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Supercritical water oxidation of quinoline with moderate preheat temperature and initial concentration

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Abstract

This work reports an experimental study on supercritical water oxidation of quinoline. Moderate preheat temperature (420°C-510°C) and initial concentration (1wt%-10wt%) are selected to address the possibility of utilizing the heat released during the reaction, in order to realize high conversion rate at relatively low preheat temperature. The effects of temperature, residence time, oxidation ratio, pressure and concentration are analyzed. The results show that considerable conversion can happen at relatively low preheat temperature, while increase in temperature will significantly promote the complete conversion. The yield of carbon dioxide increases with the residence time but there is an upper limit due to the stronger dependence on oxidizer concentration, for which an estimated reaction order is 1.90. When the quinoline concentration is larger than 8wt%, clear exothermic peaks with temperature rise about 100°C are detected. These exothermic peaks can be interpreted as a sign of ignition interrupted by the heat loss to the surrounding salt bath. An analogy is made between the start temperatures of these exothermic peaks and the ignition temperatures reported in methanol and isopropanol hydrothermal flame research. We conclude that quinoline solutions can be ignited without co-fuels, at comparable ignition temperature as methanol and isopropanol around 450°C.

Keywords: supercritical water oxidation (SCWO), heat release, quinoline, initial concentration, preheat temperature, ignition

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1. Introduction

Supercritical water oxidation (SCWO) is a promising wet waste treatment technology [1]. At conditions exceeding its critical point (P=22.1MPa, T=374.15°C), water presents gas-like transport properties and liquid-like solvent characteristics. Most organics and non-polar inorganic molecules such as oxygen, nitrogen and dioxide carbon are miscible with supercritical water. Therefore, refractory organics dissolved in supercritical water can be oxidized quickly and completely. On the other hand, as heat is released during the SCWO process, this technology is also prospected to utilize the chemical energy stored in organic wastes[2].

There has been some research on SCWO of organics, ranging from real waste[3, 4, 5, 6] to model compounds[7, 8, 9], among which aromatic and N-containing compounds are considered to be the more refractory ones. DiNaro et al.[10] investigated the SCWO of benzene at temperature ranging from 479°C to 587°C with initial benzene concentration from 0.4 to 1.2 mmol/L. Complete conversion of benzene with stoichiometric oxygen at 246 bar was achieved only when the temperature was higher than 575°C. Pinto et al.[11] conducted a series of SCWO experiments on quinoline with the concentration of about 0.3mmol/L, indicating that 100% TOC removal was not achieved until the temperature approached 650°C. Also the research on DBU(1,8-diazabicyclo[5.4.0]undec-7-ene) by Al-Duri et al.[12] has shown that temperature is the main factor enhancing the oxidation.

The previous experimental studies are mainly focused on concentration around the level of one mmol/L. Converting this to the chemical oxygen demand (COD), which is a key parameter in the waste water treatment field, it corresponds to about 3000mg/L, which is quite lower than the COD of real waste where it is always around 50000-100000 mg/L. Higher COD usually means that more heat is released during the reaction. In the research mentioned above, the heat release effects are neglected, which is reasonable for low concentration cases. However, when it comes to high-concentration real waste, we should reconsider this. Actually, there has been some research on high-concentration methanol (90000-420000mg/L

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COD)[13] and isopropanol (72000-120000mg/L COD)[14]. This group of research is classified as hydrothermal combustion which is regarded as a promising approach to solve the corrosion and plugging problems in preheaters, since the preheat temperature can be decreased and then the preheaters are not subjected to the temprature range most dangerous for material corrosion and salt deposition[15, 16]. With the regime of hydrothermal flame, it is not necessary to heat the feedstock up to the reaction temperature. Instead, the reaction temperature, in other words the flame temperature, is reached through the heat release from the oxidation reactions. Hence, complete conversion is more easily achieved, considering that preheating the feedstock to the desired reaction temperature (nearly 600°C) is not an easy job in a commercial SCWO system.

To the best of our knowledge, studies on the hydrothermal flame regime are limited in simple alcoholic materials. Cabeza et al.[17] have found that it is impossible to sustain a hydrothermal flame using exclusively ammonia as fuel. They recommend to use isopropanol as co-fuel to sustain the hydrothermal flame. Sobhy et al.[18] have tested naphthalene oxidation in a methanol-air hydrothermal flame, and found that the flame temperature was declined when adding naphthalene. Using a co-fuel will increase the operating cost, because not only the purchase of co-fuel but also the extra oxygen demand caused by the co-fuel is expensive. Therefore, it is very interesting to explore the possibility of igniting, or at least utilizing the released heat of, the exclusive refractory compounds.

For this purpose, we investigate the supercritical water oxidation of 1wt%-10wt% quinoline (26700-267000mg/L COD), at relatively low preheat temperature (420°C-510°C). The influence of preheat temperature, residence time, pressure and initial concentration are analyzed. Special attention is paid to the temperature variation inside the reactor in order to explore the heat release effects.

2. Experimental Method

2.1. Materials

Quinoline (C_9H_7N, 98% purity, Tianjin Fuchen Chemical Reagents Co., Ltd.) is selected as an aromatic N-containing compound to be investigated in this research. In preparation of the experiments, a specific concentration quinoline solution (1-10wt%) is made with deionized water. The solution is stored in a brown flask and shakes well before use. The oxidizer used is oxygen (O_2, 99.999% purity, Baoguang Gas Co., Ltd), except for the comparative study where hydrogen peroxide (30%H_2O_2, Tianjin Fuchen Chemical Reagents Co., Ltd.) is used. Helium (99.999% purity, Shanghai Youjiali Liquid Helium Co., Ltd) is also added as an inner standard composition to facilitate the gas composition analysis. In the process of organic liquid phase analysis, ethyl acetate (99.8% purity, Tianjin Kemiou Chemical Reagent Co., Ltd.) is used as extraction agent.

To predict the heat release during quinoline oxidation, the enthalpy-of-formation of each species is looked up from the NIST database[19] and the enthalpy-of-reaction is calculated:

$$\underset{200.52}{C_9H_7N} + \underset{0}{10.75O_2} = \underset{-393.51}{9\,CO_2} + \underset{-241.83}{3.5\,H_2O} + \underset{0}{0.5N_2} \quad {}_{\text{kJ/mol}}$$

$$\Delta H_r = -4588.52kJ/mol$$

2.2. Apparatus and experimental procedure

Apparatus used in this research is a set of batch reactors in combination with a salt bath heater and a multiple gas injection and evacuation system (see Figure 1). The reactor is assembled from SS 316 tube (o.d. 1/2 in., thickness 0.083in., length 100mm), with one end plugged by a Swagelok fitting cap and another connected with a high pressure and high temperature valve through a Swagelok fitting 1/2 in. to 1/4 in. reducer, as shown in Figure 2. For the reactors used to detect the inner temperature rise, a tee connecter is assembled instead. The salt bath is a mixture of sodium nitrate and sodium potassium nitrate, heated electrically and controlled with a feedback thermocouple inside the bath. The gas system provides oxygen, helium and vacuum options for the reactors.

Three pressures (23MPa, 25MPa, 28MPa) and four preheat temperatures (420°C, 450°C, 480°C, 510°C) conditions are investigated in our research. For each temperature and pressure set, we look up the corresponding density of water from the NIST database[19]. This density multiplied by the reactor volume is the amount of solution to be added into the reactor.

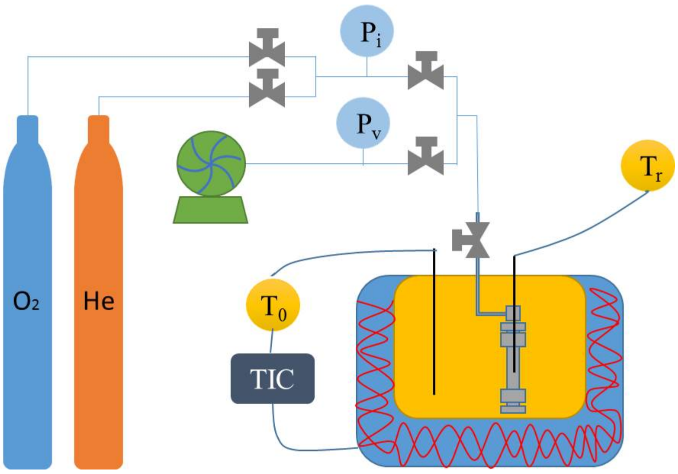


Figure 1: Experimental apparatus

For the case of hydrogen peroxide as oxidant, it is the amount of quinoline solution plus the water from hydrogen peroxide. After all liquid is added in the reactor, the reactor is sealed well, connected to the gas system and vacuumed. Then 0.2MPa Helium and specific amount of oxygen is injected in sequentially. The pressure in the feed pipeline is monitored to make sure that the amount of oxygen meets the desired oxidation ratio. The evacuation and injection process is repeated three times to eliminate the remaining air in the reactor. Afterwards, when the salt bath is heated-up and the temperature is stable, reactors are submerged into the salt and the timer is started. After the specified residence time (1-10min), the reactor is taken out and quenched by a cold-water bath. Staying still for 8 hours, to reach gross separation, gas and liquid products are analyzed sequentially.

2.3. Products analysis

The gas products are analyzed by a Beifen-Ruili GP-3420A gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a SUPELCO 60/80 mesh Carboxen 1000 packed column. Connecting the gas valve to the sampling port of GC and opening the valve gently, we can have the gas products fill the sample tube. Then with argon (Ar) as carrier gas, the volume fractions of helium (He), hydrogen (H_2), oxygen (O_2), nitrogen (N_2), carbon monoxide (CO), methane (CH_4), carbon dioxide (CO_2), ethylene (C_2H_4) and acetylene (C_2H_6) are determined sequentially, under the programmed column temperature

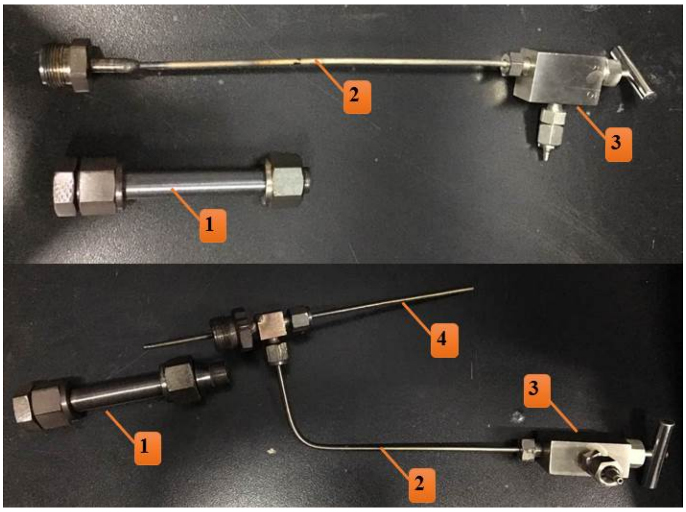


Figure 2: Assembly of batch reactors(1: reactor tube; 2: gas pipe; 3: gas valve; 4: thermocouple insert)

of 50°C (kept for 13.5min) to 105°C (kept for 20min) in 50°C/min, then to 180°C (kept to infinite) with 50°C/min. Then the absolute amount of each component is obtained by reference to the a priori known amount of helium.

After analysis of the gas products, reactors are opened and the liquid products are collected into clean vials. In most cases, there is no explicit phase interface appears, since the organic concentration is already decreased to the level of its solubility in water after reaction. Then the liquid samples are diluted 50-200 times by distilled water and analyzed by a Euro TOC analyzer (ET 1020A) using the nondispersive infrared absorption method. The total carbon (TC), total organic carbon (TOC) and total inorganic carbon (TIC) are determined at the same time. Some selected samples are used to analyze the organic composition in the liquid products. Before each test, 1 ml ethyl acetate and 0.3 ml sample are added into a centrifuge tube and centrifuged 10 minutes at 3000rpm. Then the organic components is extracted into the ethyl acetate phase in the upper layer. This upper layer is collected and analyzed by a Shimadzu GC-MS-QP2010 Plus analyzer equipped with a Rtx-5 capillary column. The components are identified through comparison with the NIST08 and NIST08s library, and quantified roughly by the peak areas.

2.4. Case specification and data processing

Each case is specified by the initial quinoline concentration, preheat temperature, residence time, oxidation ratio and pressure. The preheat temperature indicates the steady temperature of the salt bath. The residence time counts from the moment when the reactor is submerged into the salt bath. The oxidation ratio denotes the ratio of the added oxygen over the oxygen demanded to oxidize the quinoline to CO_2, H_2O and N_2 completely.

With the products analysis methods described above, the mole number of each gaseous product and the mole number of total organic and inorganic carbon in the liquid product can be obtained. The yield of each product is calculated through dividing the mole number of carbon in each product by the mole number of carbon in the reactant. In all cases, the sum of CH_4, C_2H_4 and C_2H_6 yields are lower than 0.01. Therefore, only CO_2, CO, TOC and TIC are counted for the carbon balance. Since CO_2 is the final product of quinoline oxidation, the CO_2 yield presents the complete conversion rate of quinoline. The TOC yield reflects the clarity of the output liquid.

The GC-MS results provide the organic composition remaining in the liquid products. Based on the semi-quantitative fraction of each components, an analysis of the reaction pathway is conducted in section 3.1.

3. Results and Discussions

3.1. Effect of temperature and residence time

The CO_2 yields at different preheat temperature and residence time are shown in Figure 3. It shows that temperature has a positive effect on CO_2 yield. At each residence time, 30°C increase in temperature will lead to 0.1-0.2 increase in CO_2 yield. Another observation is that the reaction starts earlier at higher temperature. For the temperatures of 420°C and 450°C, minor reaction occurs in the first two minutes, which is shown by the fact that the CO_2 yields are below 0.1. At temperatures of 480°C and 510°C, the CO_2 yield is fairly high within two minutes. This can be explained by the observed temperature trace after the reactor is submerged in the salt bath. As shown in Figure 4, when the reactor is

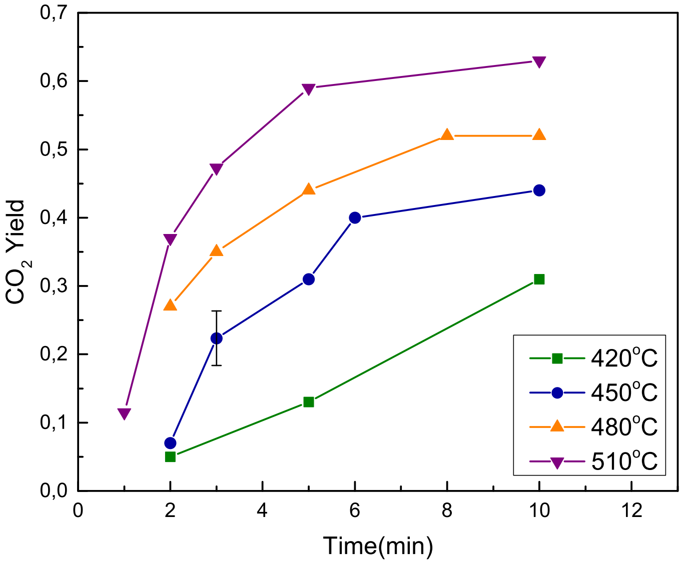


Figure 3: CO_2 yields as function of the residence time (1wt%, P=25MPa, OR=1)

submerged in the salt batch, the temperature inside the reactor rises rapidly. The higher the salt temperature is, the more rapidly the temperature rises. For the case that the salt bath temperature is set at 480°C, the temperature inside the reactor reaches 450°C in 1 minute, while it takes 2 minutes to reach the same temperature for the case that the salt bath temperature is set at 450°C. Hence, considerable conversion takes place one minute earlier at the 480°C condition than at the 450°C condition. This illustrates that reaction can happen at a relatively low temperature and increasing temperature accelerates the reaction rate and promotes the complete conversion.

Figure 5 shows the product distribution as function of the residence time at 450°C and 480°C conditions. The products are composed of CO, CO_2, TIC, TOC and undetected fractions, of which the sum is one reflecting the carbon balance. It is observed that there are considerable undetected fractions at low residence time, but this fraction declines as the time increases. Meanwhile, the CO_2 yields increase but the TOC yields change a little. We guess that the undetected carbon fraction is some type of highly volatile species which can hardly be detected by the GC-TCD and easily evaporates from the collected liquid samples. There is no reference in the former quinoline SCWO research[11] about the carbon balance analysis. Whereas in the study on the hydrothermal liquefaction of nannochloropsis

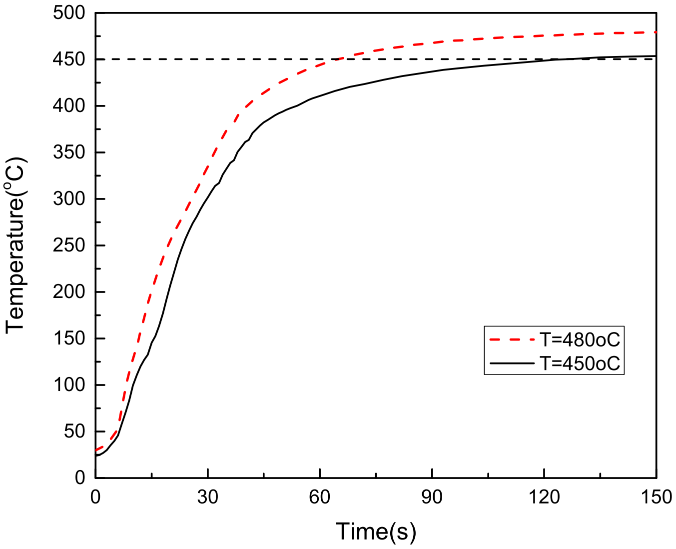
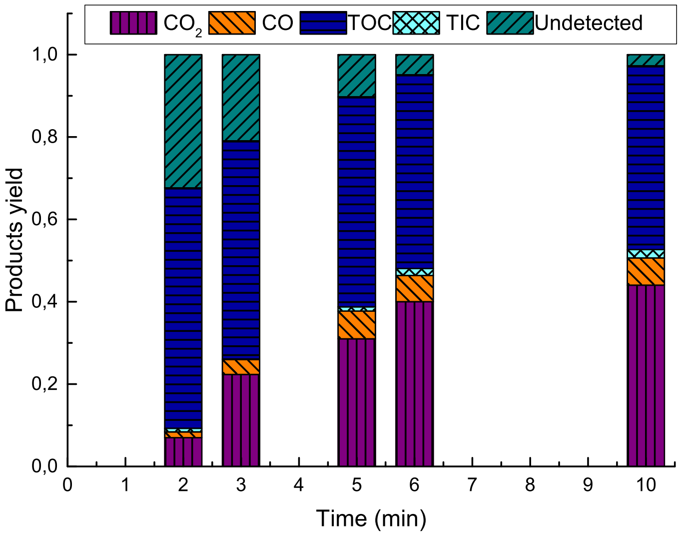


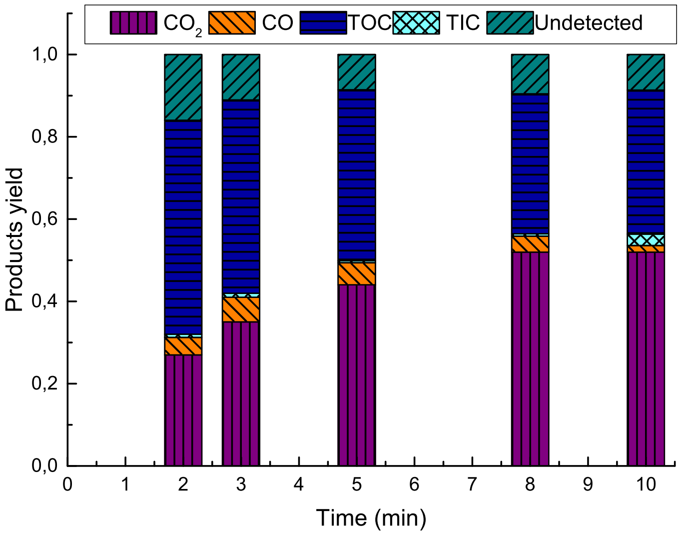
Figure 4: Temperature profile inside the reactor after submerged into salt bath (1wt%, P=25MPa, OR=1)

sp, Valdez et al.[20] also presume that the difference between one and the sum of all the detected products yields is the yield of volatile species. In their research, the reported volatile yield increases steadily with both time and temperature (250°C to 400 °C), with the highest volatile yield equal to 0.4 reached at 400°C. As our temperature conditions are all above 400°C, highly volatile species are produced more readily. In addition, due to the oxidation atmosphere, the volatile species convert to gaseous products (CO and CO_2) as residence time and temperature increase. With a residence time of 10 minutes, the lowest undetected fraction can be decreased down to 0.02 at the preheat temperature of 450°C. It shows the point that the conversion of highly volatile species to gaseous products maybe the controlling step for complete oxidation of quinoline.

Another point to be discussed here is that the TOC yield changes little with the increase in residence time. Referring to the research by Pinto et al.[11] , removal of TOC was very low (less than 10%) at temperature below 500°C and within a residence time of 4-9s. As the residence time is extended to larger values in our research, the conversion rate is much improved but there seems to be an asymptotic value. To explore this further, we determined the liquid products with the GC-MS method. The results are shown in Table 1. The major component of the organic liquid product is quinoline. Other secondary components are



(a) preheat temperature is 450°C



(b) preheat temperature is 480°C

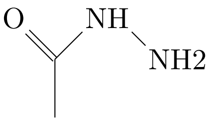
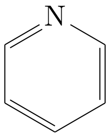
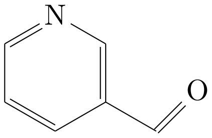
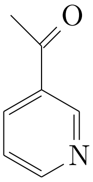
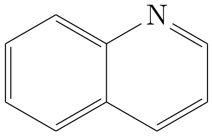
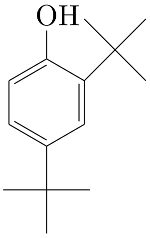
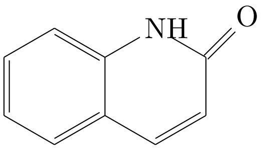
Figure 5: Product distribution as function of the residence time (1wt%, P=25MPa, OR=1)

quinolinone, pyridine and its derivatives, acethydrazide and phenolics. All these components suggest a reaction route where the benzene ring is opened first and the opening of the pyridine ring is a little slower, which is accordance with the work of Gong et al. [6]. Furthermore, a reaction pathway can be proposed as quinoline → secondary components → volatile species → gaseous products. From the fact that the main component in the liquid product is still quinoline, we can conclude that the decomposition of quinoline to secondary components only happens at the beginning. With the progress of reaction, active oxidizers are mostly consumed by the secondary components and the volatile species. The remaining quinoline does not react too much. Hence the TOC yield decreases very slowly. The effect of oxidizer will be illustrated further in the next section.

3.2. Effect of oxidation ratio and alternative oxidizer

Four oxidation ratios are tested from 0.5 to 2.0. As shown in Figure 6, the increase in oxidation ratio brings a significant change towards the complete conversion of quinoline. This is easy to understand, as the reaction rate is directly proportional to n-th power of the concentration of the reactants. In the low concentration quinoline SCWO research by Pinto et al.[21], the fitted reaction order for oxygen is 0.36, with the integral method approximation that $-ln(1-X) = kt[\mathrm{O_2}]_0^b$, where X is the global conversion rate of quinoline to CO_2, k is the reaction rate coefficient and t is the residence time. Applying this formula to the X at different $[\mathrm{O_2}]_0$, where k and t are the same, the reaction order of oxygen b is obtained as 1.90. This indicates that the dependence on oxygen concentration becomes larger at the present conditions. It is known that the SCWO reaction is actually a series of elementary reactions, which involves initiation, propagation and termination. The higher quinoline concentration and lower preheat temperature at the present conditions can induce changes in all these three stages and result in the increase of global reaction order. It should be pointed out that this conclusion is based on the integral method approximation for isothermal reactions. In this work, the temperature keeps increasing in the first two minutes, which means that k is dependent on t. Although the temperature integral on time is the same for all cases used in this kinetic fitting, more precise calculation can be conducted using the non-isothermal

Table 1: GC-MS analysis of liquid products (reaction condition: 1wt%, P=25MPa, T=450°C, OR=1, t_r=5min)

Retention time (min)	**Components**	**Fraction(%)**
4.015	 Acethydrazide	0.60
4.381	 Pyridine	1.55
16.183	 Pridylaldehyde	0.24
21.753	 Pridylethanone	0.08
28.004	 Quinoline	94.57
39.975	 2,4-Di-tert-butylphenol	0.42
46.38	 Quinolinone	2.54

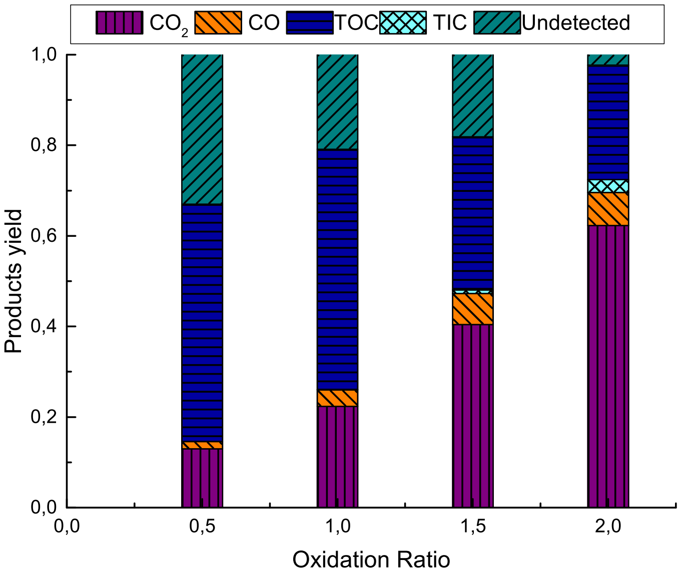


Figure 6: Product distribution at different oxidation ratio (1wt%, P=25MPa, T=450°C, t_r=3min)

reaction kinetic model proposed by Hietala et al. [22].

The difference between hydrogen peroxide and gaseous oxygen as oxidizer is investigated, with the results shown in figure 7. It is obvious that using hydrogen peroxide as oxidizer strongly increases the yield of CO_2. This can be explained by the radical accumulation mechanism [23]:

$$RH + O_2 = R + HO_2 \tag{1}$$

$$RH + HO_2 = R + H_2O_2 \tag{2}$$

$$H_2O_2 = 2\,OH \tag{3}$$

The reaction is initiated by the collision of quinoline (presented as RH) and oxygen, producing HO_2 and H_2O_2 radical sequentially. Then the branching reaction that one H_2O_2 produces two OH radicals largely accelerates the accumulation of radicals, providing plenty of OH radicals to oxide the hydrocarbons. However, when hydrogen peroxide is used as oxidizer, it may bypass the relatively slow steps (1) and (2). Hence hydrogen peroxide is a more effective oxidizer for providing OH radicals more directly. On the other hand, hydrogen peroxide is liquid at the initial state and can mix with quinoline solution more easily

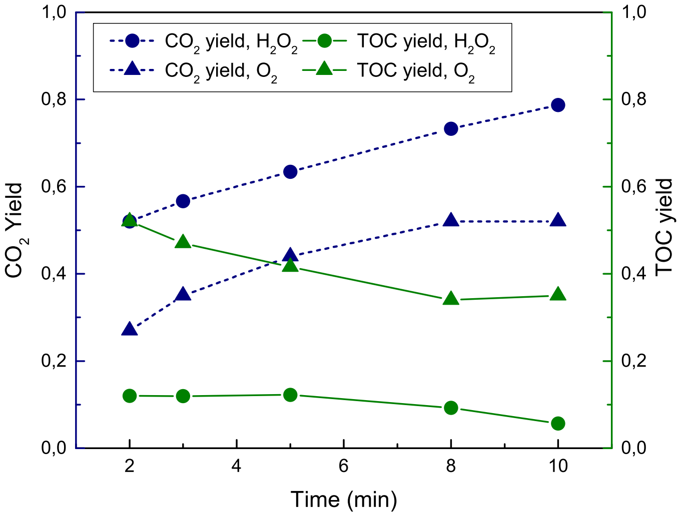


Figure 7: Different CO_2 and TOC yield profiles with gaseous oxygen and hydrogen peroxide as oxidizer respectively (1wt%, T=480°C, P=25MPa, OR=1)

than gaseous oxygen. It should be kept in mind that hydrogen peroxide is a type of strong oxidizer even at ambient condition.

3.3. Effect of pressure and density

The product distribution at three different pressures are shown in Figure 8. It shows that the increase in pressure can promote the conversion to CO_2. As described in the experimental section, the pressure variation is achieved by changing the amount of quinoline solution added to the reactor. Actually, the pressure also affects the reaction rate through its effect on the concentration of reactants. The fact is that reaction rates increase with the concentration of reactants. However, it is also stated in literature that the increase in pressure may lead to the increase of ionic product, and hence suppress the radical reactions[24]. Nevertheless, results here indicate that the enhancement by increase of concentration is stronger than the suppression by increase of ionic products.

3.4. Effect of quinoline concentration

In this section, we report on the effect of gradually increasing the concentration of quinoline solution. Figure 9 shows the temperature profiles during the reaction at four different concentrations with the same oxidation ratio and preheat temperature. It indicates that

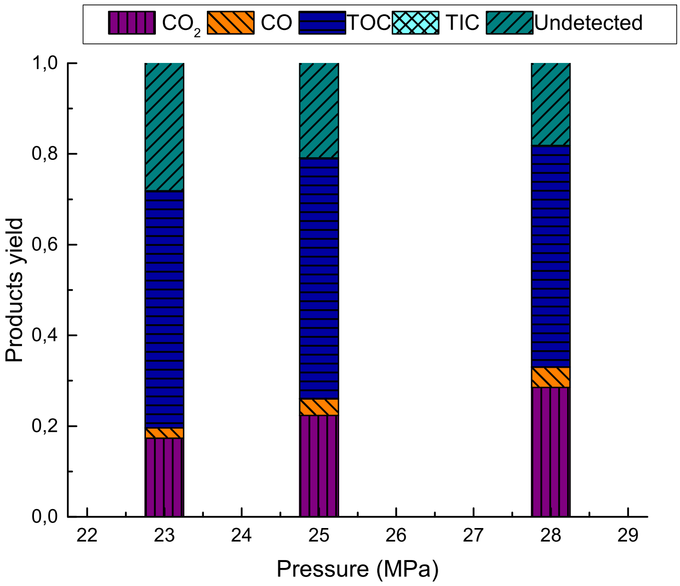


Figure 8: Product distribution at different pressure (1wt%, T=450°C, OR=1, t_r=3min)

with the increase in quinoline concentration, the temperature rise inside the reactor becomes steeper. Especially when the concentration reaches 8wt%, a temperature peak appears. And for the concentration of 10wt%, the amplitude of the temperature peak exceeds 100°C.

This is what we expected. Actually, for an adiabatic process, a 100°C temperature rise would be observed already for 1wt% quinoline solution. As listed in the section 2.1 *Materials*, the completed oxidation of 1mol quinoline will release 4588.52kJ heat. We can calculate that 1wt% quinoline solution contains 0.0775mol quinoline per kilogram and it will release 355.7kJ/kg heat. This amount of heat could bring a temperature increase from 400°C to 548°C for the 1wt% quinoline solution, by counting the internal energy values of water at constant volume[19]. Nonadiabatic operation explains why no temperature peak is observed at 1wt% and 5wt% conditions. Considering the setup, the reactor is immersed in a salt bath, which is kept stable at a specific temperature. The heat transfer rate through the molten salt is rather high and the mass of quinoline solution inside the reactor is quite small compared to the mass of the salt or the mass of the reactor wall. Therefore, for the low-concentration quinoline solution, the heat release rate is not high enough to offset the heat loss to the surroundings. No distinct temperature rise can be observed. With the

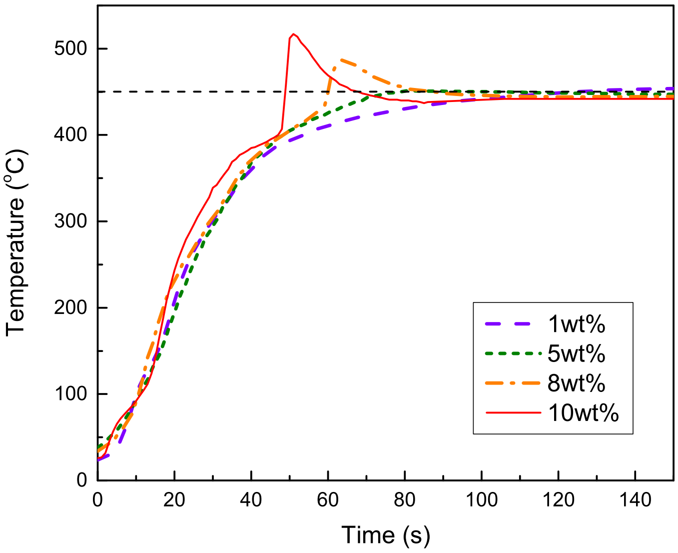


Figure 9: Temperature profiles inside the reactor at different quinoline concentration (T=450°C, P=25MPa)

increase in quinoline concentration, the heat release rate increases and exceeds the heat loss rate, so that the exothermic peaks are observed.

The effect of concentration on product distribution is shown in Figure 10. With the increase in quinoline concentration, the conversion rate to CO_2 strongly increases. Even though no temperature peak is observed for the 5wt% case, the CO_2 yield increases to more than three times of that for 1wt%. This indicate that the reaction is indeed more intense at higher concentration. Specifically, assuming a first order reaction, the complete conversion rate of quinoline would be $X = 1 - e^{-kt}$, where $k = k_0 e^{-E/RT}$ is the reaction rate coefficient and t is the residence time. For the same temperature and residence time, the complete conversion rate would be the same when the rate constant k_0 and activation energy E remain unchanged. However, from the results we can conclude that at higher concentration, higher k_0 and/or lower E would apply. This result agrees with the findings from Vogel et al. [25] for methanol SCWO.

Another benefit from high concentration would be the temperature rise caused by heat release. According to the above formulas, the conversion rate will increase exponentially with temperature. For the 10wt% case, heat release leads the temperature rise to about 510°C, and hence the CO_2 yield increases to nearly 0.9. The duration of this temperature

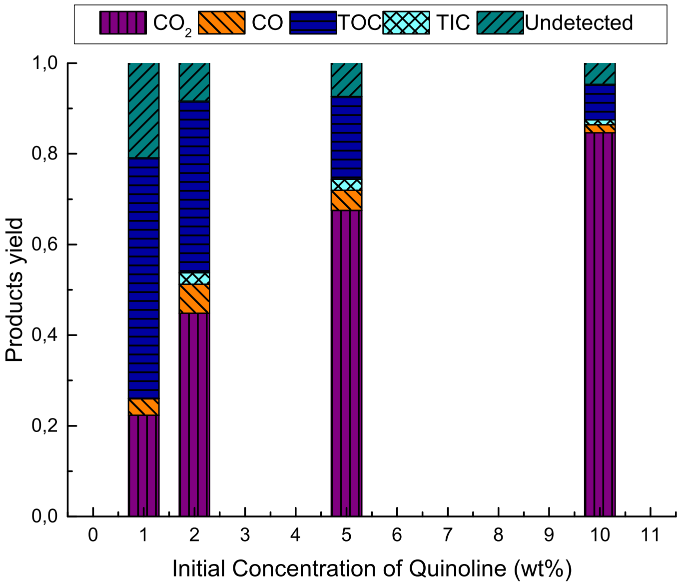


Figure 10: Product distribution at different quinoline concentration (T=450°C, P=25MPa, t_r=3min, OR=1)

peak is only 20s, otherwise the enhancement would be stronger. It is again due to the heat loss. With the temperature increase inside the reactor, the difference in temperature between the reactants and the salt bath becomes larger. Hence the heat loss rate exceeds the exothermic rate and then the temperature falls down. Fortunately, a commercial setup will not use salt bath heating. At a larger scale, close to adiabatic operation is possible and it is possible to obtain benefit from a higher and wider temperature peak.

An interesting property is the temperature when the exothermic peak starts. For the 8wt% case, the temperature starts to rapidly rise at about 425°C, while for 10wt%, it is below 400°C. The exothermic peak can be regarded as a signal of the ignition of hydrothermal flames, but interrupted by heat loss. Therefore, we can make an analogy between this exothermic start temperature and the ignition temperature. It indicates that ignition temperature decreases when the fuel concentration increases. For comparison, the ignition temperature of 15wt%-20wt% methanol is about 480°C [13] and that of 5wt% isopropanol is about 470°C [14]. The “ignition temperature” of quinoline here is lower than that of methanol and quinoline, but there are two factors that should be kept in mind. Firstly, the comparison is made at different fuel concentration and it is still questionable whether the same mass concentration of different fuels can be seen as an identical condition for ignition comparison. Secondly, the flow patterns can also affect the ignition temperature which is illustrated in our previous work [23]. Nevertheless, the results here indicate that quinoline can be ignited at comparable temperature as methanol and isopropanol.

4. Conclusion

Considerable conversion can happen at relatively low preheat temperature, while increase in temperature will significantly promote the complete conversion. The CO_2 yield increases with the residence time but there is an upper limit due to the stronger dependence on oxidizer concentration, for which an estimated reaction order is 1.90. Gaseous oxygen is less active than hydrogen peroxide due to the slow radical initiation reaction, but more practical. Pressure has positive but weak influence on the conversion. Exothermic peaks are observed for 8wt% and 10wt% quinoline with temperature increase around 100°C. The temperature rise is weaker than what we expect because of the rapid heat loss to the salt bath. Besides the exothermic effect, a high concentration condition can decrease the global activation energy and/or increase the reaction rate constant. It is proved that quinoline has comparable “ignition temperature”as methanol and isopropanol. With good reactor and insulation design, it is promising to ignite quinoline without co-fuels, giving possibility to run SCWO process in the regime of hydrothermal flame with low operation cost.

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