The Journal of Supercritical Fluids 140 (2018) 356–363

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

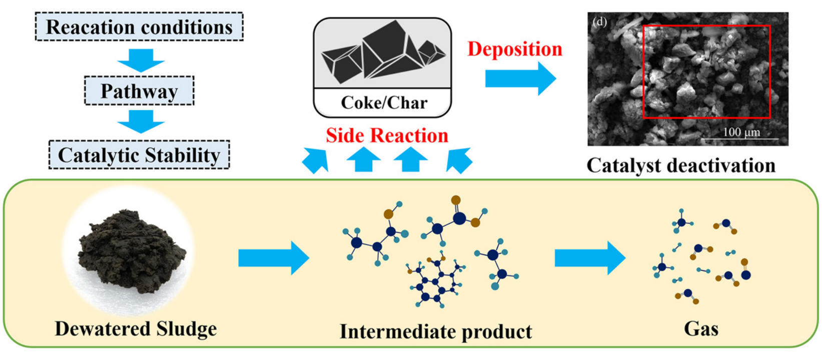
journal homepage: www.elsevier.com/locate/supflu

Influence of reaction conditions on the catalytic activity of a nickel during the supercritical water gasification of dewatered sewage sludge

Chenyu Wang[a], Wei Zhu[a,b,*], Cheng Chen[a], Hao Zhang[a], Naixi Lin[a], Ying Su[c]

[a] College of Environment, Hohai University, Nanjing 210098, PR China
[b] National Engineering Research Center of Water Resources Efficient Utilization and Engineering Safety, Hohai University, Nanjing, Jiangsu 210098, PR China
[c] College of Civil Engineering, Yancheng Institute of Technology, YanCheng, Jiangsu 224051, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Catalytic activity
Dewatered sewage sludge
Nickel
Supercritical water gasification

ABSTRACT

Dewatered sewage sludge with different moisture contents was treated with a nickel catalyst in supercritical water in a batch quartz tube micro-reactor at different temperatures and reaction times. The catalytic activity of the nickel wire catalyst was investigated. Because of the gradual deactivation of the catalyst, the hydrogen yield decreased by 8–72% after five catalytic cycles. The temperature has the largest influence on the deactivation rate of the nickel catalyst. The decline rate of the hydrogen yield decreased from 67% to 8% when the temperature was increased from 400 °C to 500 °C. SEM, EDS and TPO were used to characterize the spent catalyst. The results showed that the deactivation of the nickel catalyst is caused by the deposition of char/coke on the catalyst surface. Finally, the relationship between the reaction conditions and catalyst deactivation was investigated from the viewpoint of the organic matter degradation pathway.

1. Introduction

Dewatered sewage sludge (DSS) is an inevitable by-product of sewage treatment, which easily causes secondary environmental pollution if not appropriately disposed. Because of its high moisture content and complex organic components, DSS disposal and treatment has become an urgent problem in many cities. Supercritical water gasification (SCWG) technology can use the water in the DSS to simultaneously decompose organic matter and produce hydrogen, and this has attracted widespread attention in the field of DSS disposal.

Because of the complex organic matter components of DSS, the hydrogen yield is rather low if SCWG is performed without a catalyst.

* Corresponding author at: College of Environment, Hohai University, Nanjing 210098, PR China.
E-mail address: zhuweiteam.hhu@gmail.com (W. Zhu).

https://doi.org/10.1016/j.supflu.2018.07.018
Received 26 May 2018; Received in revised form 17 July 2018; Accepted 17 July 2018
Available online 18 July 2018

Table 1
Recent reports on the deactivation of metal catalysts in SCWG.

Reactant	Catalyst	Deactivation phenomena	References
methanol	Nickel wire	After three cycles, the conversion rate of methanol was reduced from 80% to 10%–20%.	Dileo et al. [9]
lignin	Ru/C, Ru/Al_2O_3	After recycling the catalyst, the gas yield decreased by 20%–60%	Osada et al. [10]
glucose	Ni/Al_2O_3	The hydrogen yield decreased from 1.4 mol/kg OM to 0.6 mol/kg OM	Lu et al. [11]
glucose	Ni/γ-Al_2O_3	The hydrogen yield decreased after 8 h of continuous use	Zhang et al. [12]
glycerol	Ru/TiO_2	The surface area of the catalyst decreased and the conversion rate of glycerol decreased	Zöhrer et al. [13]
lignin	Ni/Al_2O_3-SiO_2	After two cycles, the gasification rate of lignin was reduced by 13.8%.	Guan et al. [14]
isopropanol	Ru/TiO_2	After 50 h of operation, the degradation rate of isopropanol decreased by more than 50%.	Peng et al. [15]
microalgae	Ru	After 100 h of operation, the catalyst showed sulfur poisoning.	Peng et al. [16]
humic acid	Ni/Al_2O_3-SiO_2	The hydrogen yield is close to that without a catalyst	Gong et al. [17]

The hydrogen yield can be effectively improved by adding a catalyst. Common catalysts include carbon catalysts, alkali catalysts, and metal catalysts. Matsumura et al. [1] and Xu et al. [2] conducted experiments on various carbon catalysts and showed that they can significantly increase the hydrogen yield but the catalytic activity needs to be improved for reaction temperatures above 600 °C, which will increase energy consumption. Alkali catalysts include NaOH, KOH, etc. Masaru et al. [3] added NaOH during the gasification of lignin, and the hydrogen yield increased four-fold; Xu et al. [4] also reported the effects of KOH, K_2CO_3, and Na_2CO_3 on the production of hydrogen from the gasification of DSS in supercritical water. However, alkali catalysts are homogeneous catalysts and are therefore difficult to recover and reuse and will cause corrosion to the reactor. As heterogeneous catalysts, metal catalysts can effectively increase the hydrogen yield in the gasification of biomass [5,6] and are easily recycled. In particular, Ni catalysts are widely used because of their low price and good catalytic activity. The Ni catalysts promote hydrogen production in SCWG of DSS has been reported in previous paper [7,8]. However, many scholars have reported the deactivation of metal catalysts, and relevant data from the recent literature are summarized in Table 1.

As can be seen from Table 1, the deactivation of metal catalysts is a widespread occurrence. However, current research often focuses on single compounds or biomass, and reports on complex matter such as DSS are very rare. In addition, Yoshida et al. [18] performed experiments on cellulose and lignin and pointed out that intermediate products will reduce the activity of the Ni catalyst, and changes in the reaction conditions will significantly influence the progress of the reaction and the formation of products. However, studies on the influence of the reaction conditions on the deactivation of catalysts are lacking.

Therefore, nickel wire was selected as the catalyst. SCWG experiments were performed in a miniature quartz tube. The hydrogen yield was measured after each test. Moreover, the catalyst was recovered and further reused in five experiments. Finally, the catalyst was characterized. The aim of the study was to explore (1) the catalytic activity of nickel catalysts in the SCWG process of complex DSS, (2) whether the reaction conditions will affect the stability of catalytic activity of the catalyst, and (3) if catalyst deactivation occurs, what is the mechanism of deactivation.

2. Materials and methods

2.1. Materials

The DSS was taken from a sewage treatment plant in Nanjing, China. The basic properties of the DSS are shown in Table 2. The original sludge was freeze-dried and sieved into a dry sludge powder after grinding.

Nickel wire was purchased from Aladdin Chemistry Co., Ltd. and used as the nickel catalyst. The nickel wire was 1 mm in diameter and 99.9% pure. It was rubbed with sandpaper before use to remove nickel oxide from the surface.

The quartz tube was purchased from China Lianyungang Quartz Products Co., Ltd and had an inside diameter of 2 mm and an outer diameter of 6 mm.

Table 2
Properties of the tested dewatered sewage sludge.

Organic matter (wt%) [a]	Ash (wt%)[a]	Ultimate analysis (wt%)[a]					HHV (MJ/kg)[c]	treatment process
		C	H	N	S	O[b]		
40.8	59.2	19.5	3.7	3.18	0.17	14.25	9.45	domestic sewage

[a] On an air-dried basis.
[b] By difference (O% = 100% – C% – H% – N% – S%).
[c] Higher heating value (HHV) calculated by the Dulong Formula: HHV(KJ/kg) = 0.3393C + 1.443(H–O/8) + 0.0927S + 0.01494N.

2.2. Experimental apparatus and procedure

Using a quartz capillary as a batch reactor, a certain amount of dry DSS powder was weighed with a precision scale and carefully added to a quartz tube. Subsequently, according to the set moisture content of the DSS, a certain amount of deionized water was added to the quartz tube with a micro-syringe. Then, a certain length of nickel wire, determined from the mass of the sludge, was added. Finally, the quartz tube was sealed with an oxyhydrogen flame. The length of the quartz tube after sealing was 16 cm (i.e. volume is 502 mm^3). According to the IAPWA-IF97 thermodynamic parameters of water and steam, it is determined from the volume of the reactor and the amount of water added, that the pressure could reach 23 MPa at the set reaction temperature. The mass of the sludge, quality of the deionized water, and length of the nickel wire used in each experiment are given in Table 3.

During the experiment, the muffle temperature was raised to the preset temperature and placed in a sealed quartz tube, the quartz tube quickly reached the reaction temperature within 3 s, and then timing

Table 3
Reaction conditions and sample addition.

No.	temperature (°C)	time (min)	moisture content[a] (wt%)	Amount		catalyst loading[b]
				dry sludge (g)	water (μL)	
Blank	400	10	75	0.0183	55	0.007 g DSS/cm Ni wire
400-10-75	400	10	75	0.0183	55	
450-10-75	450	10	75	0.0133	40	
500-10-75	500	10	75	0.0116	35	
400-5-75	400	5	75	0.0183	55	
400-15-75	400	15	75	0.0183	55	
400-10-65	400	10	65	0.0257	55	
400-10-90	400	10	90	0.0073	55	

[a] Moisture content = mass of water/mass of wet sludge, wet sludge = dry sludge + water.
[b] Catalyst loading = (mass of DSS)/(length of nickel wire), and the mass of DSS include mass of dry sludge and water (i.e. mass of wet sludge).