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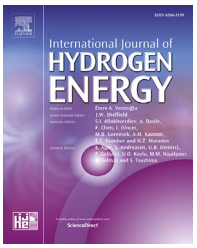

Gasification of unsymmetrical dimethylhydrazine in supercritical water: Reaction pathway and kinetics

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ABSTRACT

Unsymmetrical dimethylhydrazine (UDMH) is a high N-containing (as much as nearly 50%) substance. Traditional treatment methods such as incineration will inevitably cause the formation of nitric oxide and secondary pollution. Supercritical water is a preferred transformation medium due to its unique physicochemical properties. However, at present most of studies are limited to supercritical water oxidation (SCWO) which tends to produce hydrogen nitrate resulting in corrosion to the reactor. To conquer this problem, we propose supercritical water gasification (SCWG) technology which is in a reducing environment, realizing both harmless treatment and resource utilization. In order to promote its industrialization process, the reaction pathways and kinetic parameters should be studied. In this paper, the reaction pathways and kinetics of UDMH in supercritical water were conducted under the conditions of 400 °C–550 °C in quartz reactor, which avoids the catalytic effect on the reaction kinetics. From the resource utilization perspective, the most abundant quantitatively detectable gaseous product is methane, together with less hydrogen, carbon monoxide and ethane orderly. All these gaseous products are combustible. The maximum of carbon efficiency is 90.25% at 550 °C, 10 min. In the point of view of harmless treatment, the organic compounds contained in the residual liquid are detected with ^{1}H NMR, FTIR and GC/MS. Results show that UDMH could be fully degraded within 3 min and the ultimate organic compounds in the residual liquid are mainly dimethylamino acetonitrile and trimethylamine. In addition, a reaction pathway for UDMH disposed in supercritical water is developed. Finally, the quantitative kinetic model for describing the gaseous products and ammonia-nitrogen in the residual liquid is brought forward. The pyrolysis activation energy for UDMH in supercritical water is 49.98 ± 7.38 kJ/mol.

Introduction

Pollution is the price we pay for economic growth in an ever-increasing pace. Much effort has been made to deal with it, which is still a worldwide threat to overwhelm us. Hazardous waste is one of the most dangerous varieties of pollution that will do a great harm to human beings and surroundings if cannot be properly treated. Unsymmetrical dimethylhydrazine (UDMH) is considered to be a kind of hazardous waste

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because of its high toxicity. Owning the advantages of high specific impulses, high thrust levels and better thrust control [1], UDMH is used as a source of propellant for military and space programs [2] in many countries, such as Russia, China and the U.S [3]. However, it has a high potential to exacerbate the environment and the human health [4].

Table 1 gives a brief list with respect to comparison of different approaches to decompose UDMH waste water. Apart from traditional methods (such as adsorption, incineration), the mostly used method is oxidation, which has the disadvantage of forming the known highly carcinogenic N-dimethylhydroxylamine (NDMA) for the reason of UDMH oxidation [5]. As such, new way of treatment for UDMH still needs exploring. It is reported that SCWG technology can deal with various organic waste, such as sewage sludge [6], waste paper [7], vinasses generated during the alcohol process [8], garbage and industrial wastes [9], with the advantage of high reaction rate, harmless treatment and resource utilization. So it is worth making an attempt to dispose UMDH with SCWG.

The properties of water above its critical point are quite different from those of liquid water under ambient conditions. The number and persistence of hydrogen bonds are both diminished and the dielectric constant is much lower, which is one of the reasons why organic wastes enjoy complete miscibility in SCW. On the other hand, the dissociation constant (K_w) for SCW is much higher than it is for ambient liquid water, which makes it an ideal solvent for organic compounds [18–23]. Supercritical water has been proved to be a good medium to treat many kinds of organic substances [24–31].

Research concerning the transformation of nitrogen in supercritical water has been studied by many researchers. Killilea's group [32] reportedly studied the distribution of nitrogen under the conditions of SCWO, finding that most of nitrogen in any oxidation state is converted to N_2, as well as trace of N_2O that could be eliminated via catalytic reduction or operating the SCWO process at higher temperature. Quinoline used as a model nitrogen-containing compound, also under SCWO environment, Yuan [33] obtained a reduction of total nitrogen to 85% with the presence of sulfided NiMo catalyst, and put forward the denitrogenation pathway. In Liu's [34] work, the transformation mechanism of nitrogen is given. With no nitrogen-containing gaseous products being detected, the concentration of inorganic nitrogen in the residual liquid, mainly in the form of ammonia-nitrogen, increased with the increase of temperature and prolonging of reaction time.

Although many attempts have been made to dispose wastes containing UDMH, there are still several problems to be tackled. For example, conventional thermal methods, such as incineration in flame, consume much energy and lead to the formation of large amounts of secondary pollutants [35]. SCWO process has accomplished many challenges in recent years, but in terms of UDMH disposal, highly carcinogenic substance such as NDMA could be formed in the process of SCWO. Beyond that, corrosion imposed by hydrogen nitrate is one of bottlenecks remaining to be solved. Compared to SCWO, SCWG can slow down the rate of corrosion and recycle part of energy contained in the wastes, realizing resource utilization. However, the gasification mechanism and kinetic model of UDMH in SCWG process are not readily accessible.

Table 1 – Comparison of different approaches to decompose UDMH waste water.

Method	Experimental condition	Advantages	Disadvantages	Reference
Activated carbon fiber adsorption	Temperature: 25 °C, processing time: 3 h	No toxic compound formed	Low processing efficiency	[10]
Catalytic fenton oxidation	Room temperature, reaction time: 1.5 h	No toxic substance formed	Long reaction time, adsorption will cause secondary pollution	[11]
Catalytic oxidation	Temperature: 25–75 °C, half time: 1–300 min, pH: 7,9	The iron-containing catalysts are stable in neutral media	Formation of toxic compounds, low handling capacity	[12]
Microwave catalytic oxidation	Microwave power 490 W, irradiation time 9 min, H_2O_2 dosage 1 mL and activated carbon dosage 1 g per 100 mL UDMH sewage	High degradation rate	Long reaction time, low handling capacity	[13]
Ultraviolet induced chlorination	Temperature: 40–125 °C, degree of irradiation: 0.1–1.0 W per liter, pH 5	Suitable for multiple pollutants, clean effluent	Long reaction time, complex system, operating at certain pH	[14]
Magnetic carbon nanocomposite	Room temperature, contact time: 30 min, pH 6	High removal efficiency	Long reaction time, secondary pollution, limited pH range	[15]
Chemical oxidation	Room temperature, reaction time 30 days, adding oxidant	High effectiveness with strong oxidant	Mostly produce toxic compounds, long reaction time	[16]
Hybrid cavitation	Near room temperature, pressure: 7 bar, reaction time: 40 min, pH: 2–7.4	High removal efficiency, no oxidant needed, no toxic products	Low processing efficiency	[17]

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