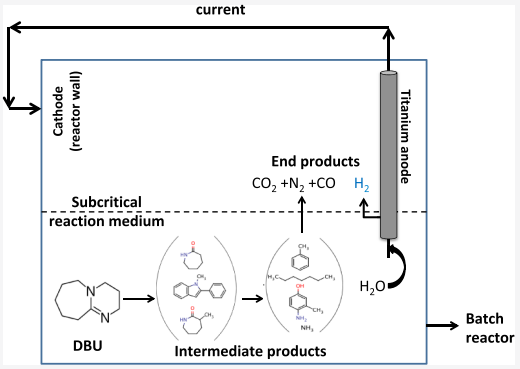
I&EC research
Industrial & Engineering Chemistry Research
pubs.acs.org/IECR
Article

Electrolytic Oxidation of 1,8-Diazabicyclo[5.4.0]undec-7-ene in Hot-Compressed Water on a Titanium Electrode

Ceren Orak and Aslı Yüksel Özşen*

Cite This: *Ind. Eng. Chem. Res.* 2020, 59, 19153−19161
Read Online

ABSTRACT: The nitrogen-containing heterocyclic organic compound, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), was chosen to prepare a model solution to represent nitrogen-containing industrial waste streams. A hybrid reactor system was designed to combine electrolysis with wet oxidation in hot compressed water using a titanium electrode. The effects of current density, NaOH concentration, and reaction time on DBU and total organic carbon (TOC) removal were investigated via Minitab 18 software to clarify the main and interaction effects. Statistical analysis shows that the NaOH concentration and current density had significant effects on DBU removal. The highest DBU (91.2%) and TOC (45%) removal was observed at the lowest DBU concentration (3 mM) for 90 min of reaction time. Last, the effect of temperature on DBU and TOC removal was investigated. TOC removal was described with the first-order reaction kinetic model. Rate constants were determined as 0.0025, 0.041, and 0.050 min^{-1} at 200, 240, and 280 °C, respectively. The activation energy was calculated as 79.86 kJ/mol.



INTRODUCTION

Wastewater could contain many organic compounds that consist of heteroatoms such as nitrogen and phosphorus produced in various industrial processes.[1−3] Nitrogen-containing organic compounds could be present in pesticides, insecticides, drugs, dyes, and pharmaceuticals.[4,5] Consequently, they could be present in many wastes such as pharmaceutical and textile wastewaters. Additionally, they could also exist in coke plant wastewater.[6] These hazardous compounds could enter the agricultural fields through various industrial and pharmaceutical effluents and could cause severe damage to the human and environmental health. Hence, before discharging these wastewaters, the properties of wastewater (i.e., nitrogen and organic matter content) should meet the discharging standards.[6] Otherwise, these compounds could be detected in ground and surface waters and they cause an increase over the algal and bacterial population in drinking water.[4] Upon decomposition of nitrogen-containing organic compounds, they release ammonia, which is highly refractory and requires stringent conditions to achieve total mineralization.[4−8] Furthermore, mutagenic and carcinogenic compounds could form as degradation products, and thus, long-term health problems could result from these compounds.[7,9] For instance, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is a nitrogen-containing heterocyclic organic compound, an amidine base, which exists as a pale yellow or colorless liquid under ambient conditions. It is used as a dehydrohalogenation agent in the alkylation and acylation of active methylene compounds in the pharmaceutical, dye, and cosmetic industries.[8,10] Petroleum and chemical industries produced wastewater at high amounts, and this wastewater contains heterocyclics (i.e., DBU) which are nonbiodegradable and chemically stable. In the literature, these compounds were degraded by incineration and very dangerous byproducts such as dioxins formed. Additionally, even at low concentrations, highly toxic nonbiodegradable compounds were also observed as byproducts.[11,12] This type of compounds show resistance against the biological treatment so that there has been strong research interest in alternative methods for the treatment of nitrogen-containing wastewaters. New greener solutions such as advanced oxidation methods or their combinations are promising to eliminate the byproducts of nitrogen-containing wastewaters.[6,8] DBU, which is a nitrogen-containing compound, also poses a significant threat to the aqueous environment, as it is water-soluble and chemically stable under ambient conditions and present in wastewater generated from these industries.[8,10] Therefore, it was chosen as a model nitrogen-containing compound for this study. Ochuma et al. (2007) studied DBU degradation using a

Received: May 22, 2020
Revised: September 30, 2020
Accepted: October 6, 2020
Published: October 15, 2020

https://dx.doi.org/10.1021/acs.iecr.0c02562
Ind. Eng. Chem. Res. 2020, 59, 19153−19161

pilot-scale photocatalytic oxidation reactor having a TiO_2-coated 15 pores-per-inch alumina reticulated foam monolith under UV light irradiation, and 100% DBU and almost 23% total organic carbon (TOC) removal were achieved.[8] It could be deduced that lower TOC removal could be achieved by photocatalytic oxidation. Compared to other wastewater treatment processes, advanced oxidation in hot compressed water (HCW) or subcritical water is considered a green technology. Water is called subcritical water if its temperature varied between 100 and 300 °C and when its pressure changed between 1 and 50 MPa, whereas water is called supercritical water if the temperature and pressure of water exceed the critical pressure and temperature (374 °C and 22.1 MPa, respectively). HCW has more ion value (10^{-11} at 250 °C) than water (10^{-14} at room temperature), and it also shows different properties compared to ambient water. For instance, subcritical water has a lower dynamic viscosity and a relatively low dielectric constant than its values under normal conditions.[8] Various wastewaters which contain Orange G, rhodamine B, maxilon blue GRL, paracetamol, and so forth were treated using HCW.[13−16] For instance, Emire et al. carried out a study on the degradation of paracetamol under subcritical conditions in the presence of hydrogen peroxide and oxygen. The degradation of paracetamol was achieved as 100 and 68% using hydrogen peroxide and oxygen, respectively. Yuksel et al. studied the degradation of Orange G by hydrothermal electrolysis. 99% TOC removal was observed at 180−250 °C temperature and 7 MPa pressure. Based on this study, complete mineralization was obtained by the addition of Na_2CO_3 as an electrolyte in a very short reaction time.[13] Consequently, hydrothermal electrolysis is a promising and greener solution for wastewater treatment by means of the efficiency of TOC removal, and no nontoxic byproducts formed during hydrothermal electrolysis of wastewaters. Moreover, hydrothermal electrolysis does not require the addition of an external oxidant such as air or hydrogen peroxide, rather the required oxidant is generated by applying current. Additionally, higher TOC removal compared to photocatalytic oxidation could be achieved by hydrothermal electrolysis. In addition, this method could provide complete mineralization of nitrogen-containing wastewaters without formation of any harmful or toxic end products. Therefore, a hybrid hydrothermal electrolysis reactor system with a volume of 450 mL was designed for the treatment of nitrogen-containing resistant compounds (i.e., DBU) in wastewaters. In this system, a titanium cylindrical electrode was used as an anode, and a reactor wall (also made of titanium) acted as a cathode. As only high-temperature water was used as a reaction medium under enough pressure to maintain its liquid state, this hybrid treatment system is environmentally friendly and promotes a greener solution for the treatment of wastewaters containing resistant organic compounds. To clarify the effect of parameters, which are the NaOH concentration (0.01 and 0.05 mM), current density (0 and 0.0027 mA/cm^2), and reaction time (30, 60 and 90 min), a general full factorial design was performed, and the results were discussed statistically. Additionally, the effects of temperature (200, 240, and 280 °C) and the initial concentration of DBU (3, 6, and 12 mM) on the removal of DBU and TOC in this hybrid reactor system were investigated. A kinetic study was carried out, and the intermediate products were identified by gas chromatography−mass spectrometry (GC−MS) analysis.

MATERIAL METHODS

Chemicals. The chemicals used in the study were sodium hydroxide (Merck, analytical grade) and DBU (Sigma-Aldrich, ≤99.0%). As an electrolyte, instead of using chlorine-containing salts, sodium hydroxide was chosen to prevent the reactor from corrosion.

Experimental Setup and Procedure. A special hydrothermal electrolysis reaction system (450 mL) made of stainless steel was designed for the treatment of DBU-containing model solution. In this reactor system, a specially designed cylindrical titanium electrode (D: 12 mm, L: 94 mm) was used as an anode. The reactor wall also made of titanium acted as a cathode. An auxiliary view of this hybrid reactor and titanium electrode is shown in Figure 1.

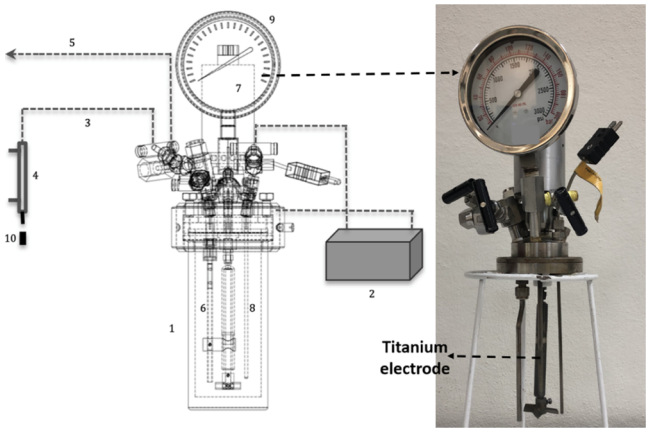


Figure 1. Auxiliary view of the hydrothermal electrolysis reactor: (1) electrical heater, (2) dc power controller, (3) liquid sampling tubing, (4) heat exchanger, (5) gas sample collector, (6) anode, (7) rotor, (8) thermocouple, (9) pressure gauge, (10) sampling vial.

The reactor was filled with 200 mL of 6 mM DBU. This DBU concentration was chosen based on the literature and concentration range of DBU (0.1 and 10 mM) that may be present in the wastewater-containing[10,27,28] model solution, and NaOH solution at a desired concentration (0.01−0.05 M) was added. Then, in order to remove the air inside the reactor, nitrogen gas was passed through the reactor to purge the system. After that, it was heated up to the desired reaction temperature (200, 240, or 280 °C) and it was continuously stirred to obtain a homogeneous reaction solution. After the system reached the desired reaction temperature, constant current (1 A) was applied for hydrothermal electrolysis experiments, whereas for hydrothermal degradation experiments, no current was passed through the electrodes. Then, the reaction was carried out for a certain reaction time (0−90 min). The experimental conditions were chosen based on the features of the experimental setup and a previous study.[13] At the end of the reaction duration, the heater was turned off and the reactor was cooled by cooling water with stirring until the temperature was reduced to 40 °C to take the sample. Finally, the product solution was collected for further analysis.

A general full factorial design was applied at 95% significance level via Minitab 18 software to understand the effects of NaOH concentration, current density, and reaction time on the removal of DBU and TOC from the aqueous solution, and the levels of factors are given in Table 1. These experiments were carried out using 6 mM DBU solution at 240 °C and they

https://dx.doi.org/10.1021/acs.iecr.0c02562
Ind. Eng. Chem. Res. 2020, 59, 19153−19161

Table 1. Levels of Factors (NaOH Concentration, Current Density, and Reaction Time) for the General Full Factorial Design

factors	levels of factors		
NaOH concentration, *M*	0.01	0.05	
current density, mA/cm^2	0.0000000	0.0027	
reaction time, min	30	60	90

were duplicated. Besides, the effect of initial DBU concentration (3, 6, and 12 mM) on the removal of DBU was investigated using 0.01 M NaOH concentration by applying a current density of 0.0027 mA/cm^2 at 240 °C for 30−90 min of reaction time. Moreover, the effect of temperature (200, 240, and 280 °C) on the DBU and TOC removal was investigated using 6 mM DBU and 0.01 M NaOH and by passing 0.0027 mA/cm^2 of the current density between electrodes for 30, 60, and 90 min of reaction time. A reaction kinetic model and reaction rate constants were derived for the DBU removal, and the activation energy was calculated based on the obtained data.

Analysis of Products. The liquid product solution was analyzed via high-performance liquid chromatography (HPLC) to determine DBU removal. HPLC analysis for DBU was carried out using a Fortis UniverSil C18 column at 50 °C column temperature. In this analysis, a mobile phase consisting of acetonitrile (A phase) and 0.1 vol % phosphoric acid−ultra pure water solution (B phase) was used, and the samples were analyzed by a gradient method. In this method, at the beginning of analysis, 100% B phase was fed, and then, between 8 and 10 min of analysis, 5% B phase was continued to be fed. At 10.01 min, 100% B phase was started to be fed and then 100% B phase was continued to be fed. The details of analysis conditions and the method for DBU analysis via HPLC are given in Table 2. The calibration curve was obtained

Table 2. Conditions for HPLC Analysis of DBU

HPLC	Agilent 1100 series	
column type	Fortis UniverSil C18	
operating temperature	50 °C	
mobile phase	A: acetonitrile, B: 0.1% H_3PO_4	
flow rate	1 mL/min	
detector	UV−vis (230 nm)	
analysis method	gradient method	
	time (min)	B phase (%)
	0	100
	8	5
	10	5
	10.01	100
	12	100

using DBU (≤99.0%, GC) solutions at certain concentrations (10, 20, 50, 100, and 200 ppm) and the method development and validation were achieved by repeating the analysis of DBU solutions several times; the calibration curve for DBU is given in Figure 2.

TOC in the liquid product solution was analyzed with a Shimadzu TOC-Vcph (TNM-1/SSM-5000A). For the liquid product identification, GC−MS (Agilent 6890 N/5973 N Network, USA) was used.

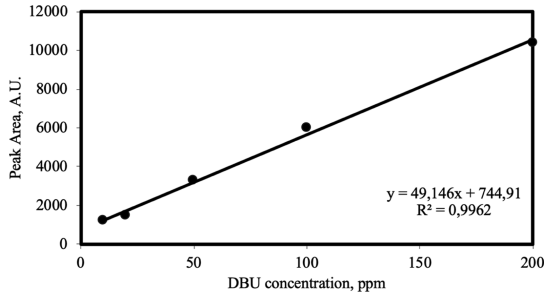


Figure 2. DBU calibration curve.

RESULTS AND DISCUSSION

DBU removal (%) is calculated using eq 1 and the results of experimental design (Minitab 18) for DBU removal are given in Table 3.

$$\text{DBU removal \%} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f represent the initial and final concentrations of DBU, respectively.

Table 3. Experimental Design and Response as Percent Removal of DBU

exp. no.	NaOH concentration, *M*	current density, mA/cm^2	reaction time, min	DBU removal, %
1	0.01	0	30	82.9
2	0.05	0	30	84.6
3	0.05	0	60	87.3
4	0.05	0	90	90.3
5	0.01	0.0027	90	72.3
6	0.05	0.0027	30	94.6
7	0.01	0	90	79.1
8	0.01	0.0027	30	76.9
9	0.01	0.0027	90	84.7
10	0.05	0.0027	90	96.7
11	0.05	0	60	88.7
12	0.01	0	60	79.6
13	0.05	0.0027	60	95.5
14	0.01	0.0027	60	78.3
15	0.01	0	30	56.9
16	0.01	0.0027	30	62.7
17	0.05	0	30	83.5
18	0.05	0.0027	90	97.4
19	0.05	0.0027	60	97.1
20	0.05	0	90	88.9
21	0.05	0.0027	30	95.3
22	0.01	0	90	68.9
23	0.01	0.0027	60	78.3
24	0.01	0	60	61.2

Table 4 presents a summary of ANOVA results for DBU conversion values. In this table, *P*-values (less than $\alpha = 0.05$) for each affecting parameter are given individually to consider the interactions between the parameters. The R^2 with a value of 76.59% indicates that the model is well fit to the observed response.

Based on Table 4, it could be concluded that two-way and three-way interactions of factors do not have a significant effect on DBU removal as their *P*-values are higher than 0.005, so that the interaction parameters were eliminated and the model

https://dx.doi.org/10.1021/acs.iecr.0c02562
Ind. Eng. Chem. Res. 2020, 59, 19153−19161

Table 4. Statistical Analysis Results for Converted DBU with 95% of Confidence Level

source	degree of freedom	sum of squares	mean square	*F*-value	*P*-value
model	11	2424.99	220.45	3.57	0.019
linear	4	2344.92	586.23	9.49	0.001
NaOH concentration	1	1981.98	1981.98	32.08	0.000
current density	1	252.85	252.85	4.09	0.066
time	2	110.09	55.04	0.89	0.436
2-way interactions	5	49.46	9.89	0.16	0.973
NaOH concentration*current density	1	34.32	34.32	0.56	0.470
NaOH concentration*time	2	7.05	3.53	0.06	0.945
current density*time	2	8.09	4.05	0.07	0.937
3-way interactions	2	30.61	15.31	0.25	0.784
NaOH conc.*current density*time	2	30.61	15.31	0.25	0.784
error	12	741.33	61.78		
total	23	3166.33			

was modified. The reduced ANOVA table and the Pareto chart for the main factors are given in Table 5 and Figure 3, respectively.

Table 5. Statistical Analysis Results for Converted DBU with 95% of Confidence Level (Reduced Model)

source	degree of freedom	sum of squares	mean square	*F*-value	*P*-value
model	4	2344.92	586.23	13.56	0.01919
linear	4	2344.92	586.23	13.56	0.00107
NaOH conc.	1	1981.98	1981.98	45.85	0.00010
current density	1	252.85	252.85	5.85	0.06593
time	2	110.09	55.04	1.27	0.43573
error	19	821.41	43.23		0.97255
lack-of-fit	7	80.07	11.44	0.19	0.47041
pure error	12	741.34	61.78		
total	23	3166.33			

Figure 3. Pareto chart for the affecting factors (NaOH concentration, current density, and time) on DBU removal percentage.

The Pareto chart explains the importance of individual effects of factors. For a 95% confidence level and 12 degrees of freedom, the *t*-value is equal to 2.093. The vertical line in the chart indicates the minimum statistically significant effect magnitude for 95% confidence level. As $F_{0.05,1,12} = 4.75$, all the factors with the F value higher than 4.75 are significant. Consequently, the results imply that the reaction time do not have a significant effect on DBU removal statistically, whereas the NaOH concentration and current density have a significant effect on DBU removal. The residual and main effects plots for DBU removal are given in Figures 4 and 5, respectively.

The difference between the experimental removal values and the predicted ones are explained with residual values, and if all points are close to the straight line, then it could be concluded that the data are normally distributed.[17] Figure 4 shows that the experimental points, except one point, were reasonably aligned suggesting a normal distribution in the range of −10 and +10, and there is also an outlier. A main effect exists, while the mean response changes across the level of a factor. The sign of the main effect indicates the directions (positive or negative) of the effect. It can be deduced from Figure 5 that the effect of NaOH concentration was characterized by a greater degree of departure from the overall mean, and thus, the NaOH concentration had a positive effect on the removal of DBU. Current density also had a positive effect on DBU removal; however, its effect was lower relative to NaOH concentration. Moreover, the effect of reaction time slightly decreased for 90 min of reaction time.

Effect of NaOH Concentration. NaOH concentration is the most important factor for hydrothermal electrolysis of DBU according to ANOVA results, and hence, the investigation of the NaOH concentration effect on DBU removal was carried out at various concentrations (0, 0.001, 0.01, and 0.05 M) using 6 mM DBU solution on applying 0.0027 mA/cm^2 of current density at 240 °C for different reaction times (30, 60, and 90 min). Figure 6 shows the effect of NaOH concentration on DBU removal. The highest DBU removal (almost 97%) was observed using 0.05 M NaOH. As the concentration of NaOH increased, the removal of DBU also increased for all reaction durations. In the literature, it was also found that increased NaOH concentration resulted in higher conversion of glycerol under hydrothermal electrolysis conditions.[13] Therefore, it could be deduced that as the electrolyte concentration increases, the ionic conductivity increases, and thus, the removal efficiency increases.

Although DBU conversion was observed in the absence of NaOH on applying 0.0027 mA/cm^2 of current density at 240 °C, 29.6% TOC removal was achieved for 90 min of reaction time. However, when 0.05 M NaOH was used as an electrolyte, 29.6 and 41.0% of TOC removal were achieved for 60 and 90 min of reaction time, respectively. In order to achieve a higher DBU removal efficiency and TOC in a shorter reaction time, an electrolyte should be used and HCW was not solely adequate.

https://dx.doi.org/10.1021/acs.iecr.0c02562
Ind. Eng. Chem. Res. 2020, 59, 19153−19161

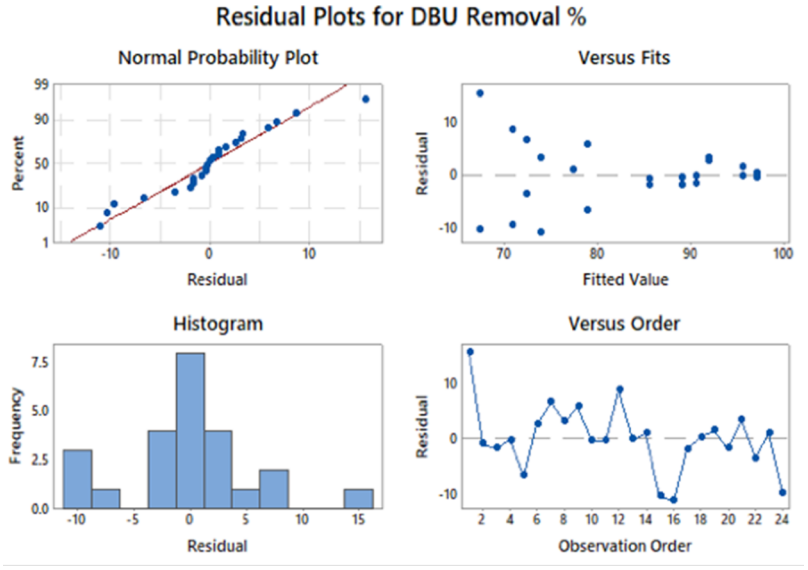


Figure 4. Residual plots for DBU removal.

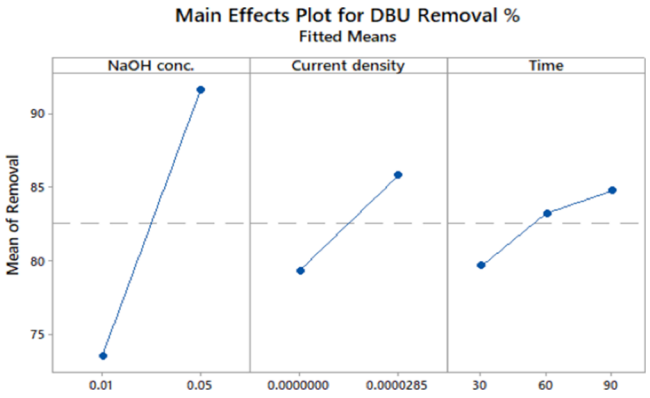


Figure 5. Main effects' plot for DBU removal.

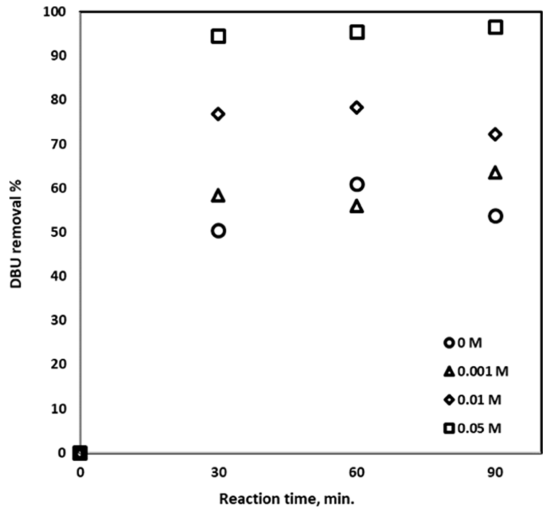


Figure 6. Effect of NaOH concentration on DBU removal (reaction conditions: C_{DBU} = 6 mM, current density = 0.0027 mA/cm^2, and T = 240 °C).

Effect of Current Density. During the electrolysis of water under normal conditions (room temperature and pressure), hydrogen and oxygen gases form by splitting of water. However, if the electrolysis of water is carried out under subcritical conditions, then the formation of oxygen gas could be controlled and only hydrogen gas formation could be achieved. The schematic illustration of electrolysis of water under normal and subcritical conditions is given in Figure 7.[18]

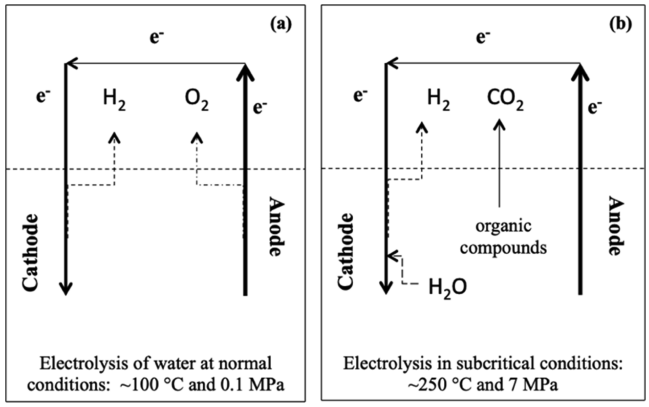


Figure 7. Electrolysis under normal (a) and subcritical (b) conditions.

Therefore, in hydrothermal electrolysis, there is no need for an oxidizer or/and catalyst as water behaves as a catalyst under subcritical conditions.[19] Moreover, any organic solvent is not required for this process, so that it is greener and environmentally benign for the treatment of wastewater. During hydrothermal electrolysis, several oxidants such as H$^\bullet$ and OH$^\bullet$ form as in the subcritical reaction region, molecules of water vapor are ionized around the anode and bombard each other, and thus, free hydroxyl radicals, ions, and sometimes hydrogen atoms form. Besides, water molecules are broken into hydrogen, oxygen, and hydrogen peroxide in the liquid reaction region.[19−21] The possible reactions for the formation of these radicals are shown in eqs 2−6. Among the formed oxidants, OH$^\bullet$ is the strongest one; however, the lifetime of OH$^\bullet$ is very short so that the secondary oxidants form by the destruction of OH$^\bullet$ to continue the degradation of organic compounds.

https://dx.doi.org/10.1021/acs.iecr.0c02562
Ind. Eng. Chem. Res. 2020, 59, 19153−19161

$$H^{\bullet} + H^{\bullet} \rightarrow H_2 \quad (2)$$

$$H^{\bullet} + OH^{\bullet} \rightarrow H_2O \quad (3)$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \quad (4)$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (5)$$

$$OH^{\bullet} + HO_2^{\bullet} \rightarrow H_2O + O_2 \quad (6)$$

Consequently, the current density is an important parameter for hydrothermal electrolysis so that the effect of this parameter was also investigated at different current densities, which are 0 mA/cm^2 (0 A), 0.0007 mA/cm^2 (0.25 A) and 0.0027 mA/cm^2 (1 A). The hydrothermal electrolysis of DBU takes place using 6 mM DBU solution at 240 °C applying the current for different reaction times (30, 60, and 90 min). The results are given in Figure 8. Based on the results, the increased

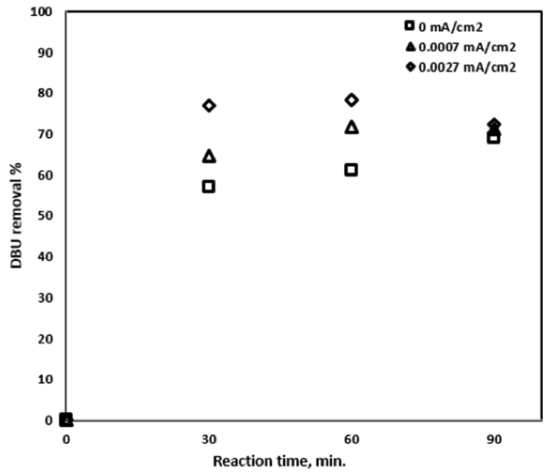


Figure 8. Effect of current density on DBU removal (reaction conditions: C_{DBU} = 6 mM, T = 240 °C, C_{NaOH} = 0.01 M).

current density promoted the DBU removal % for 30 and 60 min of reaction time. However, almost the same DBU removal efficiency was observed at 90 min of reaction time. Whereas no TOC removal was observed on applying 0 mA/cm^2 current density for 30 and 60 min of reaction time, 11.5 and 31.1% of TOC removal were obtained on applying 0.0027 mA/cm^2 current for 30 and 60 min of reaction time, respectively. Besides, TOC removal % was achieved at 90 min of reaction time as 11.1 and 31.1% on applying 0 and 0.0027 mA/cm^2 current density, respectively. Hence, while approximately the same TOC removal was observed in 30 min on applying current, it could be obtained in 90 min in the absence of current. Therefore, for short reaction times, TOC removal could not be achieved without applying current. Additionally, toxic byproducts were observed in the absence of current density, while this hazardous byproduct could be eliminated by applying current based on the GC−MS results of end products. Thus, increased current density results in increased TOC removal %. In the literature, it was found that *p*-nitrophenol degradation as well as TOC removal during hydrothermal electrolysis of glucose increased with respect to increased current densities.[22,23] Moreover, amidines such as DBU could decompose by pyrolysis under subcritical conditions in the absence of an oxidant; however, low TOC removal could be achieved when no current was applied to the system (0 mA/cm^2).[24] Consequently, applying current to the system greatly contributes to DBU and TOC removal. Besides, there is no need for an oxidant in this hybrid system, and no usage of an oxidant is an advantage to eliminate harmful end or side products during the wastewater treatment. Consequently, this hybrid hydrothermal electrolysis system is an environmentally friendly and greener solution for the treatment of organic contaminants in wastewater.

Initial DBU Concentration Effect. The effect of the initial concentration of DBU (3, 6, and 12 mM) on DBU and TOC removal was investigated, and the results are shown in Figure 9.

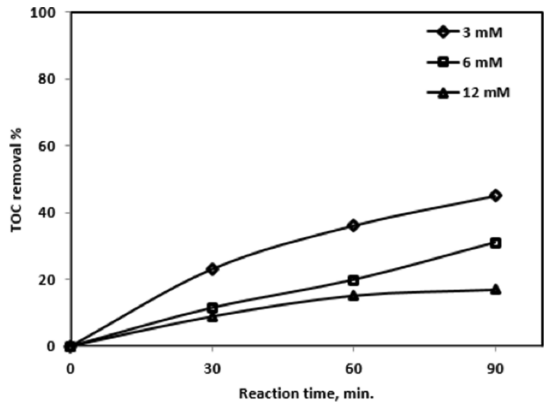


Figure 9. Initial DBU concentration effect on TOC removal % (reaction conditions: C_{NaOH} = 0.01 mM, current density = 0.0027 mA/cm^2, and T = 240 °C).

As a result, the highest DBU (91.2%) and TOC removal (45%) were observed at the lowest concentration of DBU for all reaction times. A similar DBU removal efficiency was observed for 6 and 12 mM initial DBU concentrations at 30 min of reaction time.

GC−MS Analysis. The main products of hydrothermal electrolysis of DBU at the specified reaction temperature (240 °C), NaOH concentrations (0.1 and 0.5 M), current densities (0 mA/cm^2 and 0.0027 mA/cm^2), and for 30, 60, and 90 min of reaction time under subcritical conditions were identified by GC−MS. The major products of hydrothermal electrolysis of DBU under subcritical conditions were found as methylcaprolactam, 1-methyl-2 phenyl indole, caprolactam, 4-amino-3-methylphenol nitrobenzene, and toluene. Among them, nitrobenzene (2.27 min of retention time) and toluene (3.17 min of retention time) could cause significant hazards on aquatic life on long-term exposure, and they also have serious effects on human health.[25,26] However, these compounds were eliminated by applying current. The intermediates of hydrothermal electrolysis of DBU are listed in Table 6.

Table 6. GC−MS Results for the Main Compounds of Hydrothermal Electrolysis of DBU[a]

retention time, min	compounds
4.04	1-methyl-2-phenylindole
15.71	caprolactam
20.62	4-amino-3-methylphenol
24.72	*N*-methylcaprolactam

[a]Current density: 0.0027 mA/cm^2, T: 240 °C, C_{DBU}: 6 mM, C_{NaOH}: 0.01 M, t: 60 min.

https://dx.doi.org/10.1021/acs.iecr.0c02562
Ind. Eng. Chem. Res. 2020, 59, 19153−19161

The major products of hydrothermal electrolysis of DBU under subcritical conditions were found as 4-amino-3-methylphenol, caprolactam, methylcaprolactam, and 1-methyl-2 phenyl indole. Among them 4-amino-3-methylphenol and caprolactam can cause skin or eye irritation, yet, they are relatively less hazardous than DBU. DBU is a corrosive, irritant, and acute toxic compound, and it could be said that the major products of hydrothermal electrolysis of DBU are less hazardous than those of DBU. Consequently, thanks to hydrothermal electrolysis, highly toxic end products do not form, and thus, hydrothermal electrolysis is a greener solution for treatment of wastewaters containing hazardous compounds that are resistant to degradation.

Reaction Temperature Effect. The effect of temperature on DBU and TOC removal was also investigated, and the results are given in Figure 10. According to the results, as the

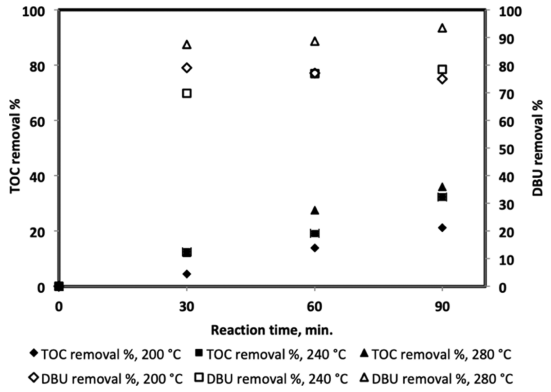


Figure 10. Temperature effect on TOC and DBU removal % (reaction conditions: C_{DBU} = 6 mM, C_{NaOH} = 0.01 M, and current density = 0.0027 mA/cm^2).

temperature and reaction time increase, the TOC removal percentage also increased. However, the DBU removal percentage was almost the same for all reaction conditions at 200 °C. When 1 A current (current density = 0.027 mA/cm^2) was passed in hydrothermal electrolysis at high temperatures (240 and 280 °C), there was a slight increase in DBU removal.

To take into account the effect of current density on DBU and TOC removal, the experiments of the kinetic study were performed by applying a direct current. To determine the reaction kinetic model and rate constants, the first- and second-order reaction kinetic models were applied by assuming that the reaction only depended on the DBU concentration and temperature. Among the applied kinetic models, TOC removal % show the best fit to the first-order reaction kinetic model. The R^2 values and reaction rate constants for the first-order model for TOC removal % are given in Table 7 and the linearized first order kinetic data are shown in Figure 11.

The first-order reaction rate constants were found as 0.0025, 0.0041, and 0.005 min^{-1} at 200, 240, and 280 °C, respectively.

Table 7. Calculated Values of R^2 and Rate Constants for the First-Order Reaction Model

temperature, °C	R^2, first order	first-order kinetic rate constant, min^{-1}
200	0.97	0.0025
240	0.98	0.0041
280	0.99	0.005

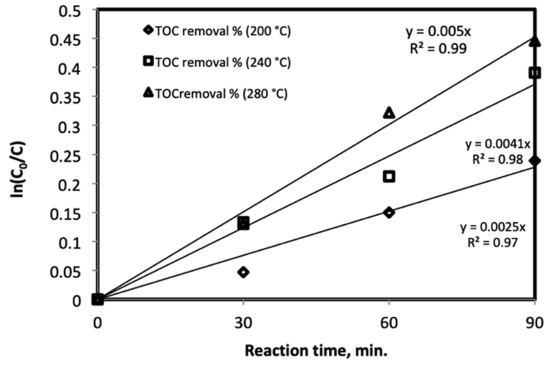


Figure 11. Linearized first-order kinetic plot.

As expected, as the temperature increased, the rate constants also increased. The activation energy was determined by the Arrhenius equation as 79.86 kJ/mol.

This study and related studies in the literature are summarized in Table 8 and a comparison of studies is briefly performed. Ochuma et al. studied the degradation of DBU by photocatalytic oxidation, and the experiments were carried out in the presence of suspended TiO_2 and using TiO_2-coated monolith for comparison. Based on the results, the highest DBU (100%) and TOC (~23%) removal were achieved for 60 min of reaction duration using a TiO_2-coated (12 wt %) reticulated foam photocatalytic reactor.[8] Al-Duri and her colleagues studied the DBU and (dimethyl formamide) DMF degradation by noncatalytic supercritical water oxidation (SCWO), and hydrogen peroxide was used as an oxidant in this study. Whereas DBU was completely degraded after 450 °C of reaction temperature, almost 90% TOC removal (highest TOC removal) was observed after 600 °C.[27] Another study related to DBU degradation and its kinetic modeling was carried out under supercritical conditions by Al-Duri and Alsoqyani, and it was found that the addition of isopropyl alcohol (IPA) to the reaction media has a positive contribution to the yield of DBU and TOC removal, and the highest TOC removal was obtained as ~99% for 5 mM initial DBU concentration at 525 °C, 10 h of reaction time, and [IPA]/[DBU] = 1. The reaction kinetic model could be described by the pseudo-first order kinetic model and the global power law kinetic model.[28] Based on these studies, it could be said that the usage of IPA provides an enhancement of the efficiency of SCWO to obtain higher TOC values at relatively lower temperatures. To conclude, it could be said that the DBU degradation reaction can be described by the first- or pseudo-first-order reaction model. SCWO shows higher efficiency due to TOC removal compared to photocatalytic oxidation; however, SCWO requires extremely harsh reaction conditions to achieve higher TOC removal. According to the literature, caprolactam, 3-methyladenine, 2,6-dimethyl-4-hydroxybenzaldehyde, 3-methoxy-4,5,6-trimethylphenol, and 4-amino-5-formamidomethyl-2-methylpyrimidine are the five intermediate products of photocatalytic degradation of DBU, and some of them have hazardous effects on human and environmental health.[8] In this study, DBU degradation by hydrothermal electrolysis was investigated, and it was found that the DBU removal efficiency depended on the NaOH concentration and current density based on statistical results. Hence, the increase in the NaOH concentration and current density is directly effective over DBU removal. For instance, 58.3% of DBU removal was achieved at 240 °C by applying 1 A current

https://dx.doi.org/10.1021/acs.iecr.0c02562
Ind. Eng. Chem. Res. 2020, 59, 19153−19161

Table 8. Comparison with Literature

reference	model compound	process	TOC removal, %, conversion of compound, %	kinetic model
Ochuma et al. 2007[8]	DBU	photocatalytic oxidation	~23% TOC removal, 100% DBU conversion	first-order kinetic model
Al-Duri et al., 2008[27]	DBU and DMF	SCWO	>90% TOC removal (600 °C), 100% DBU conversion (after 450 °C)	pseudo-first-order, integral power rate law, and power law models
Al-Duri and Alsoqyani, 2017[28]	DBU	SCWO	~99% TOC removal (525 °C)	pseudo first order and the global power law models
this study	DBU	hydrothermal electrolysis	97.4% DBU removal (240 °C), ~35% TOC removal (280 °C)	first-order kinetic model

(current density = 0.027 mA/cm^2) in the presence of 0.001 M NaOH for 30 min of reaction time; however, 97.4% was achieved using 0.05 M NaOH under the same reaction conditions. The highest TOC removal (~35%) was achieved by applying 1 A current (current density = 0.027 mA/cm^2) in the presence of 0.01 M NaOH for 90 min of reaction time at 280 °C. It might be possible to reach higher TOC removal efficiencies (which are similar to TOC removal efficiencies in SCWO) for longer reaction times. The end products of this process were analyzed via GC−MS and, based on the results, some of them are relatively less hazardous than DBU and some are not hazardous. Thus, it could be said that hydrothermal electrolysis is more effective than photocatalytic oxidation for TOC removal, and it presents moderate reaction conditions than SCWO. Additionally, hydrothermal electrolysis can be considered as a greener route for degradation of DBU because of the less harmless and unhazardous end products.

CONCLUSIONS

DBU, a nitrogen-containing compound, was chosen as a model solution to demonstrate the applicability of hydrothermal electrolysis, a hybrid green technology employed for the degradation of nitrogen-containing organic contaminants. In this study, the NaOH concentration, current density, and reaction temperature as effective parameters on DBU and TOC removal were investigated. Based on Minitab results, the NaOH concentration and current density had a significant effect on the removal of DBU statistically. Additionally, the initial DBU concentration effect was investigated and the highest DBU (91.2%) and TOC (45%) removal were observed at the lowest concentration (3 mM) for 90 min of reaction time. Besides, a kinetic study was carried out to investigate the effect of temperature on TOC removal and it followed the first-order reaction kinetic model, and rate constants were determined as 0.0025, 0.041, and 0.050 min^{-1} for 200, 240, and 280 °C, respectively. Additionally, the activation energy was calculated as 79.86 kJ/mol.

AUTHOR INFORMATION

Corresponding Author

Aslı Yüksel Özşen − *Department of Chemical Engineering and Geothermal Energy Research and Application Center, Izmir Institute of Technology, 35430 Urla, Izmir, Turkey;* orcid.org/0000-0002-9273-2078; Email: asliyuksel@iyte.edu.tr

Author

Ceren Orak − *Department of Chemical Engineering, Izmir Institute of Technology, 35430 Urla, Izmir, Turkey*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.iecr.0c02562

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was financially supported by a Marie Curie Career Integration Grant (FP7-PEOPLE-2012- CIG) with a project number PCIG11-GA-2012-321741. We would like to thank Orkan Dal and Emre Demirkaya for their help in some experiments. We would also like to thank "Environmental Reference Research and Development Center" at the Izmir Institute of Technology for their support in product analysis.

REFERENCES

(1) Navarro, P.; Gabaldón, J. A.; Gómez-López, V. M. Degradation of an azo dye by a fast and innovative pulsed light/H_2O_2 advanced oxidation process. *Dyes Pigm.* **2017**, *136*, 887−892.

(2) Elhorri, A. M.; Belaid, K. D.; Zouaoui−Rabah, M.; Chadli, R. Theoretical study of the azo dyes dissociation by advanced oxidation using Fukui indices. DFT calculations. *Comput. Theor. Chem.* **2018**, *1130*, 98−106.

(3) Azizi, A.; Alavi Moghaddam, M. R.; Maknoon, R.; Kowsari, E. Innovative combined technique for high concentration of azo dye AR18 wastewater treatment using modified SBR and enhanced Fenton process as post treatment. *Process Saf. Environ.* **2015**, *95*, 255−264.

(4) Klare, M.; Scheen, J.; Vogelsang, K.; Jacobs, H.; Broekaert, J. A. C. Degradation of short-chain alkyl- and alkanolamines by TiO_2- and Pt/TiO_2-assisted photocatalysis. *Chemosphere* **2000**, *41*, 353−362.

(5) Reddy, M. P.; Srinivas, B.; Durga Kumari, V.; Subrahmanyam, M.; Sharma, P. N. An integrated approach of solar photocatalytic and biological treatment of N-containing organic compounds in wastewater. *Toxicol. Environ. Chem.* **2004**, *86*, 127−140.

(6) Li, Y.; Gu, G.; Zhao, J.; Yu, H. Anoxic degradation of nitrogenous heterocyclic compounds by acclimated activated sludge. *Process Biochem.* **2001**, *37*, 81−86.

(7) Muz, M.; Dann, J. P.; Jäger, F.; Brack, W.; Krauss, M. Identification of mutagenic aromatic amines in river samples with industrial wastewater impact. *Environ. Sci. Techol.* **2017**, *51*, 4681−4688.

(8) Ochuma, I. J.; Osibo, O. O.; Fishwick, R. P.; Pollington, S.; Wagland, A.; Wood, J.; Winterbottom, J. M. Three-phase photocatalysis using suspended titania and titania supported on a reticulated foam monolith for water purification. *Catal. Today* **2007**, *128*, 100−107.

(9) Jurado-Sánchez, B.; Ballesteros, E.; Gallego, M. Occurrence of aromatic amines and N-nitrosamines in the different steps of a drinking water treatment plant. *Water Res.* **2012**, *46*, 4543−4555.

(10) Ochuma, I. J.; Fishwick, R. P.; Wood, J.; Winterbottom, J. M. Optimisation of degradation conditions of 1,8-diazabicyclo[5.4.0]-undec-7-ene in water and reaction kinetics analysis using a cocurrent downflow contactor photocatalytic reactor. *Appl. Catal. B Environ.* **2007**, *73*, 259−268.

(11) Al-Duri, B.; Pinto, L.; Ashraf-Ball, N. H.; Santos, R. C. D. Thermal abatement of nitrogen-containing hydrocarbons by non-

catalytic supercritical water oxidation (SCWO). *J. Mater. Sci.* **2008**, *43*, 1421−1428.
(12) Pinto, L. D.; dos Santos, L. M. F.; Al-Duri, B.; Santos, R. C. Supercritical water oxidation of quinoline in a continuous plug flow reactor-part 1: effect of key operating parameters. *J. Chem. Technol. Biotechnol.* **2006**, *81*, 912−918.
(13) Yuksel, A.; Sasaki, M.; Goto, M. Complete degradation of Orange G by electrolysis in sub-critical water. *J. Hazard. Mater.* **2011**, *190*, 1058−1062.
(14) Cheng, K.; Wei, Y.; Hui, W.; Jie, Z.; Shengji, W.; Tianming, Y.; Jianbo, P. Effect of Cu (II) on degradation and decolorization of rhodamine B in subcritical water. *Chem. Res. Chin. Univ.* **2017**, *33*, 643−647.
(15) Emgili, H.; Yabalak, E.; Görmez, Ö.; Gizir, A. M. Degradation of Maxilon Blue GRL dye using subcritical water and ultrasonic assisted oxidation methods. *GU J. Sci.* **2017**, *30*, 140−150.
(16) Emire, Z.; Yabalak, E.; Görmez, Ö.; Gizir, M. Solubility and degradation of paracetamol in subcritical water. *J. Serb. Chem. Soc.* **2017**, *82*, 99−106.
(17) Safa, Y.; Bhatti, H. N. Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk. *Desalination* **2011**, *272*, 313−322.
(18) Serikawa, R. M. Wet electrolytic oxidation of organic sludge. *J. Hazard. Mater.* **2007**, *146*, 646−651.
(19) Yuksel, A.; Sasaki, M.; Goto, M. A new green technology: hydrothermal electrolysis for the treatment of biodiesel wastewater. *Res. Chem. Intermed.* **2011**, *37*, 131−143.
(20) Miller, D. J.; Hawthorne, S. B. Method for determining the solubilities of hydrophobic organics in subcritical water. *Anal. Chem.* **1998**, *70*, 1618−1621.
(21) Savage, P. E. Organic chemical reactions in supercritical water. *Chem. Rev.* **1999**, *99*, 603−622.
(22) Dai, Q.; Lei, L.; Zhang, X. Enhanced degradation of organic wastewater containing p-nitrophenol by a novel wet electrocatalytic oxidation process: Parameter optimization and degradation mechanism. *Sep. Purif. Technol.* **2008**, *61*, 123−129.
(23) Sasaki, M.; Yamamoto, K.; Goto, M. Reaction mechanism and pathway for the hydrothermal electrolysis of organic compounds. *J. Mater. Cycles Waste* **2007**, *9*, 40−46.
(24) Shriner, R. L.; Neumann, F. W. The Chemistry of the Amidines. *Chem. Rev.* **1944**, *35*, 351−425.
(25) Holder, J. W. Nitrobenzene carcinogenicity in animals and human hazard evaluation. *Toxicol. Ind. Health* **1999**, *15*, 445−457.
(26) Kim, K.-H.; Szulejko, J. E.; Raza, N.; Kumar, V.; Vikrant, K.; Tsang, D. C. W.; Bolan, N. S.; Ok, Y. S.; Khan, A. Identifying the best materials for the removal of airborne toluene based on performance metrics - A critical review. *J. Clean. Prod.* **2019**, *241*, 118408.
(27) Al-Duri, B.; Pinto, L.; Ashraf-Ball, N. H.; Santos, R. C. D. Thermal abatement of nitrogen-containing hydrocarbons by non-catalytic supercritical water oxidation (SCWO). *J. Mater. Sci.* **2008**, *43*, 1421−1428.
(28) Al-Duri, B.; Alsoqyani, F. Supercritical water oxidation (SCWO) for the removal of nitrogen containing heterocyclic waste hydrocarbons. Part II: System kinetics. *J. Supercrit. Fluids* **2017**, *128*, 412−418.

https://dx.doi.org/10.1021/acs.iecr.0c02562
Ind. Eng. Chem. Res. 2020, 59, 19153−19161