



# Furfural degradation through heat-activated persulfate: Impacts of simulated brine and elevated pressures

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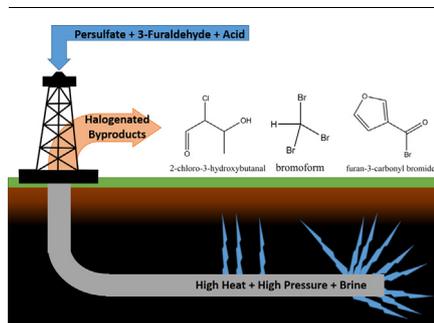
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## HIGHLIGHTS

- Furfural degradation in lab simulated hydraulic fracturing brine with persulfate.
- Novel activation of persulfate using extreme pressures.
- Persulfate activation at borehole conditions including heat, varying pH, and iron.
- Identified reaction byproducts showed formation of halogenated organics in brine.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

Persulfate is used as an oxidizing breaker in hydraulic fracturing fluids to breakdown gelling agents and clean out wellbores. Persulfate may be activated using conditions like those encountered in the wellbore, producing strong oxidizing radicals that degrade organic compounds. Thus, this study examined persulfate activated transformation of organic additives in a simulated hydraulic fracturing brine by investigating the transformation of furfural. Pseudo-first-order reactions kinetics of furfural degradation in conditions that mimic a fracture, including high temperature, acidified pH, ferric sulfate, and a laboratory simulated hydraulic fracturing brine, were established. The activation energies for furfural removal in acidic (pH 2.54) hydraulic fracturing brine was  $105.6 \text{ kJ mol}^{-1}$  without ferric sulfate and  $105.1 \text{ kJ mol}^{-1}$  with  $23.3 \text{ mg L}^{-1}$  ferric sulfate. A high-pressure reactor was used to simulate the effects of pressure on persulfate activation. Increasing pressure was shown to increase activation of persulfate at  $55^\circ\text{C}$ . Applying 3000 psi to the reactor nearly halved the apparent furfural activation energy compared to experiments at atmospheric pressure. Finally, reaction byproducts were presented with the findings showing that halogenated organic byproducts form in hydraulic fracturing brine during persulfate use.

## 1. Introduction

Increasing population and energy production continue to place demands on water resources [1]. In response to the energy demand, the

US has turned to natural gas, with most extraction achieved through hydraulic fracturing of unconventional reservoirs [2,3]. Hydraulic fracturing has become a public concern as industry practices have impacted the environment [4,5].

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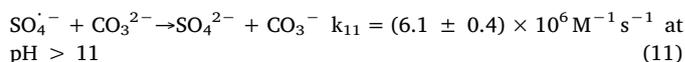
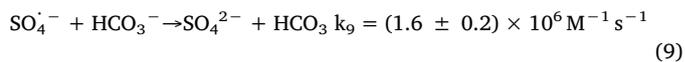
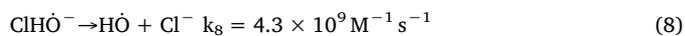
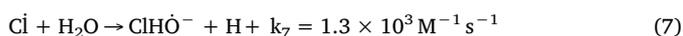
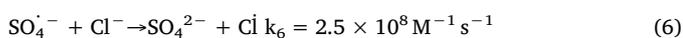
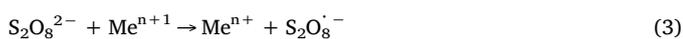
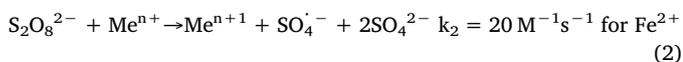
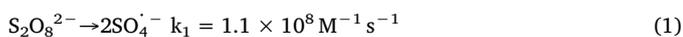
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Adding chemical agents to the large quantities of water used to fracture a single well degrades the water quality, which then requires proper treatment or disposal [6,7]. In the Marcellus region alone, over 350 organic species have been reported by hydraulic fracturing companies [8]. Additives used depend on the day-to-day conditions of the well, but include surfactants, gelling agents, biocides, and breaking agents [9–12]. Chemical transformations occur because of high downhole temperatures and pressures; however, the reactions are different for each chemical agent [13,14]. For instance, breaking agents decompose target gelling agents to smaller molecular components to allow fluid and gas to return to the well surface. Enzyme breakers react with the gelling agent at specific sites, while non-selective, “delayed” breakers oxidize the nearest constituent. Furthermore, as the fluids extract materials from the geological formation, high inorganic salt concentrations, or total dissolved solids (TDS), are introduced to the mixture [4]. Sodium persulfate, a delayed breaker used in hydraulic fracturing [15], forms sulfate and hydroxyl radicals with activation by conditions encountered during a fracture, such as elevated temperature, acid addition, and iron concentrations as shown in Reactions (1) to (5) [9,16–22]. Persulfate concentration used may vary between 0.125 and 47 mmol L<sup>-1</sup>, depending on the well location and formation conditions [9].

Little information on how high pressure influences the chemistry of hydraulic fracturing has been published. Previous studies have investigated the transformation of glutaraldehyde, an organic biocide used in hydraulic fracturing, under high pressure conditions [14]. Kahrilas et al. determined that high pressure did not impact the hydrolysis of glutaraldehyde [14]; however, the use of oxidizers was not considered in this study. Current studies that consider the use of oxidizers, such as persulfate, do not consider the high pressures reached in the well bore [9,11]. Under high pressure, oxidizers likely accelerate chemical transformation and the formation of unintended byproducts. When halogens, such as those contained in hydraulic fracturing brine or the shale rock, are present, reactions with persulfate may lead to the formation of halogenated organic byproducts, which have been detected in produced water [23]. Halogenated organic byproducts are regulated by the EPA as they are associated with cancer, birth defects, cytotoxicity, genotoxicity, and other adverse health effects [24–30].

In addition to increasing potential for halogenated organic byproduct formation, TDS (5000 mg L<sup>-1</sup> to greater than 200,000 mg L<sup>-1</sup>) [4,31–33] and brine content (32,000 to 148,000 mg L<sup>-1</sup> chloride, 720 to 1600 mg L<sup>-1</sup> bromide, and 9100 to 55,000 mg L<sup>-1</sup> carbonate species) [4,34–37] in hydraulic fracturing wastewater varies between fractures and may scavenge radicals formed from persulfate activation, as shown in Reactions 6–11, requiring additional persulfate use [11,38–40]. Ions compete for the radicals, but the extent depends on pH [38,41]. Hydrochloric acid added by hydraulic fracturing companies [6,10,42,43] may increase radical quenching at low concentrations or decrease quenching at higher concentrations [17,44,45]. Additionally, downhole temperatures may reach 140 °C, which would rapidly activate persulfate and breakdown organic additives [46]. To date, the impact of extreme downhole pressures, which may exceed 6000 psi [46], on persulfate activation have not been investigated.



The objective of this study is to determine the impacts elevated pressures and the presence of TDS has on furfural degradation and formation of transformation byproducts in laboratory simulated hydraulic fracturing brine. The chemical changes that occur over the course of a fracture were investigated using one model additive, 3-furfuraldehyde or “furfural” (a component of an enzyme breaker called “LEB-10X” and proppant material), and a laboratory composed hydraulic fracturing brine [9,12,47,48]. Extreme pressures were studied by observing changes in furfural degradation rates and transformation byproducts using persulfate in the brine. Conditions used in this study, including temperature, pressure, persulfate concentration, brine content, pH, and iron concentrations, were used to simulate those experienced during the hydraulic fracturing process [9].

## 2. Experimental

### 2.1. Chemicals

All solutions were prepared using deionized water produced by a Milli-Q Plus water purification system (Darmstadt, Germany). 3-furfuraldehyde or furfural was purchased from Sigma Aldrich (St. Louis, MO 63103). Optima grade hexane and 97% tribromomethane stabilized with ethanol were purchased from Fisher Scientific (Pittsburgh, PA 15275, USA). Inorganic salts, aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) (> 99%), ferric sulfate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) (99%), hydrochloric acid (HCl), potassium bromide (KBr) (> 99%), potassium chloride (KCl) (99%), potassium sulfate (K<sub>2</sub>SO<sub>4</sub>) (99%), sodium bicarbonate (NaHCO<sub>3</sub>) (> 99%), sodium hydroxide (NaOH), sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) (> 98%), sodium chloride (NaCl) (> 99%), and potassium iodide (KI) (> 99%) were purchased from Fisher Scientific (Pittsburgh, PA 15275, USA). LEB-10X, an enzyme breaker, and WGA, a gelling agent, were obtained from Weatherford International (Houston, Texas, USA).

### 2.2. Batch oxidation experiments at ambient pressure

Solutions containing 120 mg L<sup>-1</sup> (1.25 mmol L<sup>-1</sup>) furfural and hydraulic fracturing brine were prepared 24 h prior to starting the experiments. Furfural is used in hydraulic fracturing additive LEB-10X, an enzyme breaker, which are used in concentrations ranging from 1 to 400 mg L<sup>-1</sup> [6,9]. Based on this value, the concentration of furfural in the fluids will be less than 400 mg L<sup>-1</sup> and 120 mg L<sup>-1</sup> was used in these experiments for ease of measurement. Hydraulic fracturing brine solution was composed of 1 g L<sup>-1</sup> (17.1 mmol L<sup>-1</sup>) sodium chloride, 20 mg L<sup>-1</sup> (0.27 mmol L<sup>-1</sup>) potassium chloride, 25 mg L<sup>-1</sup> (0.14 mmol L<sup>-1</sup>) potassium sulfate, 15 mg L<sup>-1</sup> (0.13 mmol L<sup>-1</sup>) potassium bromide, 15 mg L<sup>-1</sup> (0.18 mmol L<sup>-1</sup>) sodium bicarbonate, and 15 mg L<sup>-1</sup> (0.044 mmol L<sup>-1</sup>) aluminum sulfate [49]. Iron activation of the persulfate was performed by adding 23.3 mg L<sup>-1</sup> (0.058 mmol L<sup>-1</sup>) ferric sulfate to the brine. pH was adjusted to 2.54 using 0.07% hydrochloric acid, to achieve acidic conditions used in the industry, and measured with Fisher Scientific Accumet XL600 benchtop pH meter (Pittsburgh, PA 15275, USA) [6,50,51].

Batch experiments were performed in triplicate using 100-mL volumes in 125-mL amber borosilicate volatile organic carbon jars closed with Teflon-lined screw caps. Jars were placed in a shaking water bath at 20, 30, 40, 55, or 60 °C 12 h prior to experiment start. To initiate

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