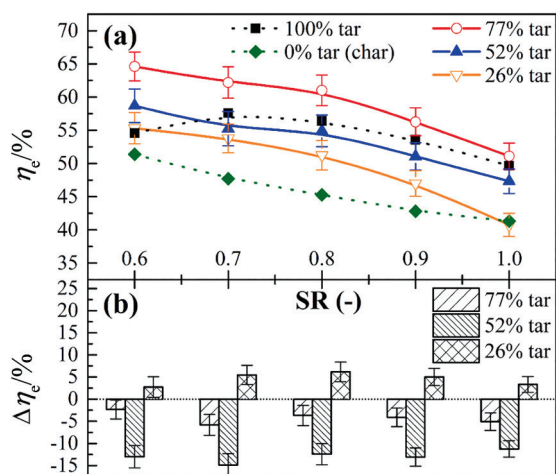


Fig. 6. Synergetic NO reduction by binary reagent of tar/char at varied SRs but a typical reaction temperature of 900 °C: (a) NO reduction, (b) Synergetic difference: “Sets 7–9” in Table 3.

75% char under such SRs were respectively 5.6% and −1.8%. Thus, the synergetic promotion effect shown by $\Delta\eta_e$ was obviously higher for the fuel-rich condition at lower SR and also for the binary mixture with the lower char content (or higher py-gas content). Indeed, the fuel-rich reburning condition (lower SRs) forms a reducing atmosphere to enhance NO reduction by all reagents including char, tar and py-gas [23, 27]. On the other hand, the gas components CO, H₂, and CH₄ in py-gas would positively affect the NO reduction reactions by char, as will be analyzed in the Section 3.4. This refers actually to the identified synergetic effect between py-gas and char on NO reduction.

Fig. 5(a) shows that the realized η_e by the binary reagent tar/py-gas increased with raising the percentage of tar in the mixture at all the tested SRs, but it obviously did not exceed the level achieved by 100% tar (tar reagent). It was previously proved that tar enables the best NO reduction among char, tar and py-gas [8]. The result suggests that the positive synergetic effect on NO reduction was not observed for the tar/py-gas mixture, and mixing py-gas into gaseous tar led to negative effect on NO reduction by tar and thus had the negative $\Delta\eta_e$ in Fig. 5(b). Consistent results were obtained also by Duan *et al.* [14] who investigated NO reduction by biogas with and without tar mixed. They reported that the mixing model tar compound such as toluene played a positive role on reducing NO by reburning biogas.

Fig. 6(a) shows the η_e realized by the binary reagent tar/char at varied SRs and mixing percentages of tar. Again, η_e increased with raising tar content at all SRs, and at the same mass rate of 0.15 g·min^{−1} the η_e obtained at 77% tar in the tar/char mixture exceeded the level achieved by 100% tar only. Nonetheless, the corresponding synergetic difference shows that the capability of this binary reagent for reducing NO was not as good as expected because in Fig. 6(b) the $\Delta\eta_e$ for 77% tar mixture at all tested SRs was negative (−5%). Similar to Fig. 5(b), only the mixture with 26% tar caused a positive $\Delta\eta_e$. Thus, for the mixture of tar with another reagent (char or py-gas), the lower the tar content, the more synergetic effect could be.

Overall, we can summarize that the interaction between char and non-condensable volatile gas (py-gas) improved their NO reduction capability, and the synergetic effect was more significant for the mixture with the higher py-gas proportion. Between tar and other reagents (either char or py-gas) it caused a positive synergetic effect only when the tar content is relatively low, for example below 26%. At the tested temperature of 900 °C, the decomposition of tar massively occurs at certain amounts of oxygen to enhance the NO-reduction required oxidative cracking of tar [8, 28]. When any other reagent is present, it should compete with tar in capturing the available oxygen. This causes the oxygen-lean atmosphere for oxidative cracking of tar, and coke/soot may be conversely formed through polymerization and graphitization under [17, 29]. It is well known that soot particles are nonporous and have limited porosity [29, 30], indicating a weak ability to occur the heterogeneous NO reduction reaction, even though there were some studies reporting positive effect [31, 32]. In comparison, a strong reducing atmosphere was reported to effectively enhance the heterogeneous NO reduction by char, possibly due to the porous structure and catalytic ash components in char [21, 22, 33, 34]. Consequently, the competition in capturing oxygen by other reagents would surely accelerate the NO reduction reactions by char to demonstrate the positive synergetic effect.

Fig. 7 shows the surface morphology and elemental distribution given by the scanning electron microscope-energy dispersive spectroscopy (SEM-EDS) for the residue samples collected in our reburning experiments. The SEM images and EDS spectra of unreacted char and tar-derived coke were respectively from the tests using char/py-gas and tar/py-gas mixtures (Sets 2 and 5) at 900 °C and a reburning SR of 0.7. It is obvious in the SEM images

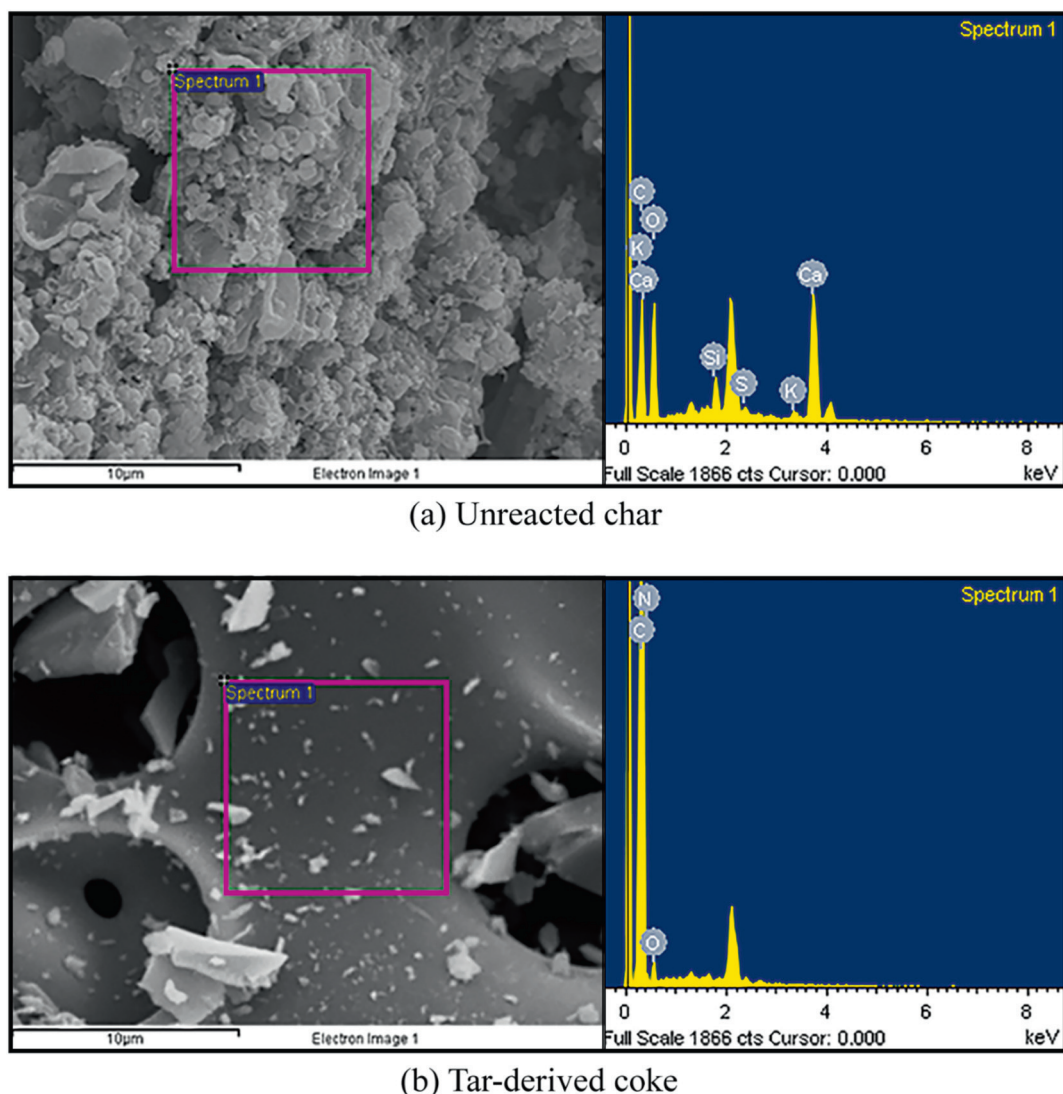


Fig. 7. SEM images and EDS spectra of reburning residues collected from experiments (Sets 2 and 5 in Table 3) at typical temperature of 900 °C and an SR of 0.7.

that char has the typical porous morphology [35] even though it was partially burned during reburning, whereas the surface of coke particle exhibits a flat, smooth, and less textured appearance [36, 37]. The EDS spectra show that the composition of the char surface consists of K and Ca metals which are known to be catalytic for NO reduction reactions [33, 38]. These identifications further explain the distinctive effect of each reagent on the above-observed synergistic NO reduction results.

3.3. Variation with temperature and residence time

Fig. 8 shows the achieved η_e at different temperatures of 800, 900, and 1000 °C under a typical fuel-rich condition (SR = 0.7) for three binary reagents of char/py-gas, tar/py-gas and tar/char at equal mass proportion of approximately 1:1. For comparison the NO reduction efficiencies realized by individual reagents at the same feeding mass rate of 0.15 g·min⁻¹ were plotted in parallel. Raising temperature from 800 to 1000 °C increased the η_e for char/py-gas, tar/py-gas and tar/char reagents by 24.9%, 44.5% and 39.2%, respectively. The order is in correspondence of their CH/NO ratios of 8.56, 11.21, and 9.88. Thus, the higher CH/NO ratio is beneficial to NO reduction so that here the highest dependence on temperature is for the tar/py-gas mixture. Nonetheless, for all

binary reagents their increases in η_e from 900 to 1000 °C were less significant than from 800 to 900 °C.

Compared with the realized NO reduction by individual reagents of char, tar and py-gas [8], the increases in η_e with raising temperature did not diminish in 900–1000 °C. It means that the synergistic effect between two reagents for NO reduction was not enhanced by increasing reaction temperature. As discussed in the Section 3.2, only the interaction between char and py-gas improved the NO reduction by their mixture at 900 °C. At rather higher temperatures of up to 1000 °C, the accelerated char oxidation as well as ash melting may inhibit NO reduction by char [21, 39], while in the oxygen-lean atmosphere tar would be decomposed into coke/soot other than reducing radicals at high temperatures [17, 29]. It is because at high temperatures the oxidation reactions for all reagents are accelerated more. Thus, for a CFBDC system treating DSL [5], the reburning zone temperature at the intermediate position of its riser should be around 900 °C in order to develop the synergistic NO reduction effects of DSL pyrolysis products.

The effect of residence time on synergistic NO reduction by binary reagents was studied at 900 °C and a reburning SR of 0.7. The tested residence time varied in 0.6–2.9 s corresponding to five sampling ports along the axial direction of the reaction zone shown in Fig. 9. For comparison, the figure shows also our previously

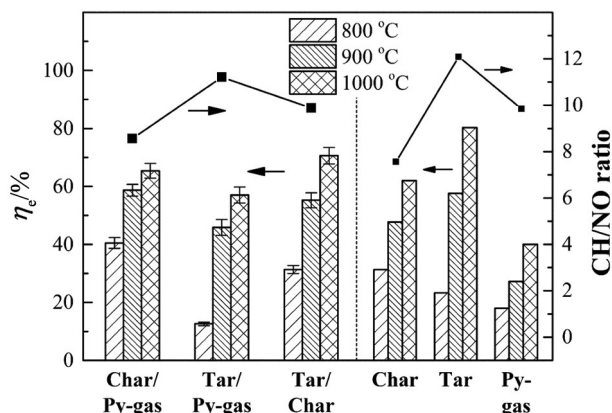


Fig. 8. NO reduction efficiencies by binary reagents with a mass ratio of 1:1 at different temperatures but an SR of 0.7 (Sets 2, 5, 8 in Table 3) and their comparison with efficiencies for individual reagents.

reported η_e by individual reagents char, tar and py-gas varying with residence time. Increasing the residence time facilitated the NO reduction, but a slow increasing tendency manifested for all the binary mixtures. This is similar to the variation tendency with residence time shown for the gas-phase homogeneous NO reductions by gaseous tar or py-gas. We found that the heterogeneous NO reduction by char became dominant only for long reaction time [8], for example, above 1.2 s. Mixing tar or py-gas reagent into char obviously shifted the gas–solid heterogeneous NO reduction to high levels by char in a short residence time. The result complies with the reports of Shu *et al.* [22] and Luan *et al.* [24] who tested the reburning of raw biomass (without pyrolysis) and proved that the residence time little affected its enabled NO reduction when it was above 0.6 s. Thus, the synergetic actions of pyrolysis products on NO reduction, cause the high reaction efficiency, come into play in a short residence time in comparing with that enabled by char. This is much helpful to practical systems in which too long residence time in the fuel-rich reburning zone may cause incomplete combustion of reburning fuel so that the overall combustion efficiency decreases [40].

3.4. Variation with gas species

The preceding results demonstrate that char and py-gas, when fed together, can obviously improve their capabilities for reducing NO, while their mixing with tar is hard to have positive synergetic effect on NO reduction (comparing to pure tar reagent), especially when the content of tar was relatively high. The composition of py-gas, mainly consisting of CO, H₂ and CH₄ (Table 1), was shown to evidently influence the heterogeneous char–NO reaction in fuel reburning [41]. In the CFBDC system the gaseous tar passing through reburning zone of the fluidized char combustor can be further converted into secondary py-gas (*i.e.*, CO, H₂, CH₄, *etc.*) via vapor phase and char-surfaces reactions [42, 43]. Thus, the influence of such gas species (and their contents) in py-gas on heterogeneous char–NO reactions is necessary to be investigated for further understanding the mechanism of synergetic NO reduction among pyrolysis products in CFBDC.

Fig. 10 shows the η_e realized by char mixed with a gas component among CO, H₂ and CH₄ at different mass proportion. The reaction temperature was 900 °C and SR was 0.7 (fuel-rich condition). All tested gas species manifested certain effect on NO reduction by char, but different gases shared certain differences. The achieved η_e is always higher for char/gas mixture than for either individual gas or char reagent at the same feeding mass rate of reactant. Char mixed with different gases had obviously different NO reduction potentials to cause different degrees of promotion on their realized efficiencies η_e against that by char. While the realized NO reduction by char/CO mixture was not much different from the baseline by 100% char, that by char/CH₄ and char/H₂ mixture was evidently higher than the baseline. Especially for the mixture of char and H₂, its realized η_e reached 100% with all tested mass ratios of char. Noting that the efficiencies are for the same feeding mass amount of reactant, the result indicated that the biggest CH/NO molar ratio enabled the highest NO reduction efficiency for case mixing H₂ and char because H has the lowest molecular weight. For the individual reagents, the realized NO reduction efficiency followed the order of H₂ > CH₄ > CO, in accordance with their order of CH/NO ratio. Fuel gas reburning investigations [10, 44] shown that hydrocarbon gases usually facilitate the better NO reduction than non-hydrocarbon gases such as CO

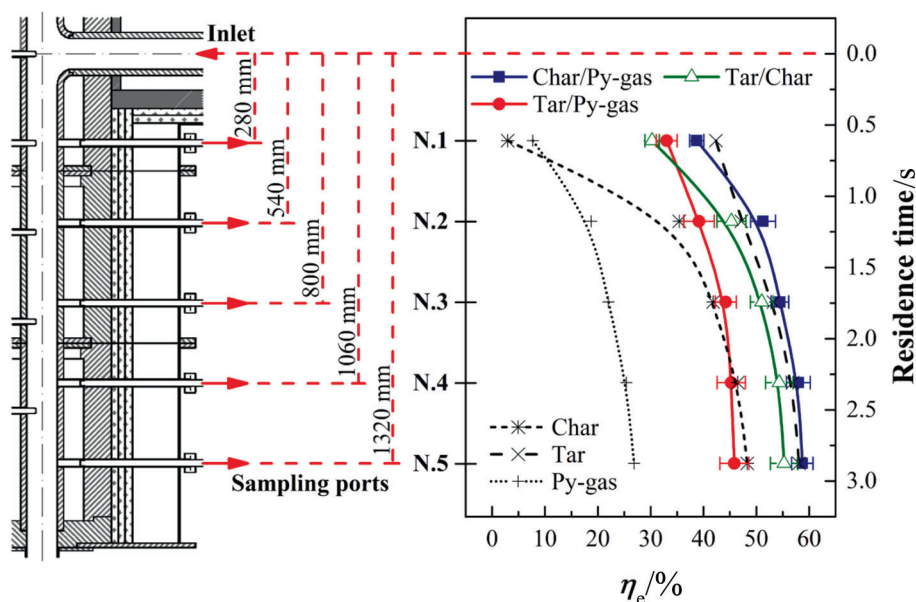


Fig. 9. Variation with residence time in reaction zone for NO reduction efficiencies by binary reagents with a mass ratio of 1:1 at 900 °C and an SR of 0.7 (Sets 2, 5, 8 in Table 3), as compared to the efficiencies by individual reagents.

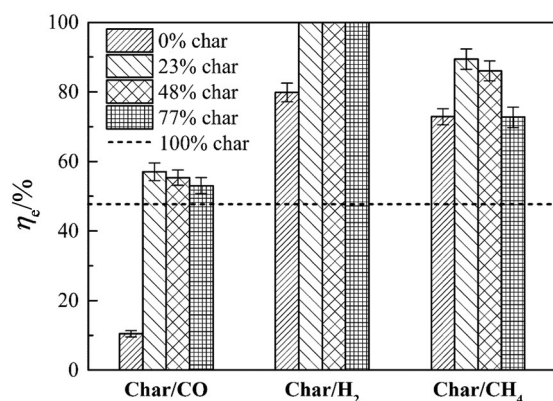


Fig. 10. NO reduction efficiency by the mixture of char with different gas species varying with proportion of char at a reaction temperature of 900 °C and an SR of 0.7 (Sets 10–21 in Table 3).

or H₂ do under the same temperature and fuel-rich condition. The result is consistent with our experiments because in our case the comparison was made on mass basis of reactant so that the efficiencies by gas species are comparable with that by char at the same basic feeding rate. Above all, from Fig. 10 we know that H₂ and CH₄ caused better synergetic effects on NO reduction than CO did when they are mixed with char.

Fig. 11(a)–(c) shows respectively the influences of CO, H₂ and CH₄ as the main components in py-gas on NO reduction by the char/py-gas binary reagent at 900 °C and SR values of 0.6–1.0. Nonetheless, the py-gas had varied proportion of CO, H₂ and CH₄ in Fig. 11(a), (b) and (c), respectively (shown by abscissa). Additionally, the proportion of components in py-gas presented in the plot did not include any inert gas species such as N₂ and CO₂. The feeding rates of reagents in these tests are based on Set 2 specified in Table 3, and the flowrates of each gas species were varied to maintain the total mass rate of all injected reactants to be equal to the feeding mass rate of py-gas specified for Set 2. Obviously, for all tests the mass ratio between char and gas reactant (with different composition) was approximately 1:1. For example, when varying CO proportion in Fig. 11(a) it was done by increasing the CO flowrate but decreasing the flowrate of simulated py-gas so that the total gas mass rate was 0.075 g·min^{−1}. This in fact decreased the proportions of other gases (H₂, CH₄) in the adopted gas reactant. In Fig. 11 the variation in CH/NO molar ratio might determine the variation tendency of NO reduction when varying the proportion of a gas component in the adopted gas reactant. For example, increasing CO proportion did not much improve the realized η_e in Fig. 11(a) because of its caused decrease in the CH/NO molar ratio. In Fig. 11(b) and (c), increasing H₂ and CH₄ proportions in gas reactant actually raised their CH/NO ratios so that their resulting η_e also increased with raising the proportions of H₂ and CH₄ in the gas reactant.

The above results show that the radical pool consisting of C and H atoms is determinative of the realized NO reduction. The presence of CO can facilitate NO reduction by char via following reactions [19, 45]:



Increasing the CO concentration in reactant gas would create more free-active sites C* to enhance reduction of NO, or CO can also react with NO as catalyzed by char. Nonetheless, increasing CO proportion diluted other gas species such as H₂ and CH₄ in reactant to decrease thus their reductions of NO. The enhancement on

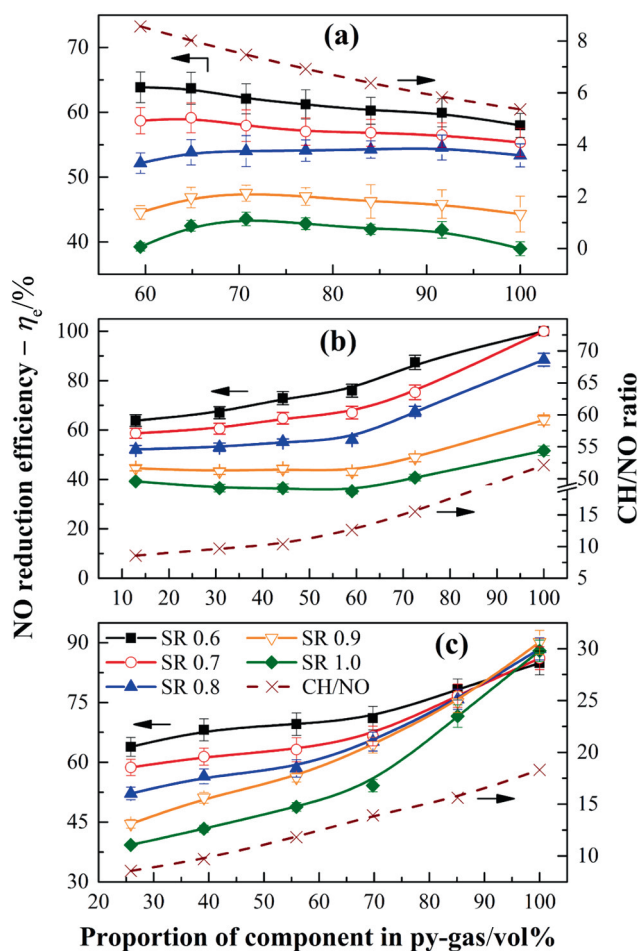
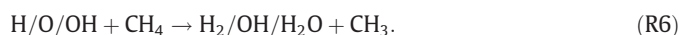


Fig. 11. NO reduction efficiency by char/py-gas reagent at a mass ratio of 1:1 but varying proportion of a specified gas component in py-gas (based on Set 2 in Table 3): (a) CO, (b) H₂, (c) CH₄.

NO reduction by the presented CO is also limited by the available catalytic sites and surfaces of char [18, 19, 34]. Thus, at higher CO proportion the realized NO reduction conversely decreased in Fig. 11(a).

In biomass volatile reburning Glarborg *et al.* [11] and Wu *et al.* [12] reported that the NO reduction by hydrocarbon radicals (CH₃) is the key reaction, and the existing H₂ in reaction zone promotes the formation of CH₃ radical via the following reactions [46]:



Nonetheless, H₂ does not always promote NO reduction as CH₄ does. In Fig. 11(b) and 11(c) the increase in η_e due to raising the H₂ proportion (up to 100%) tended to diminish at high SRs, but for CH₄ such an increase in NO reduction appeared at all tested SRs. When oxygen concentration in reaction zone is high enough, CH₄ oxidation is facilitated to form more CH₃ radicals for reducing NO but H₂ would be rapidly burned out rather than consumed through reactions R3–R5 to form oxidative radicals. This also inhibits the release of NO-reduction radical (CH₃) in reaction R6. Generally, the oxygen/reagent ratio near stoichiometric condition does not favor NO reduction especially for H₂. Fan *et al.* [10] have reported

that NO reduction by simulated biogas at an SR of 0.95 decreased with increasing H₂ proportion, whereas a reverse trend was observed when increasing the ratio of hydrocarbon species.

4. Conclusions

The synergetic effects of binary reagents (mixtures) on NO reduction were studied in an experimental drop-tube reactor to simulate the reburning conditions of biomass pyrolysis products involving in the so-called circulating fluidized bed decoupling combustion (CFBDC) process. The adopted binary reagents included mixtures of two pyrolysis products among char, tar and non-condensable py-gas derived from pyrolyzing distilled spirit lees. At a specified mass rate of 0.15 g·min⁻¹ for such binary reagents, the higher py-gas proportion enabled the better synergetic effect on NO reduction by char/py-gas reagent, but the mixtures consisting of tar only caused a positive effect when tar fraction was below 26%. Increasing reaction temperature from 800 to 1000 °C, the realized NO reduction by binary reagents generally increased but the synergetic effects of a pair of two pyrolysis products were actually not enhanced. Residence time of reagents in reaction zone exhibited certain effect on NO reduction because gaseous tar and py-gas raised efficient homogeneous reactions even at short residence time. The main gas species in py-gas such as CO, H₂, CH₄ manifested different effects on NO reduction by char/py-gas mixture (gas components adjusts py-gas composition), and the identified effect of gas component in py-gas was closely related to the corresponding CH/NO ratio. Both H₂ and CH₄ played important roles in the synergetic NO reduction, while the effect of CO was more insignificant.

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