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Interaction between 2,5-dimethylfuran and nitric oxide. Experimental and modeling study.

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Abstract

In the present work, interaction between 2,5-dimethylfuran (2,5-DMF) and NO has been investigated. The study includes experimental and modeling data on the evaluation of the influence of the temperature, stoichiometry and 2,5-DMF concentration on the NO conversion, as well as on the 2,5-DMF conversion in the presence of NO. The experiments were performed in an isothermal quartz flow reactor at atmospheric pressure in the temperature range 800-1400 K. Some of the results of the present work were compared with experimental and modeling data from an earlier study on 2,5-DMF conversion under similar conditions but in the absence of NO[1]. The results reveal that the temperature, stoichiometry and 2,5-DMF concentration play an important role on the conversion of NO. Likewise, these variables also influence the 2,5-DMF conversion regime in the presence of NO.

1. INTRODUCTION

Nitrogen oxides (NO and NO_2, referred together as NO_x) and particulate matter (PM), mainly soot, are the most critical pollutants produced by diesel engines. Due to the trade-off between the NO_x and PM emissions (mainly because NO_x formation is favored under fuel-lean conditions, while soot is formed when oxygen is lacking) it is difficult to reduce simultaneously both emissions. However, several techniques to reduce together and individually these emissions have been proposed, and fuel reformulation is one of them. In this regard, different studies demonstrate that adding oxygenates to diesel combustibles can substantially reduce PM emissions without significant effects on NO_x emissions.[2, 3, 4, 5]

A candidate to be used as an additive is 2,5-dimethylfuran (C_6H_8O; 2,5-DMF), and in addition to the experiments conducted on diesel engines,[6,7] several experimental and computational studies have explored its pyrolysis and oxidation.[8-15] However, the interaction between 2,5-DMF and pollutants such as NO, to our knowledge, has not been studied yet. Thus, in order to understand which is the principle that governs the reduction of NO in the presence of 2,5-DMF, as well as the pyrolysis and oxidation processes of 2,5-DMF in the presence of NO, both an experimental and modeling efforts are required in this field.

In this context, the aim of the present work was to perform an experimental and kinetic study on the interaction between 2,5-DMF and NO in various reaction environments. Experiments were performed under well-controlled flow reactor conditions over the temperature range of 800 to 1400 K and at atmospheric pressure. Under these conditions, the oxygen concentration was varied from pyrolytic to very fuel-lean conditions. Impact of the inlet C/N ratio value was analyzed, varying the initial 2,5-DMF concentration, i.e. varying the initial atomic C amount. On the other hand, a modeling study was performed using a detailed gas-phase chemical kinetic mechanism compiled from literature and which describes the pyrolysis and oxidation of 2,5-DMF and the interaction of NO with some hydrocarbons. Additionally, experimental data obtained in a previous work, where the experimental conditions were similar to the present work but in the absence of NO[1], have been considered to analyze the influence of the NO presence on the 2,5-DMF conversion.

2. EXPERIMENTAL SECTION

Experiments have been carried out in an atmospheric pressure gas-phase installation. It basically consists on a gas feeding system, a reaction system, and a conditioning and gas analysis system. The setup for this installation has been presented in detail elsewhere,[16,17] and is described here only briefly.

The interaction between 2,5-DMF and NO at atmospheric pressure takes place in a quartz flow reactor, designed for obtaining plug flow conditions,[18] with a reaction zone of 8.7 mm inside diameter and 200 mm in length. The reactor tube is placed in a three-zone electrically heated furnace, insuring a uniform temperature profile within ± 10 K throughout the reaction zone. 2,5-DMF, O_2 and NO, stored in gas cylinders, are fed to the reactor through mass flow controllers and together with water vapor and N_2 are injected at the top of the reactor in up to four separate streams. Water vapor, approximately 6000 ppm, is introduced in the reactor by saturating a N_2 stream through a water bubbler and N_2 is used to achieve a total flow rate of 1000 mL(STP)/min. The gas residence time (t_r) is a function of the temperature in the reaction zone and, for a given total flow rate of 1000 mL(STP)/min, is given by: t_r(s)= 195/T(K). The product gas is quenched at the outlet of the reaction zone by an air flow and, before analysis, it passes through a condenser and a filter to assure gas cleaning. The outlet gas composition is measured using a micro-chromatograph (Agilent 3000A), which detects and quantifies 2,5-DMF, CO, CO_2 and H_2, and continuous Uras 14 IR and Uras 26 IR analyzers from ABB for CO/CO_2 and NO, respectively. Also, a Fourier Transform Infrared (FTIR) spectrometer (Genesis II, Ati Mattson) is used to check the formation of some nitrogen species such as NO_2, N_2O, HCN and NH_3. The uncertainty of the concentration measurements is estimated as ±5%, except for the FTIR spectrometer, which is estimated as ±10%.

3. MODELING SECTION

The experimental results have been analyzed in terms of a detailed gas-phase chemical kinetic mechanism compiled for this investigation, in order to identify the reactions that mainly have influence on the NO conversion in the presence of 2,5-DMF, as well as the 2,5-DMF conversion in the presence of NO under the experimental conditions of the present work. The mechanism used for the simulations is the same used in our previous work focused on pyrolysis and oxidation of 2,5-DMF without NO[1], which is largely based on a work by Sirjean et al.[14] The subsets of the interactions between NO_x with some radicals, C_1/C_2 hydrocarbons, oxygenated hydrocarbons and with other compounds of interest, taken from Alzueta et al.[19] and updated in a number of works,[20,21] were added to the base mechanism. The thermodynamic data were taken from the same source as the subsets of the mechanism. Calculations were performed using the Chemkin[22] software, with the SENKIN plug flow reactor code, assuming temperature and pressure constants in the reaction zone. The full mechanism and thermodynamic data can be found in the Supporting Information.

4. DISCUSSION OF RESULTS

In this work, we have investigated the interaction between 2,5-DMF, a proposed fuel additive[14], and NO. In such a way, the NO conversion in the presence of 2,5-DMF, as well as the 2,5-DMF conversion in the presence of NO were studied. The experiments have been carried out at atmospheric pressure, from pyrolytic to very fuel-lean conditions (specifically, λ=0, 0.3, 0.7, 1, 5 and 30), using different inlet C/N ratio values (0.67 and 2) and in the temperature range of 800-1400 K. Impact of the C/N ratio value has been analyzed by keeping constant the inlet NO concentration (900 ppm) and by varying the initial atomic C amount (600 and 1800 ppm). In this way, the effect of the inlet concentration of 2,5-DMF on the NO conversion has been studied, as well as on its own conversion in the presence of NO. Table 1 summarizes the conditions for each set of experiments, which were all performed under highly diluted conditions to ensure an isothermal reaction zone. Additional experimental data were taken from previous work[1] where the 2,5-DMF conversion was investigated under the same conditions of the present work but in the absence of NO.

4.1. NO conversion in the presence of 2,5-DMF. The NO conversion, at atmospheric pressure using 2,5-DMF, has been studied for different λ values and varying the inlet C/N ratio value, i.e. varying the initial concentration of 2,5-DMF (100 and 300 ppm). Figure 1 shows the experimental data and the model predictions of the NO concentration profile as a function of temperature, for the inlet C/N ratio values of 0.67 and 2, and for all λ values studied. The top figure shows the concentration profile of NO for fuel-rich and stoichiometric conditions, the bottom for fuel-lean conditions. The modeling predictions match the experimental measurements reasonably well, although better predictions are seen for fuel-rich and stoichiometric conditions.

For $\lambda \leq 1$, the concentration of NO decreases as both the temperature and oxygen concentration increase. The model results indicate that under pyrolytic (λ=0), fuel-rich (λ=0.3 and 0.7) and stoichiometric (λ=1) conditions, the reactions between NO and the CH_3 radicals to give nitrogen species, such as HCN and H_2CN (R.1 and R.2), are an important step for the consumption of NO.

$NO+CH_3 \rightleftarrows HCN+H_2O$ (R.1)

$NO+CH_3 \rightleftarrows H_2CN+OH$ (R.2)

For T≥1275 K, the NO conversion is more pronounced because there is an increase in the formation of the CH_3 radicals by the decomposition of the 2,5-DMF. Also, with increasing the concentration of oxygen, eventually λ=0.7 and 1, the greatest reduction of NO is because in these conditions, besides R.1 and R.2, reactions between NO and the CH_3O_2 /HO_2 radicals to give NO_2 (R.3 and R.4) become important as well.

$NO+CH_3O_2 \rightleftarrows NO_2+CH_3O$ (R.3)

$NO+HO_2 \rightleftarrows NO_2+OH$ (R.4)

Reactions R.3 and R.4 become more important under fuel-lean conditions (λ=5 and 30). For these leaner conditions, the CH_3 radicals are not consumed by R.1 and R.2. Nevertheless, they react with molecular oxygen to give the CH_3O_2 radicals (R.5), which react with NO according to R.3.

$CH_3+O_2(+M) \rightleftarrows CH_3O_2(+M)$ (R.5)

On the other hand, the HO_2 radicals are formed significantly by reaction between the H radicals, produced by the decomposition of the 2,5-DMF, and the molecular oxygen, as shown in reaction R.6, reaction that is considerably favored under very fuel-lean conditions.

$H+O_2(+M) \rightleftarrows HO_2(+M)$ (R.6)

Under fuel-lean conditions (λ=30) and for the lowest temperatures considered in the present work, the calculations show that the NO concentration diminished as a result of the $NO \rightarrow NO_2$ conversion (R.3 and R.4). However, as the temperature is increased, NO_2 reacts with the radical pool, basically by the reactions R.7 or R.8, and NO begins to become dominant again. The present results suggest that the NO/NO_2 inter-conversion does not contribute to a net NO removal. In this way, under the conditions of this work, 2,5-DMF is not seen to exert negative influence on the NO emissions. However, a beneficial effect adding 2,5-DMF is not observed either.

$NO_2+H \rightleftarrows NO+OH$ (R.7)

$NO_2+O \rightleftarrows NO+O_2$ (R.8)

The no detection of HCN in none of the experiments under fuel-rich and stoichiometric conditions, suggests that under the conditions of the present work, HCN readily forms N_2 or N_2O by consecutives reactions, which can be found through model calculations, as shown below:

$HCN+CH_3 \rightleftarrows CH_3CN+H$ (R.9)

$CH_3CN+H \rightleftarrows CH_2CN+H_2$ (R.10)

$CH_2CN+O \rightleftarrows CN+CH_2O$ (R.11)

$CN+O_2 \rightleftarrows NCO+O$ (R.12)

$NCO+NO \rightleftarrows N_2+CO_2$ (R.13)

$NCO+NO \rightleftarrows N_2O+CO$ (R.14)

4.2. 2,5-DMF conversion in the presence of NO. The inlet C/N ratio, i.e. C amount, has been found to influence the NO conversion. Thus, it may be interesting to evaluate if this ratio value has also an influence on the 2,5-DMF conversion. In this context, Figure 2 shows the $[2,5\text{-DMF}]_{out}/[2,5\text{-DMF}]_{in}$ ratio values as a function of temperature for the C/N ratio values of 0.67 and 2 and for the different λ values studied. Figure 2 shows that the inlet C/N ratio is seen to have a slight influence on the 2,5-DMF only to fuel-lean conditions, i.e, λ=30 (Figure 2c), although model calculations show no appreciable influence. However, in our previous study[1], we detected that in the absence of NO and λ=30, the concentration of 2,5-DMF is seen to have a considerable influence on the its conversion, and for the higher concentration (300 ppm), the onset of the consumption of 2,5-DMF is shifted at lower temperatures (Figure 3). Calculations indicate that for λ=30 and both in the absence and presence of NO, 2,5-DMF is consumed mainly by OH-addition to form acetylene, the acetyl radical and acetaldehyde, according to the reaction R.15.

$C_6H_8O+OH \rightleftarrows C_2H_2+CH_3CO+CH_3CHO$ (R.15)

This fact suggests that the onset of the 2,5-DMF conversion, in the absence and presence of NO under very fuel-lean conditions, is determined by the concentration of the OH radicals in the reaction environment. While in the presence of NO, the OH radicals are formed by the reaction between the NO and HO_2 radicals (R.4), in the absence of NO, the principal step to the formation of the OH radicals depends on the concentration of 2,5-DMF: the reaction between the H radicals and O_2 (R.16), and the decomposition of the H_2O_2 radicals (R.17), for 100 and 300 ppm, respectively. Both the H and H_2O_2 radicals are formed from 2,5-DMF.

$H+O_2 \rightleftarrows O+OH$ (R.16)

$H_2O_2(+M) \rightleftarrows OH+OH(+M)$ (R.17)

For λ=30, 100 ppm of 2,5-DMF and in the absence of NO, the H radicals are consumed by their reactions with oxygen to yield HO_2 or to yield O and OH through reactions R.6 and R.16, respectively. The competition between both reactions diminishes the production of the OH radicals, and consequently diminishes the rate of the reaction R.15. However, H_2O_2 is only consumed by the reaction R.17 (reaction belongs to the case of 300 ppm of 2,5-DMF), consequently, the OH radicals are largely formed and increment the rate of the reaction R.15, shifting the onset of consumption of 2,5-DMF at lower temperatures.

With the aim of understanding the influence of the presence of NO on the 2,5-DMF conversion for a given inlet 2,5-DMF concentration and different λ values, Figure 4 shows an example of the comparison between the concentration profiles of 2,5-DMF, as well as the main products (CO, CO_2 and H_2), in the absence and presence of NO for 100 ppm of 2,5-DMF, λ=0, 0.7 and 30, and at atmospheric pressure. Similar trends are found for 300 ppm of 2,5-DMF (not shown). The model agrees well with the experimental data obtained, although certain discrepancies are seen for λ=30.

Under pyrolytic conditions (λ=0), the concentration profile of 2,5-DMF, as well as the concentration profile of the pyrolytic products (CO, H_2 and CO_2 in a minor amount), are not modified by the presence of NO. This suggests a similar governing chemistry in these experiments. Under these conditions, both in the absence and presence of NO, CO and H_2 are formed by decomposition of CH_3CO radicals (R.18) and by hydrogen abstraction from methyl group of 2,5-DMF to yield the resonance-stabilized 5-methyl-2-furanylmethyl radical ($R1C_6H_7O$) (R.19), respectively.

$$CH_3CO(+M) \rightleftarrows CH_3+CO(+M) \qquad (R.18)$$

$$C_6H_8O+H \rightleftarrows R1C_6H_7O+H_2 \qquad (R.19)$$

Under fuel-rich and stoichiometric conditions (λ=0.3, 0.7 and 1), the presence of NO does not influence the concentration profile of 2,5-DMF. As an example, Figure 4 shows the results obtained for λ=0.7. However, under these environments and at intermediate and high-temperatures, the presence of NO acts to diminish the formation rate of the oxidation products (CO, CO_2 and H_2). Calculations show that at low temperature (about 1125 K), the formation of CO and H_2 is initiated by reactions R.18 and R.19, respectively. This occurs for both the absence and presence of NO. Nonetheless, with increasing temperature, reactions involving other radicals, such as, CHCO and CHO, as well as some product intermediates, begin to be more important to the formation of CO and H_2. The presence of NO leads to the occurrence of competing reactions, which act to diminish the concentration of the radicals that produce CO and H_2. The formation of CO_2 is originated by the reaction of CO with the radical pool, basically with the OH radicals.

Under fuel-lean conditions (λ=5 and 30, shown as an example for λ=30 in Figure 4), the presence of NO shifts the onset of 2,5-DMF consumption to lower temperatures, advancing consequently the beginning of the formation of the combustion products (CO and CO_2). This behavior is caused by the higher concentration of the radicals in the reaction environment which react with 2,5-DMF. In the absence of NO, competing reactions occur, which reduce the formation of the radicals, as is explained above in the absence of NO, Figure 3.

Summarizing, from fuel-rich to stoichiometric conditions, and for the intermediate and high temperatures considered in this work, the presence of NO origins competing reactions, which act to diminish the formation rate of the products. On the other hand, under fuel-lean conditions and for the low temperatures of this work, the presence of NO increases the formation of the radicals which react with 2,5-DMF, shifting thus the profile concentration of 2,5-DMF at lower temperatures.

Sensitivity analyses for the conversion of CO were carried out in order to identify the reactions affecting more the results. Sensitivity plots can be found in the Supporting Information**.**

5. CONCLUSIONS

The NO conversion in the presence of 2,5-DMF and the 2,5-DMF conversion in the presence of NO have been investigated in a quartz flow reactor, at atmospheric pressure, by varying the temperature, the stoichiometry and the 2,5-DMF concentration. The experimental results have been interpreted in terms of a detailed chemical kinetic mechanism, through which the main reactions involved in the interaction between NO and 2,5-DMF, under the experimental conditions studied here, have been identified.

Experimental and theoretical results are, in general, in good agreement, and show that, for fuel-rich conditions, with increasing temperature, oxygen and 2,5-DMF concentration, the NO conversion increases. However, under fuel-lean conditions and in the intermediate and high-temperature interval, NO after reaching a minimum, starts be formed again by the reactions between NO_2 and the radical pool. In this way, the inter-conversion NO/NO_2 does not contribute to a net NO removal, and according to the conditions tested, high λ values (λ=30), high 2,5-DMF concentration (300 ppm) and low temperatures (about 900 K) result in the greatest conversion of NO to NO_2. Under the conditions of the work, 2,5-DMF is not seen to exert negative influence on the NO emissions. However, a beneficial effect adding 2,5-DMF is not observed either. On the other hand, the concentration of 2,5-DMF, both in the absence and the presence of NO, does not have an appreciable influence on the 2,5-DMF conversion under fuel-rich and stoichiometric conditions (λ=0.3 and 1). For fuel-lean conditions (λ=30), the influence of 2,5-DMF concentration on its conversion is appreciable, and is more noticeable in the absence of NO. Also, under pyrolytic conditions and for a given inlet 2,5-DMF concentration, the presence of NO does not modify the 2,5-DMF conversion regime. However, from fuel-lean to fuel-rich conditions, the presence of NO modifies the 2,5-DMF oxidation regime by varying the concentration of the radical pool.

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Notes

The authors declare no competing financial interest.

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ASSOCIATED CONTENT

Supporting Information

Detailed kinetic mechanism and thermodynamic data in Chemkin Format and sensitivity plots. This material is available free of charge via the Internet at http://pubs.acs.org.

Figure captions

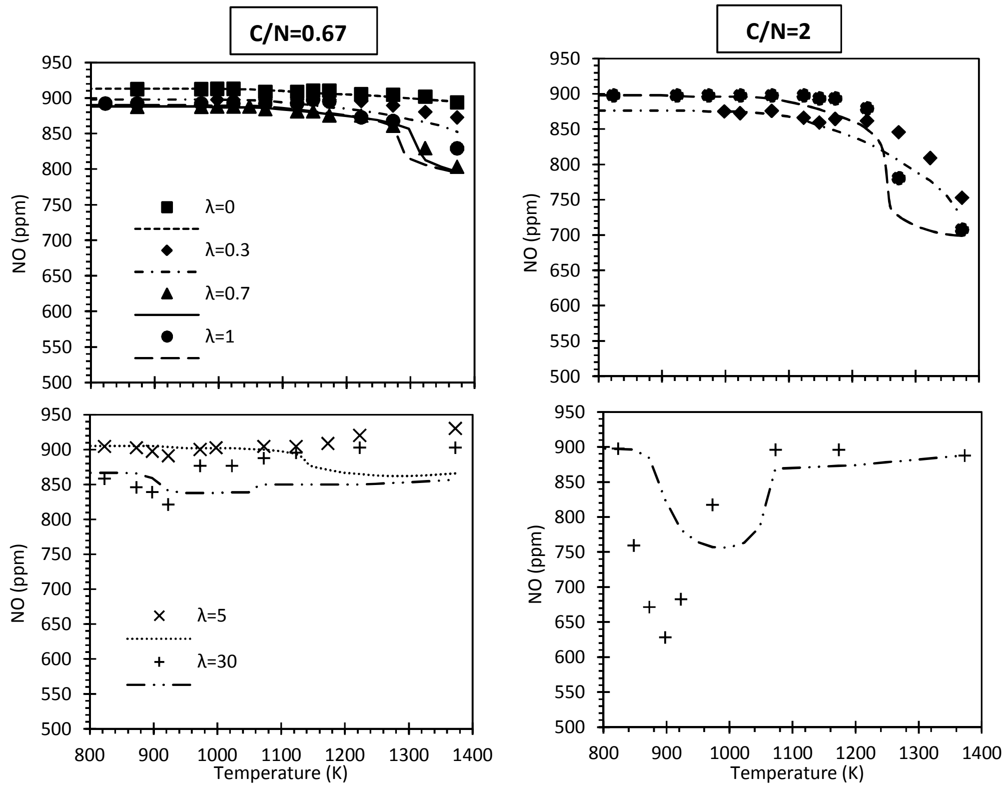
Figure 1. Concentration profile of NO as a function of temperature for C/N=0.67 and 2, at atmospheric pressure. In the top, fuel-rich and stoichiometric conditions (sets 1, 3, 4, 6, 10 and 11 in Table 1) and, in the bottom, fuel-lean conditions (sets 7, 8 and 12 in Table 1). Symbols denote experimental data and lines denote model predictions.

Figure 2. $[2,5\text{-DMF}]_{out}/[2,5\text{-DMF}]_{in}$ ratio values as a function of temperature for C/N=0.67 and 2, and λ=0.3, 1 and 30, at atmospheric pressure (2a tied to sets 3 and 10, 2b to sets 6 and 11 and 2c to sets 8 and 12 in Table 1). Symbols denote experimental data and lines denote model predictions.

Figure 3. $[2,5\text{-DMF}]_{out}/[2,5\text{-DMF}]_{in}$ ratio values as a function of temperature for λ=30, at atmospheric pressure and in the absence of NO (sets 9 and 13 in Table 1). Symbols denote experimental data and lines denote model predictions.

Figure 4. Interaction with NO of 100 ppm of 2,5-DMF, for λ=0, 0.7 and 30, and at atmospheric pressure. Full symbols: experimental data without NO. Empty symbols: experimental data with NO. Lines with full symbols: model predictions without NO. Lines with empty symbols: model predictions with NO. Data in the absence of NO correspond to sets of a previous work[1] and data in the presence of NO correspond to sets 1, 4 and 8 in Table 1 of the present work.

Figures



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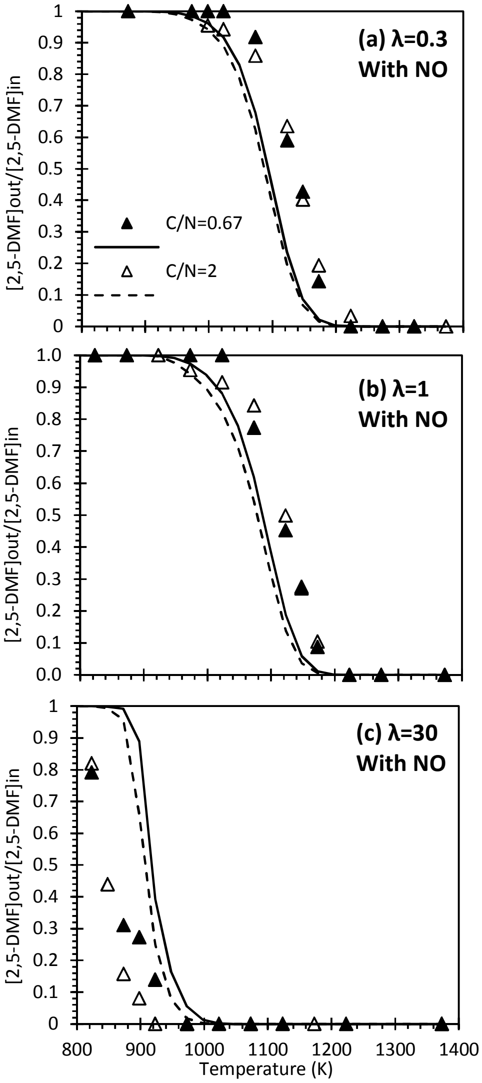

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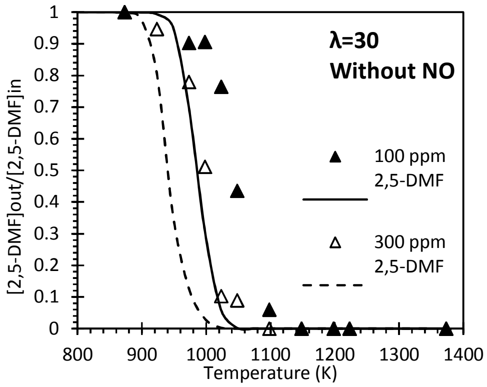

Figure 3. $[2,5\text{-DMF}]_{out}/[2,5\text{-DMF}]_{in}$ ratio values as a function of temperature for λ=30, at atmospheric pressure and in the absence of NO (sets 9 and 13 in Table 1). Symbols denote experimental data and lines denote model predictions.

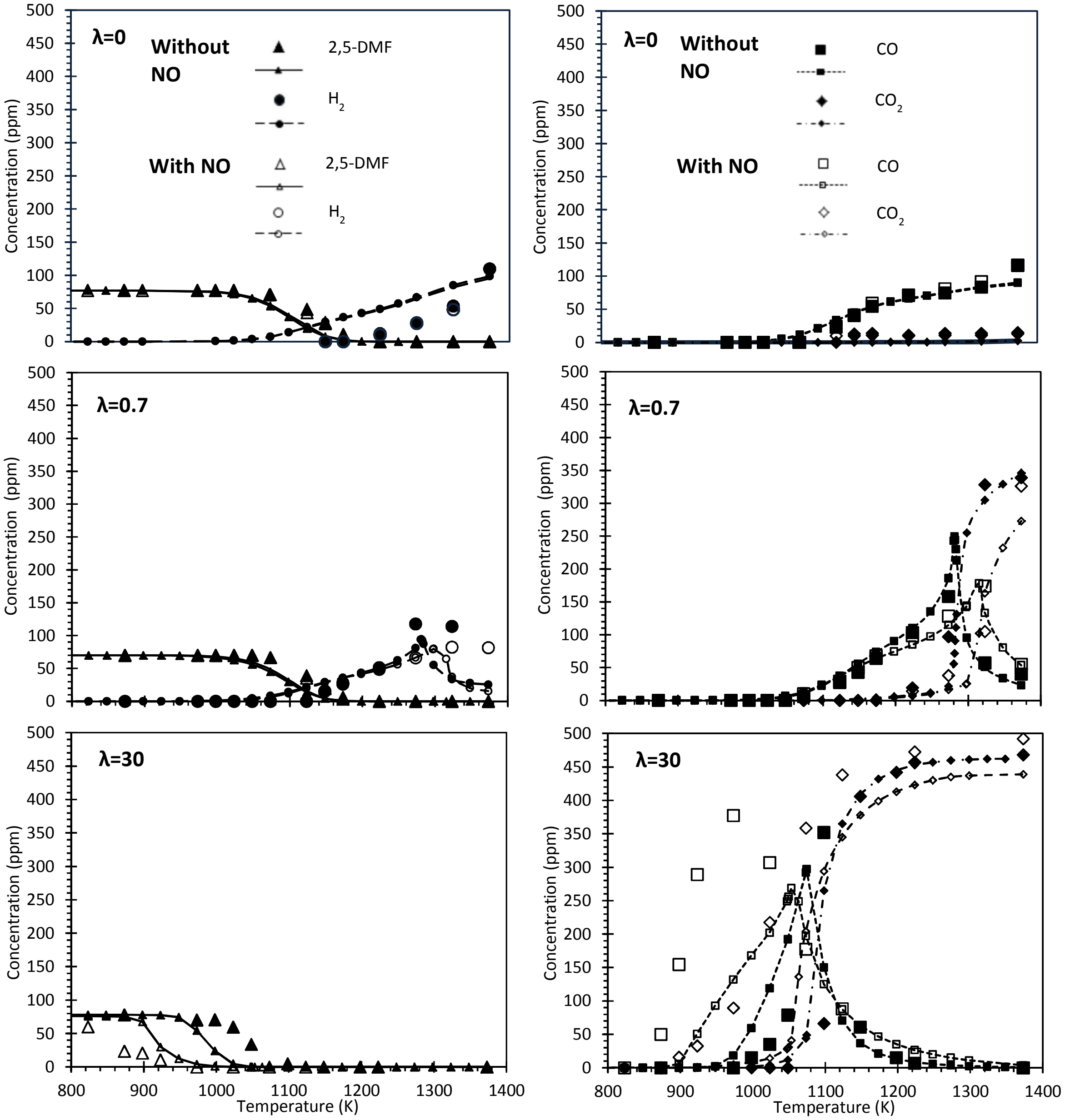

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Table

Table 1. Experimental conditions: T= 800-1400 K, flow rate=1000 mL(STP)/min, t_r(s)= 195/T(K). N_2 is used to close the balance.

set	C_6H_8O (ppm)	O_2 (ppm)	λ	NO (ppm)	C/N molar ratio	Reference[a]
1	100	0	0	900	0.67	pw
2	100	0	0	0	-	Alexandrino et al.[1]
3	100	225	0.3	900	0.67	pw
4	100	525	0.7	900	0.67	pw
5	100	525	0.7	0	-	Alexandrino et al.[1]
6	100	750	1	900	0.67	pw
7	100	3750	5	900	0.67	pw
8	100	22500	30	900	0.67	pw
9	100	22500	30	0	-	Alexandrino et al.[1]
10	300	675	0.3	900	2	pw
11	300	22500	1	900	2	pw
12	300	67500	30	900	2	pw
13	300	67500	30	0	-	Alexandrino et al.[1]

[a] pw denotes present work.

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