Heterogeneous and platinum-initiated homogeneous combustion of nitrogen-containing heterocyclic compounds in the argon and water vapor media at elevated pressure

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Abstract. The paper presents the results on the oxidation of pyrrole and pyridine in the argon and water vapor media at high pressure and uniform heating of the tubular stainless steel reactor to 823 K. Experiments were carried out with lean and stoichiometric mixtures (fuel equivalence ratio \( \phi = 0.78-1.0 \)) at their dilution level \( x_D = 36-65\% \) mol. Based on the time dependences of the reaction mixture temperature, it is revealed that oxidation proceeds via the mechanisms of homogeneous and heterogeneous reactions. It was found that the oxidation rate of pyrrole depends on the amount of corrosion products accumulated on the reactor wall. It is shown that a Pt-Rh/Pt thermocouple inserted into the center of the reaction volume intensifies pyridine oxidation in the near-surface region. The difference in the oxidation mechanisms of pyrrole and pyridine is explained by the structure of their molecules.

1. Introduction

In comparison with the conventional methods, combusting fuel directly in the heat-carrier (water vapor or supercritical water) has several advantages, of which the main are the minimization of heat losses, and the low process temperature (\( T \leq 923 \) K). Since fossil fuels and biomass contain nitrogen, localized mainly in pyrrole and pyridine structural fragments, and because pyrrole and pyridine, as well as their alkyl derivatives, are present in the composition of the product of hydrothermal conversion [1–3], the study of the oxidation features of nitrogen-containing heterocyclic compounds in the water medium is of great practical importance.

When studying pyrrole oxidation using a flow quartz reactor (700–1500 K, 0.1 MPa) it was revealed [4] that the process is mainly initiated by isomerization through thermal rearrangement into pyrroline and by hydrogen abstraction together with the formation of pyrrolyl radical. The data on pyrrole oxidation in the laminar pyrrole/O\(_2\)/Ar flames [5] indicate that N\(_2\), NO, and NO\(_2\) are the major nitrogenous products, while hydrogen cyanide, isocyanic acid, and 2-propenenitrile are the most important nitrogen-containing intermediates. Based on the results of research on the composition of pyridine oxidation products in the O\(_2\)/Ar mixture (1000–2200 K, 8.0–20 atm) using a single-pulse shock tube, a kinetic model is proposed in [6], according to which the oxidation is initiated both by the separation of the H atom from the pyridine molecule and by the bimolecular reaction of pyridine with oxygen to form an ortho-pyridyl radical. The results of comparative analysis of pyrrole and pyridine oxidation in the Ar medium (1100–1800 K, 200–560 kPa) show [7] that the ignition delay times for pyridine were consistently shorter than the corresponding delay times measured for pyrrole. When studying the effect of water vapor on the oxidation of pyridine and pyrrole (1273 K, 0.1 MPa), it was
found [8] that water inhibits NO formation, and the inhibitory effect would become stronger with a higher concentration of water. When studying the oxidation of pyridine in supercritical water (699–798 K, 27.6 MPa) using a continuous-flow reactor, it was revealed [9] that the process is initiated by the separation of the H atom from the pyridine molecule, followed by hydroxylation of the aromatic ring and formation of hydroxypyridine. According to [9], pyridine oxidation proceeds through the formation of amines first, and then ammonia as the main intermediates. When studying the oxidation of pyridine in supercritical water (22 MPa, and an excess of oxidizer by 300%) using a coiled tubular reactor and H₂O₂ as an oxidizer, it is shown [10] that when the temperature increases from 623 to 873 K, the proportion of nitrogen, converted into N₂ increases from 13 to 65%; and the maximum yield of nitrate ions and ammonia is observed at 673 and 723 K, respectively. In the present work, the effect of fuel equivalence ratio and dilution level of the reaction mixture with argon or water vapor on the product composition, as well as pyrrole and pyridine oxidation dynamics at elevated pressure were investigated for the first time.

2. Experimental procedures
The tests were performed with the use of an experimental setup [11], whose main component is the tubular reactor (with an internal diameter of 3.0 cm and the volume of 67.1 cm³) made of stainless steel. The reactor was placed in a furnace heated by a resistive heater. The heating rate was controlled using a thermo-programmer and a chromel-alumel thermocouple $T_{\text{out}}$ mounted on the outer wall of the reactor. Additionally, the reactor temperature was measured by two chromel-alumel thermocouples, located at reactor edges. The temperature of the reaction mixture $T_{\text{in}}$ was measured by a Pt-Rh/Pt (S-type) or nicrosil-nisol (N-type) thermocouple inserted into the center of the reaction volume. The reagents pressure was measured by a membrane strain gauge. The temperature and pressure measurement errors were ±0.5 K and ±0.03 MPa, respectively. Time dependences of temperature were recorded with a frequency of 10 Hz. The reagents were fed into the reactor vacuumed through the capillary, welded to the central part of the reactor sidewall via the adjusting valve. The volume of the reactor located inside the furnace (the reaction volume) was 67.1 cm³, while the volume of the reactor outside the furnace (input channel of the reactor for the thermocouple and the capillary, connecting the reactor with a valve to supply the reagent, and a valve of the pressure sensor) was 1.8 cm³.

In tests 1, 2, and 8, 9, where argon was used as a diluent, to prevent pyrrole and pyridine condensation in non-heated reactor volumes, they were filled with water. To do this, the reactor was fed with a certain amount of water injected using a syringe through the rubber diaphragm installed on the connecting branch of the reagent flow valve. Then the reactor was heated up to $T_{\text{out}} = 403$ K and thermostated for 45 min; at that, some water (≈ 1.8 cm³) was condensed in the non-heated volumes. After dropping pressure at $T_{\text{in}} = 403$ K, the water pressure in the reactor was 0.1 MPa. After cooling the reactor to 303 K, it was filled with a certain amount of pyrrole and pyridine, using syringe, argon, and oxygen to a given pressure. In tests 3–7 and 10–14, where water vapor was used as a diluent, the filling of the non-heated volumes was similar to tests 1, 2, and 8, 9. Fuel (pyrrole or pyridine), water, and oxygen to a predetermined pressure were fed into the reactor at 303 K. Then the reactor was heated at the rate of 1 K·min⁻¹ to a set temperature. After reaching the set temperature (≤ 873 K), the reactor was cooled at a rate of ≈ 6 K·min⁻¹ to room temperature. The composition and amounts of volatile reactants were determined using quadruple mass spectrometer MS 7303 according to the method [12]. After completing all tests, the corrosion of structural materials was observed due to the formation of nitric acid. Using X-ray diffraction analysis, Fe₂₆₆O₆, CrFeO₃, CuO, and Cu₃O were detected in the composition of corrosion products [11]. Tests with pyrrole were conducted in the presence of corrosion products (tests 1, 3–6) and after their removal from the reactor (tests 2, 7). When studying pyridine oxidation, corrosion products were removed from the reactor after each test.

3. Results and discussion
Table 1 shows the amount of the reagents and diluent ([Fuel], [O₂], and [D]) in the heated part of the reactor, the fuel equivalence ratio $\phi$, the dilution level $x_D$ of the mixture, the heat capacity of the
reaction mixture \( C_v \), the temperature increment of the reaction mixture in adiabatic conditions \( \Delta T_{ad} \), the reaction mixture temperature corresponding to fuel ignition \( T_{in}^{*} \), the oxidation duration \( t_{ox} \), the temperatures of the reactor wall \( T_{out}^{\text{max}} \) and the reaction mixture \( T_{in}^{\text{max}} \) corresponding to the maximum heat release, and the maximum increment of the reaction mixture temperature \( \Delta T_{\text{max}} \). The amounts of reagents and diluents were determined based on their temperature and partial pressure, as well as reactor volume occupied by gases using the reference \( P–\rho–T \) data [13]. The fuel equivalence ratio \( \phi \) was calculated based on the stoichiometry of the following reactions

\[
\begin{align*}
C_4H_8NH + 5.25O_2 &\rightarrow 4CO_2 + 2.5H_2O + 0.5N_2, \quad \Delta H^{298} = -2287 \text{ kJ mol}^{-1}, \\
C_6H_5N + 6.25O_2 &\rightarrow 5CO_2 + 2.5H_2O + 0.5N_2, \quad \Delta H^{298} = -2432 \text{ kJ mol}^{-1}.
\end{align*}
\]

Taking into account data [14], we believe that heat release during pyrrole and pyridine oxidation in the context of the present work occurs on the reactor wall and in the volume of the reaction mixture. The exothermic reactions on the reactor wall almost do not affect the indications of the thermocouple \( T_w \) due to the high heat capacity \( c = 548 \text{ J(} \text{kg} \cdot \text{K})^{-1} \) of stainless steel, as well as the stabilizing effect of the thermo-programmer, which regulates the reactor heating by reducing the heater power. Under adiabatic conditions, heat release at complete pyrrole and pyridine oxidation \((\text{Fuel}) = 10.1 \text{ and 9.9 mmol}, \quad Q = 23.1 \text{ and 24.1 kJ, respectively}) \) could have led to an increase in the reactor temperature, whose mass was \( m_w = 3.6 \text{ kg, by } \approx 12 \text{ K or the temperature of the gas contained in the reactor at homogeneous combustion – by several thousand degrees (table 1).}

| Test | Amount (mmol) | \( \phi \) | \( x_D \) | \( C_v \) | \( \Delta T_{ad} \) | \( T_{in}^{*} \) | \( t_{ox} \) | \( T_{out}^{\text{max}} \) | \( T_{in}^{\text{max}} \) | \( \Delta T_{\text{max}} \) |
|------|---------------|-------------|---------|-------|----------------|-------------|--------|---------------|---------------|-------------|
| Pyrrole | | | | | | | | | | |
| 1 | 10.1 | 53.0 | 100 | 1.00 | 61 | 3.7 | 6243 | 560 | 143 | 592 | 696 | 106 |
| 2 | 10.1 | 52.8 | 100 | 1.00 | 61 | 3.7 | 6243 | 535 | 235 | 609 | 817 | 209 |
| 3 | 10.1 | 58.0 | 60 | 0.91 | 47 | 4.7 | 4915 | 619 | 108 | 638 | 871 | 235 |
| 4 | 10.1 | 58.0 | 60 | 0.91 | 47 | 4.7 | 4915 | 608 | 82 | 622 | 827 | 208 |
| 5 | 10.1 | 61.2 | 60 | 0.87 | 46 | 4.6 | 5021 | 611 | 93 | 624 | 820 | 199 |
| 6 | 10.1 | 56.9 | 110 | 0.93 | 62 | 6.8 | 3397 | 612 | 155 | 620 | 763 | 145 |
| 7 | 10.1 | 56.9 | 110 | 0.93 | 62 | 6.6 | 3500 | 619 | 197 | 679 | 694 | 18 |
| Pyrrole | | | | | | | | | | |
| 1 | 7.4 | 45.8 | 100 | 1.01 | 65 | 3.4 | 5252 | 544 | 129 | 668 | 1641 | 977 |
| 2 | 7.4 | 46.1 | 100 | 1.00 | 65 | 3.4 | 5275 | 545 | 191 | 684 | 684 | 4 |
| 3 | 9.9 | 63.4 | 50 | 0.98 | 41 | 4.5 | 5338 | 587 | 186 | 679 | 1086 | 410 |
| 4 | 9.9 | 62.7 | 100 | 0.99 | 58 | 6.6 | 3645 | 608 | 169 | 662 | 749 | 91 |
| 5 | 9.9 | 79.8 | 50 | 0.78 | 36 | 4.9 | 4932 | 518 | 143 | 658 | 1728 | 1074 |
| 6 | 9.9 | 77.9 | 100 | 0.79 | 53 | 7.0 | 5445 | 550 | 214 | 659 | 734 | 78 |
| 7 | 9.9 | 78.7 | 100 | 0.79 | 53 | 7.0 | 5445 | 552 | 178 | 675 | 677 | 6 |

Figure 1 presents the temperature difference \( \Delta T = T_{in} - T_{out} \) versus \( T_{out} \) during the pyrrole oxidation in the argon (tests 1, 2) and water vapor (tests 3–7) media. Here and below \( T_{out} \) corresponds to a given increase in the reactor wall temperature at the rate of 1 K min\(^{-1} \), and \( T_{in} \) is the reactant temperature, measured using the internal thermocouple. It can be seen that against the background of an increase in \( T_{out}(t) \), a temperature increment \( \Delta T(t) \), caused by the ignition of \( C_4H_8NH/O_2 \) mixture, was observed in all the test. Table 1 shows that the ignition temperature of pyrrole \( T_{in}^{*} \) in the argon medium is \( \approx 50 \text{ K lower than that in water vapor (varies within the range of 608–619 K), primarily due to the lower heat capacity of the } C_4H_8NH/O_2/Ar \text{ mixture. At the same time, the ignition temperature of pyrrole } T_{in}^{*} \text{ in water vapor decreases as corrosion products accumulate on the reactor wall. Besides, the values of the} \)
reactor wall temperature $T_{\text{out}}^{\max}$, corresponding to the maximum heat release, and the maximum temperature increment of the reaction mixture $\Delta T^{\max}$, as well as the oxidation time $t_{\text{ox}}$ decrease in the presence of corrosion products. This means that the corrosion products have a catalytic effect on the oxidation of pyrrole. In this case, the heterogeneous stage precedes the homogeneous stage, whose intensity depends on the amount of oxygen unspent for heterogeneous oxidation.

Table 2 shows the values of the carbon burn-up degree $Y_C$ and the fraction of nitrogen $X_N$ converted into $N_2$, calculated by the formula proceeding from the results of the mass spectrometric analysis of oxidation products:

$$Y_C = 100\% \frac{n(CO_2)}{i\cdot n_0(C,H,N)}, \quad X_N = 100\% \frac{n(N_2)}{0.5\cdot n_0(C,H,N)},$$

(3)

Here $C,H,N$ is the symbolic representation for pyrrole or pyridine; $i$ and $j$ are the stoichiometric coefficients. From these data, it can be seen that when pyrrole is oxidized in the argon medium in the presence of corrosion products (test 1), the values of $Y_C$ and $X_N$ are less than those indicated in the absence of corrosion products (test 2) primarily due to a smaller increase in temperature $\Delta T^{\max}$ in test 1 (table 1). A decrease in the value of $\varphi$, and the accumulation of corrosion products in the reactor at a constant water vapor density (tests 3–5) contribute to an increase in the values of $Y_C$ and $X_N$. An increase in the water density (test 7) prevents complete oxidation of pyrrole not only due to a decrease in the temperature increment $\Delta T^{\max}$ because of the high heat capacity of the reaction mixture (table 1) but also due to the manifestation of cage effect [15,16].

**Figure 2** shows the change in the temperature difference $\Delta T$ depending on $T_{\text{out}}$ during the oxidation of pyridine in the argon (tests 8, 9) and water vapor (tests 10–14) media. It can be seen that when measuring the reaction mixture temperature using an S-type or N-type thermocouples, the pyridine oxidation dynamics and mechanisms differ. When measuring temperature $T_{\text{in}}$ using an N-type
thermocouple, both in the argon medium (test 9) and the water vapor (test 14), heterogeneous oxidation prevails on the reactor wall, which is indicated by a small temperature increment of the reaction mixture $\Delta T_{\text{max}}$ (table 1). When measuring the temperature $T_{\text{in}}$ using an S-type thermocouple, the dynamics of pyridine oxidation is determined by both the fuel equivalence ratio $\phi$ and the water vapor density. The ignition temperature of pyridine $T_{\text{in}}^*$ varies from 518 to 608 K and decreases with a decrease in the value of $\phi$ and the heat capacity of the reaction mixture.

**Figure 2.** Temperature dependences of difference in temperature ($\Delta T = T_{\text{in}} - T_{\text{out}}$) of reactants in the center of the reactor ($T_{\text{in}}$) and the external reactor wall ($T_{\text{out}}$) during pyridine oxidation in the argon and water vapor media.

From the comparison of the results of tests 8, 13, and 9, 14, it follows that when measuring the temperature with the Pt-Rh/Pt thermocouple, pyridine oxidation is initiated on thermocouple surface, that is, apparently, a consequence of dissociative adsorption of oxygen and pyridine on the platinum surface [17,18]. Figure 1 shows that in the Ar medium (test 8) and at a low water vapor density (test 12), oxidation was accompanied by detonation; at that, the maximum temperature increment of the reaction mixture was $\Delta T_{\text{max}} = 977$ and 1074 K, respectively (table 1). A decrease of the oxygen content in the reaction mixture and an increase in the water vapor density contributed to a decrease in the maximum temperature increment $\Delta T_{\text{max}}$. Besides, at a high water vapor density, pyridine oxidation was accompanied by numerous short-term temperature jumps $\Delta T$ against the background of a slight temperature increment of the reaction mixture (curves 11 and 13, fig. 2). Obviously, these temperature jumps on the Pt-Rh/Pt thermocouple were initiated by the oxygen, accumulated progressively on its surface. The high density and heat capacity of water vapor could prevent the spread of pyridine oxidation into the gas phase.

As it can be seen in table 2, the lowest values of the carbon burn-up degree $Y_C$ and the nitrogen fraction $X_N$ converted into $N_2$ were detected when the amount of $O_2$ in the reaction mixture was close to stoichiometric and high water vapor density (test 11), while the highest values were detected at the excess of $O_2$ and low water vapor density (test 12). As in the case of pyrrole oxidation, this indicates that the high density of water vapor prevents complete oxidation of the fuel. On the other hand, the presence of small amounts of water vapor contributes to an increase in the oxidation rate of pyridine that is manifested by a lower temperature $T_{\text{out}}^{\text{max}}$, which corresponds to the maximum heat release when pyridine is oxidized in water vapor (test 12) as compared to its oxidation in the Ar medium (test 8). According to [19], one of the reasons for this may be the additional generation of OH radicals when water molecules dissociate on the platinum surface in the presence of adsorbed oxygen.

The difference in the dynamics and oxidation mechanisms of pyrrole and pyridine is explained by the structure of their molecules. The presence of an N–H bond in the pyrrole molecule can contribute...
to its adsorption on the surface of metal oxides, and increase the contribution of heterogeneous oxidation. The formation of a pyrrolyl radical at the initial stage of oxidation [4,7] and the capture of active species, such as O, OH, H, and HO₂ by this radical can inhibit pyrrole ignition.

Conclusion
In this paper, the oxidation of pyridine and pyrrole in the argon and water vapor media at a high density of reagents and diluents was studied for the first time. It is established that the oxidation of both fuels occurs according to the heterogeneous and homogeneous reaction mechanisms. When oxidizing pyrrole, the contribution of heterogeneous oxidation increases with the accumulation of corrosion products on the reactor wall. When measuring the reaction mixture temperature with a Pt-Rh/Pt thermocouple, pyridine oxidation is initiated on its surface due to dissociative adsorption of oxygen and pyridine. In the argon medium, at a low density of water vapor, pyridine oxidation is accompanied by detonation. The highest degree of nitrogen removal from pyrrole and pyridine in the composition of N₂ is achieved with an excess of oxygen at \( T \geq 750 \) K and a low density of water vapor. Increasing the density of water vapor reduces the contribution of heterogeneous reactions and prevents complete combustion of fuel. The results obtained can become the basis for the development of environmentally friendly technologies for combusting fossil fuels, biomass, and organic waste in water vapor and supercritical water.

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