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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

27 1. Introduction

28 Supercritical water oxidation (SCWO) is a promising wet waste treatment technology
29 [1]. At conditions exceeding its critical point ($P=22.1\text{MPa}$, $T=374.15^\circ\text{C}$), water presents
30 gas-like transport properties and liquid-like solvent characteristics. Most organics and non-
31 polar inorganic molecules such as oxygen, nitrogen and dioxide carbon are miscible with
32 supercritical water. Therefore, refractory organics dissolved in supercritical water can be
33 oxidized quickly and completely. On the other hand, as heat is released during the SCWO
34 process, this technology is also prospected to utilize the chemical energy stored in organic
35 wastes[2].

36 There has been some research on SCWO of organics, ranging from real waste[3, 4, 5,
37 6] to model compounds[7, 8, 9], among which aromatic and N-containing compounds are
38 considered to be the more refractory ones. DiNaro et al.[10] investigated the SCWO of
39 benzene at temperature ranging from 479°C to 587°C with initial benzene concentration
40 from 0.4 to 1.2 mmol/L. Complete conversion of benzene with stoichiometric oxygen at
41 246 bar was achieved only when the temperature was higher than 575°C . Pinto et al.[11]
42 conducted a series of SCWO experiments on quinoline with the concentration of about
43 0.3mmol/L, indicating that 100% TOC removal was not achieved until the temperature
44 approached 650°C . Also the research on DBU(1,8-diazabicyclo[5.4.0]undec-7-ene) by Al-
45 Duri et al.[12] has shown that temperature is the main factor enhancing the oxidation.

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

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

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

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

78 **2. Experimental Method**

79 *2.1. Materials*

80 Quinoline (C₉H₇N, 98% purity, Tianjin Fuchen Chemical Reagents Co., Ltd.) is selected
81 as an aromatic N-containing compound to be investigated in this research. In preparation of

82 the experiments, a specific concentration quinoline solution (1-10wt%) is made with deion-
83 ized water. The solution is stored in a brown flask and shakes well before use. The oxidizer
84 used is oxygen (O₂, 99.999% purity, Baoguang Gas Co., Ltd), except for the comparative
85 study where hydrogen peroxide (30%H₂O₂, Tianjin Fuchen Chemical Reagents Co., Ltd.)
86 is used. Helium (99.999% purity, Shanghai Youjiali Liquid Helium Co., Ltd) is also added
87 as an inner standard composition to facilitate the gas composition analysis. In the pro-
88 cess of organic liquid phase analysis, ethyl acetate (99.8% purity, Tianjin Kemiou Chemical
89 Reagent Co., Ltd.) is used as extraction agent.

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

92



94

$$95 \quad \Delta H_r = -4588.52 \text{kJ/mol}$$

96 2.2. Apparatus and experimental procedure

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

106 Three pressures (23MPa, 25MPa, 28MPa) and four preheat temperatures (420°C, 450°C,
107 480°C, 510°C) conditions are investigated in our research. For each temperature and pressure
108 set, we look up the corresponding density of water from the NIST database[19]. This density
109 multiplied by the reactor volume is the amount of solution to be added into the reactor.

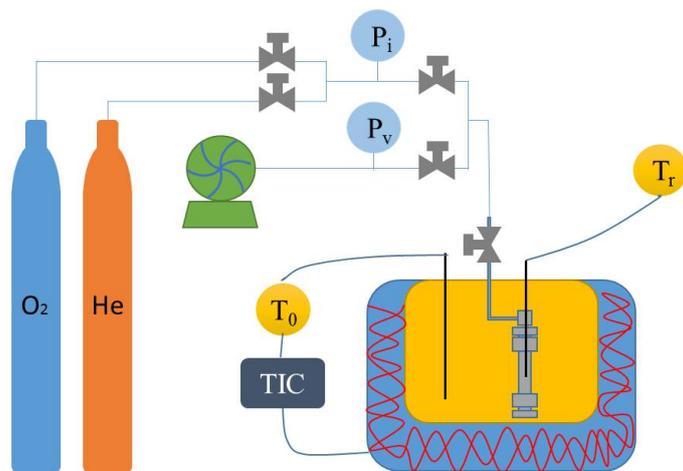


Figure 1: Experimental apparatus

110 For the case of hydrogen peroxide as oxidant, it is the amount of quinoline solution plus
 111 the water from hydrogen peroxide. After all liquid is added in the reactor, the reactor is
 112 sealed well, connected to the gas system and vacuumed. Then 0.2MPa Helium and specific
 113 amount of oxygen is injected in sequentially. The pressure in the feed pipeline is monitored
 114 to make sure that the amount of oxygen meets the desired oxidation ratio. The evacuation
 115 and injection process is repeated three times to eliminate the remaining air in the reactor.
 116 Afterwards, when the salt bath is heated-up and the temperature is stable, reactors are
 117 submerged into the salt and the timer is started. After the specified residence time (1-
 118 10min), the reactor is taken out and quenched by a cold-water bath. Staying still for 8
 119 hours, to reach gross separation, gas and liquid products are analyzed sequentially.

120 2.3. Products analysis

121 The gas products are analyzed by a Beifen-Ruili GP-3420A gas chromatograph (GC)
 122 equipped with a thermal conductivity detector (TCD) and a SUPELCO 60/80 mesh Car-
 123 boxen 1000 packed column. Connecting the gas valve to the sampling port of GC and opening
 124 the valve gently, we can have the gas products fill the sample tube. Then with argon (Ar)
 125 as carrier gas, the volume fractions of helium (He), hydrogen (H₂), oxygen (O₂), nitrogen
 126 (N₂), carbon monoxide (CO), methane (CH₄), carbon dioxide (CO₂), ethylene (C₂H₄) and
 127 acetylene (C₂H₆) are determined sequentially, under the programmed column temperature

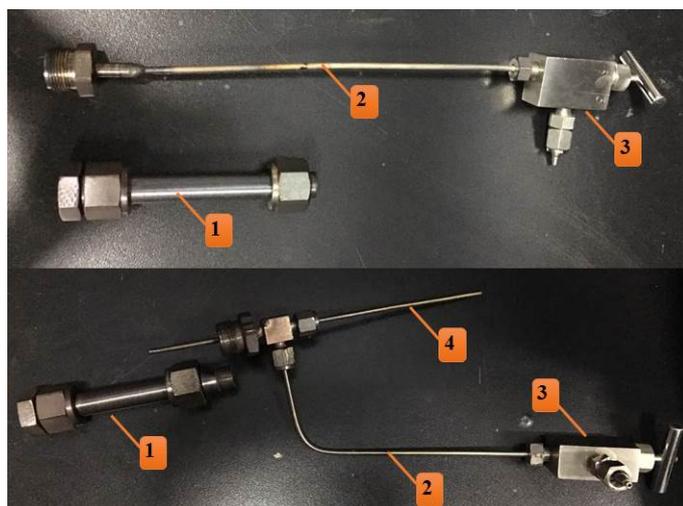


Figure 2: Assembly of batch reactors(1: reactor tube; 2: gas pipe; 3: gas valve; 4: thermocouple insert)

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

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

144 *2.4. Case specification and data processing*

145 Each case is specified by the initial quinoline concentration, preheat temperature, res-
146 idence time, oxidation ratio and pressure. The preheat temperature indicates the steady
147 temperature of the salt bath. The residence time counts from the moment when the reactor
148 is submerged into the salt bath. The oxidation ratio denotes the ratio of the added oxygen
149 over the oxygen demanded to oxidize the quinoline to CO₂, H₂O and N₂ completely.

150 With the products analysis methods described above, the mole number of each gaseous
151 product and the mole number of total organic and inorganic carbon in the liquid product
152 can be obtained. The yield of each product is calculated through dividing the mole number
153 of carbon in each product by the mole number of carbon in the reactant. In all cases, the
154 sum of CH₄, C₂H₄ and C₂H₆ yields are lower than 0.01. Therefore, only CO₂, CO, TOC
155 and TIC are counted for the carbon balance. Since CO₂ is the final product of quinoline
156 oxidation, the CO₂ yield presents the complete conversion rate of quinoline. The TOC yield
157 reflects the clarity of the output liquid.

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

161 **3. Results and Discussions**

162 *3.1. Effect of temperature and residence time*

163 The CO₂ yields at different preheat temperature and residence time are shown in Figure
164 3. It shows that temperature has a positive effect on CO₂ yield. At each residence time,
165 30°C increase in temperature will lead to 0.1-0.2 increase in CO₂ yield. Another observation
166 is that the reaction starts earlier at higher temperature. For the temperatures of 420°C
167 and 450°C, minor reaction occurs in the first two minutes, which is shown by the fact
168 that the CO₂ yields are below 0.1. At temperatures of 480°C and 510°C, the CO₂ yield is
169 fairly high within two minutes. This can be explained by the observed temperature trace
170 after the reactor is submerged in the salt bath. As shown in Figure 4, when the reactor is

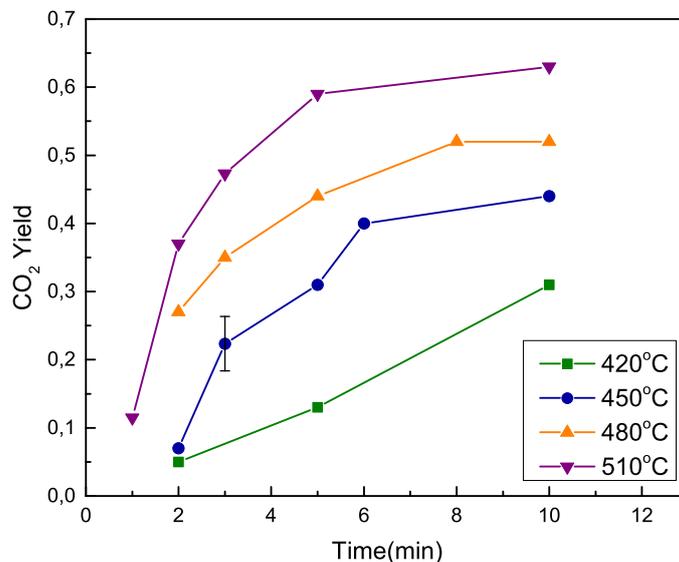


Figure 3: CO₂ yields as function of the residence time (1wt%, P=25MPa, OR=1)

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

179 Figure 5 shows the product distribution as function of the residence time at 450°C and
 180 480°C conditions. The products are composed of CO, CO₂, TIC, TOC and undetected
 181 fractions, of which the sum is one reflecting the carbon balance. It is observed that there
 182 are considerable undetected fractions at low residence time, but this fraction declines as
 183 the time increases. Meanwhile, the CO₂ yields increase but the TOC yields change a little.
 184 We guess that the undetected carbon fraction is some type of highly volatile species which
 185 can hardly be detected by the GC-TCD and easily evaporates from the collected liquid
 186 samples. There is no reference in the former quinoline SCWO research[11] about the carbon
 187 balance analysis. Whereas in the study on the hydrothermal liquefaction of nannochloropsis

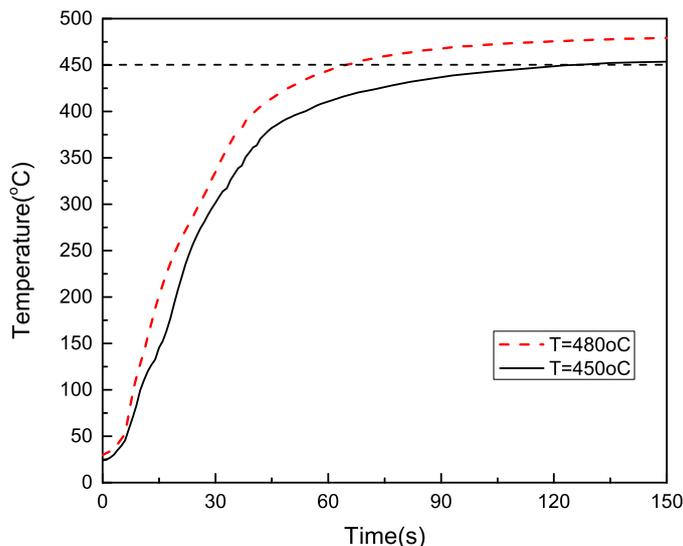
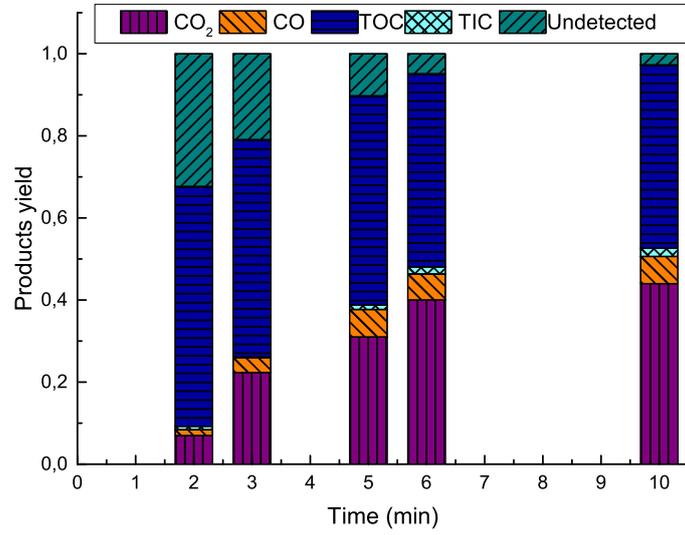


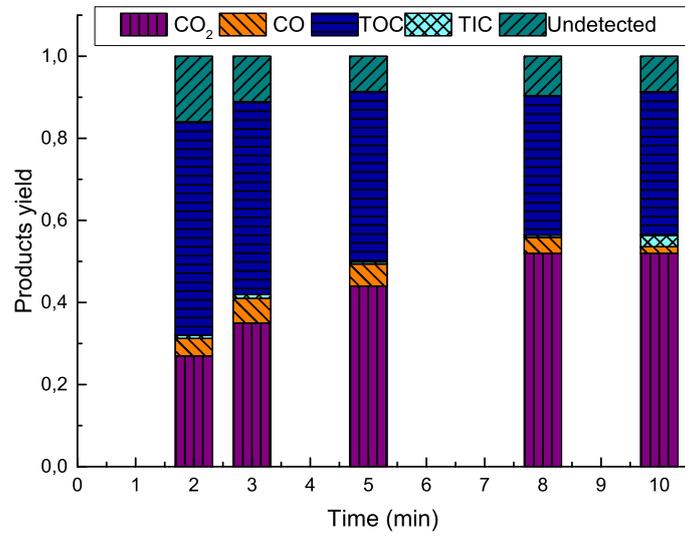
Figure 4: Temperature profile inside the reactor after submerged into salt bath (1wt%, P=25MPa, OR=1)

188 sp, Valdez et al.[20] also presume that the difference between one and the sum of all the
 189 detected products yields is the yield of volatile species. In their research, the reported
 190 volatile yield increases steadily with both time and temperature (250°C to 400 °C), with
 191 the highest volatile yield equal to 0.4 reached at 400°C. As our temperature conditions are
 192 all above 400°C, highly volatile species are produced more readily. In addition, due to the
 193 oxidation atmosphere, the volatile species convert to gaseous products (CO and CO₂) as
 194 residence time and temperature increase. With a residence time of 10 minutes, the lowest
 195 undetected fraction can be decreased down to 0.02 at the preheat temperature of 450°C. It
 196 shows the point that the conversion of highly volatile species to gaseous products maybe the
 197 controlling step for complete oxidation of quinoline.

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



(a) preheat temperature is 450°C



(b) preheat temperature is 480°C

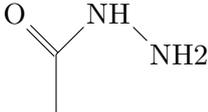
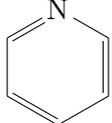
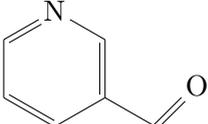
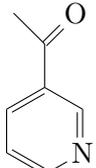
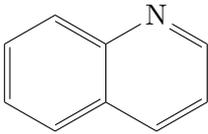
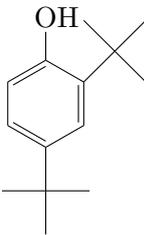
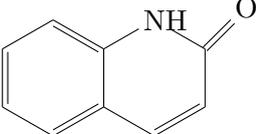
Figure 5: Product distribution as function of the residence time (1wt%, P=25MPa, OR=1)

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

215 3.2. Effect of oxidation ratio and alternative oxidizer

216 Four oxidation ratios are tested from 0.5 to 2.0. As shown in Figure 6, the increase
217 in oxidation ratio brings a significant change towards the complete conversion of quinoline.
218 This is easy to understand, as the reaction rate is directly proportional to n-th power of the
219 concentration of the reactants. In the low concentration quinoline SCWO research by Pinto
220 et al.[21], the fitted reaction order for oxygen is 0.36, with the integral method approximation
221 that $-\ln(1 - X) = kt[\text{O}_2]_0^b$, where X is the global conversion rate of quinoline to CO_2 , k is
222 the reaction rate coefficient and t is the residence time. Applying this formula to the X at
223 different $[\text{O}_2]_0$, where k and t are the same, the reaction order of oxygen b is obtained as 1.90.
224 This indicates that the dependence on oxygen concentration becomes larger at the present
225 conditions. It is known that the SCWO reaction is actually a series of elementary reactions,
226 which involves initiation, propagation and termination. The higher quinoline concentration
227 and lower preheat temperature at the present conditions can induce changes in all these
228 three stages and result in the increase of global reaction order. It should be pointed out that
229 this conclusion is based on the integral method approximation for isothermal reactions. In
230 this work, the temperature keeps increasing in the first two minutes, which means that k is
231 dependent on t . Although the temperature integral on time is the same for all cases used
232 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, $t_r=5\text{min}$)

Retention time (min)	Components	Fraction(%)
4.015	 Acetylhydrazide	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

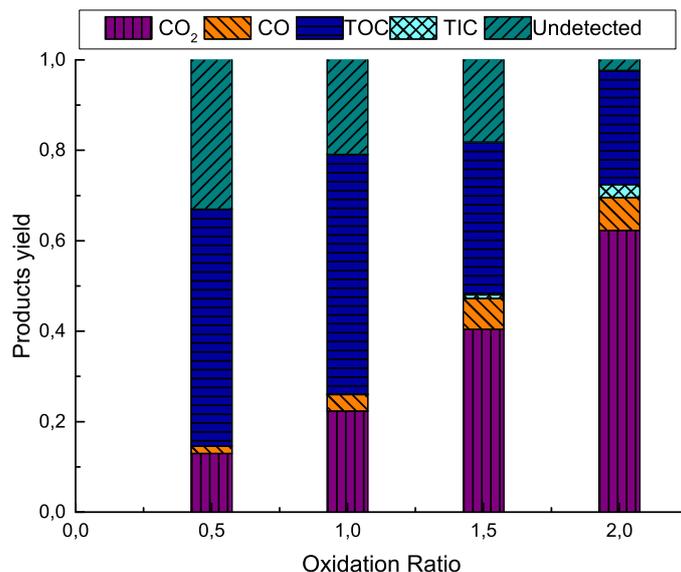


Figure 6: Product distribution at different oxidation ratio (1wt%, P=25MPa, T=450°C, t_r =3min)

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

234 The difference between hydrogen peroxide and gaseous oxygen as oxidizer is investigated,
 235 with the results shown in figure 7. It is obvious that using hydrogen peroxide as oxidizer
 236 strongly increases the yield of CO₂. This can be explained by the radical accumulation
 237 mechanism [23]:



238 The reaction is initiated by the collision of quinoline (presented as RH) and oxygen, pro-
 239 ducing HO₂ and H₂O₂ radical sequentially. Then the branching reaction that one H₂O₂
 240 produces two OH radicals largely accelerates the accumulation of radicals, providing plenty
 241 of OH radicals to oxide the hydrocarbons. However, when hydrogen peroxide is used as
 242 oxidizer, it may bypass the relatively slow steps (1) and (2). Hence hydrogen peroxide is a
 243 more effective oxidizer for providing OH radicals more directly. On the other hand, hydro-
 244 gen peroxide is liquid at the initial state and can mix with quinoline solution more easily

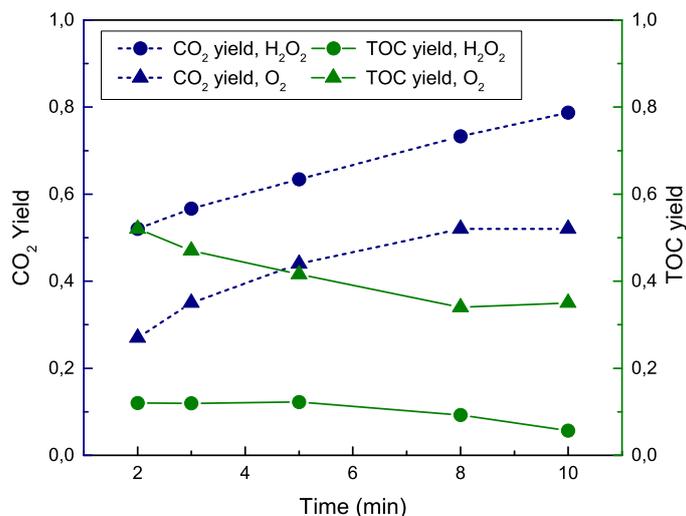


Figure 7: Different CO₂ and TOC yield profiles with gaseous oxygen and hydrogen peroxide as oxidizer respectively (1wt%, T=480°C, P=25MPa, OR=1)

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

247 3.3. Effect of pressure and density

248 The product distribution at three different pressures are shown in Figure 8. It shows that
 249 the increase in pressure can promote the conversion to CO₂. As described in the experimental
 250 section, the pressure variation is achieved by changing the amount of quinoline solution added
 251 to the reactor. Actually, the pressure also affects the reaction rate through its effect on the
 252 concentration of reactants. The fact is that reaction rates increase with the concentration
 253 of reactants. However, it is also stated in literature that the increase in pressure may lead
 254 to the increase of ionic product, and hence suppress the radical reactions[24]. Nevertheless,
 255 results here indicate that the enhancement by increase of concentration is stronger than the
 256 suppression by increase of ionic products.

257 3.4. Effect of quinoline concentration

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

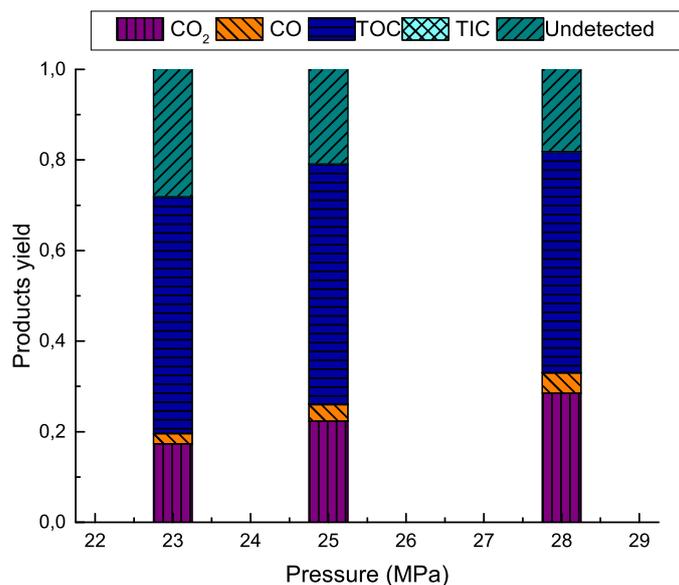


Figure 8: Product distribution at different pressure (1wt%, T=450°C, OR=1, t_r =3min)

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

264 This is what we expected. Actually, for an adiabatic process, a 100°C temperature
 265 rise would be observed already for 1wt% quinoline solution. As listed in the section 2.1
 266 *Materials*, the completed oxidation of 1mol quinoline will release 4588.52kJ heat. We can
 267 calculate that 1wt% quinoline solution contains 0.0775mol quinoline per kilogram and it
 268 will release 355.7kJ/kg heat. This amount of heat could bring a temperature increase from
 269 400°C to 548°C for the 1wt% quinoline solution, by counting the internal energy values of
 270 water at constant volume[19]. Nonadiabatic operation explains why no temperature peak is
 271 observed at 1wt% and 5wt% conditions. Considering the setup, the reactor is immersed in
 272 a salt bath, which is kept stable at a specific temperature. The heat transfer rate through
 273 the molten salt is rather high and the mass of quinoline solution inside the reactor is quite
 274 small compared to the mass of the salt or the mass of the reactor wall. Therefore, for the
 275 low-concentration quinoline solution, the heat release rate is not high enough to offset the
 276 heat loss to the surroundings. No distinct temperature rise can be observed. With the

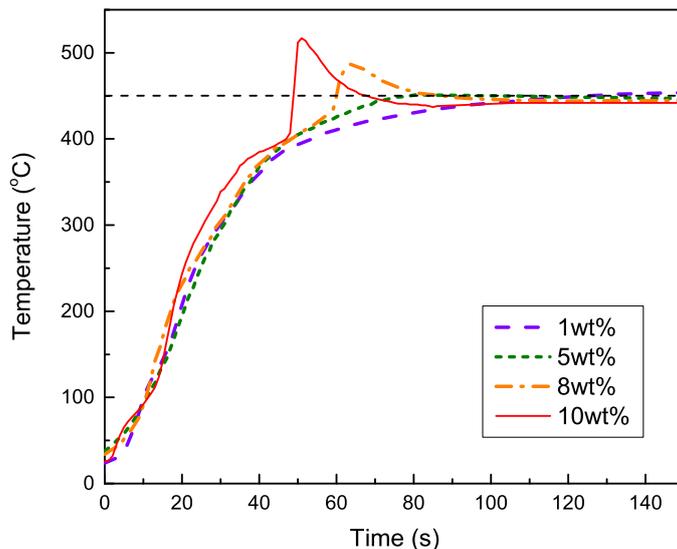


Figure 9: Temperature profiles inside the reactor at different quinoline concentration (T=450°C, P=25MPa)

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

279 The effect of concentration on product distribution is shown in Figure 10. With the
 280 increase in quinoline concentration, the conversion rate to CO₂ strongly increases. Even
 281 though no temperature peak is observed for the 5wt% case, the CO₂ yield increases to more
 282 than three times of that for 1wt%. This indicate that the reaction is indeed more intense at
 283 higher concentration. Specifically, assuming a first order reaction, the complete conversion
 284 rate of quinoline would be $X = 1 - e^{-kt}$, where $k = k_0 e^{-E/RT}$ is the reaction rate coefficient
 285 and t is the residence time. For the same temperature and residence time, the complete
 286 conversion rate would be the same when the rate constant k_0 and activation energy E remain
 287 unchanged. However, from the results we can conclude that at higher concentration, higher
 288 k_0 and/or lower E would apply. This result agrees with the findings from Vogel et al. [25]
 289 for methanol SCWO.

290 Another benefit from high concentration would be the temperature rise caused by heat
 291 release. According to the above formulas, the conversion rate will increase exponentially
 292 with temperature. For the 10wt% case, heat release leads the temperature rise to about
 293 510°C, and hence the CO₂ yield increases to nearly 0.9. The duration of this temperature

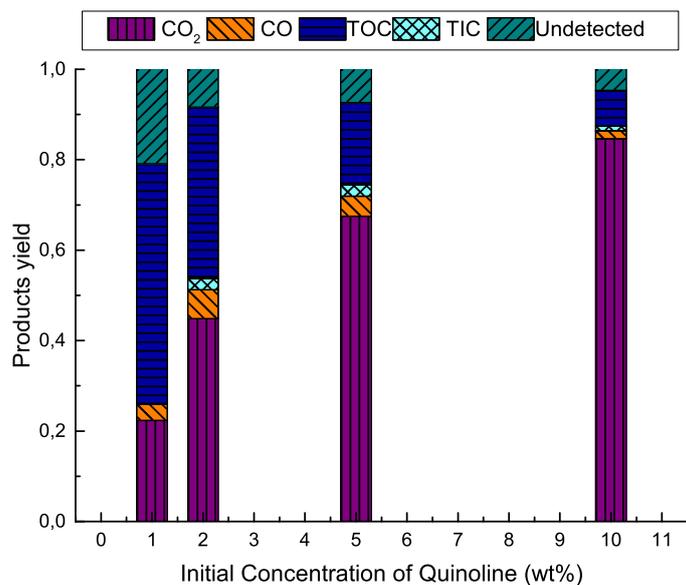


Figure 10: Product distribution at different quinoline concentration ($T=450^{\circ}\text{C}$, $P=25\text{MPa}$, $t_r=3\text{min}$, $\text{OR}=1$)

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

300 An interesting property is the temperature when the exothermic peak starts. For the
 301 8wt% case, the temperature starts to rapidly rise at about 425°C , while for 10wt%, it is
 302 below 400°C . The exothermic peak can be regarded as a signal of the ignition of hydrother-
 303 mal flames, but interrupted by heat loss. Therefore, we can make an analogy between
 304 this exothermic start temperature and the ignition temperature. It indicates that ignition
 305 temperature decreases when the fuel concentration increases. For comparison, the ignition
 306 temperature of 15wt%-20wt% methanol is about 480°C [13] and that of 5wt% isopropanol
 307 is about 470°C [14]. The “ignition temperature” of quinoline here is lower than that of
 308 methanol and quinoline, but there are two factors that should be kept in mind. Firstly, the
 309 comparison is made at different fuel concentration and it is still questionable whether the

310 same mass concentration of different fuels can be seen as an identical condition for ignition
311 comparison. Secondly, the flow patterns can also affect the ignition temperature which is
312 illustrated in our previous work [23]. Nevertheless, the results here indicate that quinoline
313 can be ignited at comparable temperature as methanol and isopropanol.

314 **4. Conclusion**

315 Considerable conversion can happen at relatively low preheat temperature, while increase
316 in temperature will significantly promote the complete conversion. The CO₂ yield increases
317 with the residence time but there is an upper limit due to the stronger dependence on
318 oxidizer concentration, for which an estimated reaction order is 1.90. Gaseous oxygen is
319 less active than hydrogen peroxide due to the slow radical initiation reaction, but more
320 practical. Pressure has positive but weak influence on the conversion. Exothermic peaks
321 are observed for 8wt% and 10wt% quinoline with temperature increase around 100°C. The
322 temperature rise is weaker than what we expect because of the rapid heat loss to the salt
323 bath. Besides the exothermic effect, a high concentration condition can decrease the global
324 activation energy and/or increase the reaction rate constant. It is proved that quinoline has
325 comparable “ignition temperature” as methanol and isopropanol. With good reactor and
326 insulation design, it is promising to ignite quinoline without co-fuels, giving possibility to
327 run SCWO process in the regime of hydrothermal flame with low operation cost.

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