Bulgarian Chemical Communications, Volume 49, Special Issue J, (pp. 290 – 296) 2017

Inherent health, safety and environmental risk assessment of nanoparticle synthesis

M. Torabifard[1], R. Arjmandi[2]*, A. Rashidi[3], J. Nouri[4], I. Mohammadfam[5]

[1] Department of Environment and Energy, Science and Research Branch, Islamic Azad University, Tehran, Iran
[2] Department of Environment and Energy, Science and Research Branch, Islamic Azad University, Tehran, Iran
[3] Nanotechnology Research Center, Research Institute of Petroleum Industry, Tehran, Iran
[4] Department of Environment and Energy, Science and Research Branch, Islamic Azad University, Tehran, Iran
[5] Department of Occupational Health and Safety, Faculty of Health, University of Medical Sciences, Hamedan, Iran

Received November 25, 2015; Revised April 27, 2017

The health and environmental effects of chemical synthesis can be assessed in the early stages of the synthesis process. The present study investigates and compares wet-chemical and hydrothermal synthesis of nanostructured metal oxides on a semi-industrial scale of 300 kg/day in Iran with respect to the health, safety and environmental risks. The Chemical Screening Tool for Exposure and Environmental Release (ChemSTEER) software was used for measuring the severity of the impact. Potentially hazardous events were determined through examining the frequency of recent events occurred during the synthesis of chemicals. After conducting the risk assessment, a pairwise comparison of the two synthesis methods was carried out based on the acceptable risk percentage and the frequency of potentially hazardous events with respect to health, safety and environmental parameters using the Expert Choice software. In accordance with the Health, Safety and Environmental (HSE) Management System, hydrothermal synthesis provided a lower inherent risk with a weight percent of 0.583 for nanostructured zinc oxide while wet-chemical synthesis yielded a weight percent of 0.417. An integrated approach to the study of the health, safety and environmental risks presenting in the early stages of synthesis can help adopt safer processes through modifying operations, changing the raw materials used and scaling up pilot plants to industrial units with higher levels of safety, so as to mitigate the hazards.

Keywords: Inherent safety, occupational health, environmental risk, nanomaterials, process design

INTRODUCTION

There is an increasing public awareness of the risks involved in the exposure to chemicals and their hazardous impacts on the environment. The poor choice of raw materials and synthesis processes and human errors are among the factors that have irreversible consequences for humans and the environment [1]. The rising rate of industrial accidents has led industries to the decision to prioritize the promotion of their health, safety and environmental standards, as these accidents entail beyond a simple economic burden and threaten human life as well as the environment. In other words, the technologies used in different industries should be directed at eliminating the health, safety and environmental hazards posed by their processes in addition to reducing operational costs [2].

Nanotechnology, which involves the design and synthesis of structures on a nanometer scale through controlling the shape and size of the synthesized materials, should also reach these safety standards. Nanotechnology is a field that has great applications in areas such as industries, health, environmental sciences, agriculture, energy, materials science and communication sciences [3]. With their distinguished features, nanomaterials have contributed to significant changes in different industries. Nanotechnology development and the increase in nanomaterial synthesis on the one hand [4], and the adverse effects of human and environmental exposure to nanomaterials on the other [3], necessitate further research for identifying the impact of these materials, especially their environmental impact.

In [3] identified starting points for the exposure assessment of nanomaterial products. Claudia et al., [5] examined the role of life cycle concepts in identifying the risks posed by nanomaterials and argued that uncertainties can be reduced through combining life cycle concepts with risk assessment and toxicological studies in nanoscience. In [6], they addressed the environmental and health effects of nanomaterials such as nanosilver, nano titanium dioxide, nano silica, nano zinc oxide and other nanomaterials in nanotextiles and façade coatings and proposed a set of environmental and health criteria for the assessment of nanomaterials' impact on human health and the environment. They argued that, in some cases, the harms of these materials is greater to humans than to the environment; however, these harms depend on the nanomaterials' life cycle and their rate of production. Monica et al. [7] presented a framework for legal issues in nanotechnology that helps explain the legal life cycle

---

To whom all correspondence should be sent:
E-mail: r.arjmandi90@gmail.com

for nanomaterial products. Savolainen et al. [8] recommended further studies on different issues pertaining to the occupational safety, health and environmental risks of nanomaterials, such as toxicological studies, nanomaterial exposure assessment and studies on nanomaterial transformation within the human body, nanomaterial structural changes and other environmental health impacts that need to be emphasized in the workplace.

Despite the importance of the cited studies examining the health and environmental impact of nanomaterials, different methods of chemical synthesis, particularly nanomaterial synthesis, and their positive and negative effects should also be studied, especially because most studies tend to emphasize the use and disposal of chemicals rather than their synthesis. The present study examines appropriate and inherently safe methods and processes of synthesis in their initial stages and investigates the technological advances that can be used to reduce potential hazards and their subsequent costs. A number of other studies have also examined the health, safety and environmental impacts of chemical synthesis and their design.

Hasim and Hurme [9] developed an inherent occupational health index for the evaluation of occupational health in the initial stages of synthesis and compared six methyl methacrylate process routes by way of three different indices. They also presented the Health Quotient Index and the concentration-based method of occupational health evaluation for the development stages of the synthesis process [10, 11] as well as the Occupational Health Index for the assessment of the synthesis process at its initial stages of engineering [12], which has been tested on the toluene hydrodealkylation process.

The Qualitative Assessment for Inherently Safer Design is another modified method developed by Rusli and Sheriff [13] to examine synthesis processes' safety at their development stage.

Gentile et al., [14] developed a fuzzy-logic-based approach to the Inherent Safety Index that is used to examine the safety of synthesis processes. The health, safety and environmental study of nanomaterial synthesis processes at their initial stages of development and a review of previous studies conducted on chemical synthesis processes and the hazardous events associated with them facilitate nanotechnology development from health, safety and environmental viewpoints.

The present study was conducted to present a suitable method of zinc oxide nanostructure synthesis that takes account of health and environmental parameters and therefore compares and carries out a health, safety and environmental risk assessment of the wet-chemical and hydrothermal synthesis of nanostructured zinc oxide under normal operating conditions and with similar production capacities at the Research Institute of Petroleum Industry (RIPI) in Tehran, Iran, in 2015.

Zinc oxide was chosen due to its special properties, such as high endurance in industrial processes and high activity at nanoscale [15], which have facilitated the use of this material in different industries.

The present study first identified and assessed the sources of pollution and potential health, safety and environmental risks in each of the discussed processes; and then, based on the determined criteria, the pairwise comparison of the processes was carried out and an appropriate method of nanostructured zinc oxide synthesis was ultimately proposed in accordance with the Health, Safety and Environmental (HSE) Management System.

MATERIALS AND METHODS

Nanostructured zinc oxide was synthesized in a research laboratory using the wet-chemical and hydrothermal methods. The wet-chemical mechanism of nanomaterial synthesis involves aqueous and non-aqueous chemical reactions and is an economical [15], simple, effective and quick process. For the wet-chemical synthesis of nanostructured zinc oxide, zinc salt crystals [$Zn\ (NO_3)_2\ H_2O$] were dissolved in a 5000 liter tank of water and drops of ammonia solution were added in to control the solution's pH and to keep it at about 10.5, thereby creating zinc hydroxide precipitate, which was then filtered, dried and calcined at 300 °C for one hour to produce nanoscale zinc oxide.

Hydrothermal synthesis involves the aqueous reaction of the intended chemical at a high pressure and temperature, resulting in a white precipitate after centrifuging, rinsing and drying [15]. This process is also economical and can easily synthesize a quality product with high morphology level and nanoscale properties.

For the hydrothermal synthesis of nanostructured zinc oxide, zinc salt crystals [$Zn\ (NO_3)_2\ H_2O$] were dissolved in a 5000 liter tank of water. The solution was warmed and pressurized to 10-20 bar and then dissolved in supercritical water flow at mixing point, resulting in a rapid heating up and a secondary reaction. The solution was then quickly cooled at a reactor outlet and larger particles were filtered on the way out. In this process, the reactor received the cooling water directly for controlling the heat generated by the reaction.

The health, safety, and environmental risk assessment of these processes was carried out using the two-dimensional method of probability of events and severity of impacts based on the Military Standard (MIL-STD), which has been previously used in a number of studies.

The Military Standard is approved for use by all Military Departments and Defense Agencies within the Department of Defense، which is a key element of systems engineering that provides a standard generic method for the identification, classification and mitigation of hazards.

The severity of impacts on humans' health and the environment was determined by the MIL-STD-882E standard based on the ChemSTEER results obtained.

The ChemSTEER was developed and approved by the US Environmental Protection Agency and demonstrates the degree of skin contact with chemicals and their inhalation in industrial and commercial processes and also shows the level of chemical dispersion in the environment, air, water and soil caused by industrial processes.

This software requires access to the chemical properties of the primary substances used, including their vapor pressure, molecular weight, density and water solubility. Operation parameters and sources of pollution and pollutant activities are then determined. The ChemSTEER presents default models. Environmental release and chemical exposure are estimated based on the operation process and the sources of pollution.

To establish the process safety, the severity of impact was determined using the process features and probable events and a structured questionnaire developed by experts in the field. The probability of events was determined using the frequency of recent events in synthesis processes and based on the MIL-STD-882B standard. After conducting the risk assessment, a pairwise comparison of the wet-chemical and hydrothermal synthesis methods was carried out in Expert Choice using the Analytic Hierarchy Process and based on the acceptable risk percentage and the frequency of potential hazardous events with respect to health, safety and environmental parameters. This method is performed according to the weighted criteria and the prioritized options using Eigen Values and is the most comprehensive multi-criteria decision-making system designed to date, as it allows the formulation of the problem in a hierarchical format and takes account of different qualitative and quantitative criteria [16].

RESULTS AND DISCUSSION

The dispersion of pollutants and the human exposure to them in nanostructured zinc oxide synthesis processes using the wet-chemical and hydrothermal methods was determined with similar annual synthesis capacities of 2000 kg using the ChemSTEER. The input data containing the raw chemical data fed to the process included the annual rate of nanostructured zinc oxide synthesis, the vapor pressure of raw materials, the molecular weight, density and water solubility of raw materials in water, the transformation of raw materials into other chemicals, the interaction of raw materials with other chemicals producing other chemicals, the physical state of raw chemicals and products and the sources of pollution in the processes. Batch production was used for both the wet-chemical and the hydrothermal processes. Table 1 presents the data pertaining to each of the processes.

Table 1. Details of the wet-chemical and hydrothermal process

Synthesis Method	Input Feed	Annual Synthesis (kg/yr)	Number of Runs per Year	Synthesis per Process (kg)	Process Time (hr)	Process Type	Type of Process Performance	Number of Exposed People	Number of Shifts
Wet Chemical	$Zn(No_3)_2.6H_2O$	2000	250	8	1	Batch	Defined Processing	5	1
Hydrothermal	$Zn(No_3)_2.6H_2O$	2000	20	100	1	Batch	Defined Processing	5	1

In the wet-chemical method, the sources of pollution in the normal synthesis of nanostructured zinc oxide include ammonia vapors produced from the primary tank, drying, calcination and storage tank. In the hydrothermal method, the sources of pollution in the normal synthesis of nanostructured zinc oxide include NOx vapors produced from the primary tank as well as from the wastewater created through the process. Each of the above sources of pollution entail health, safety, and environmental risks.

The processes' safety hazards are associated with Temperature Indicator Controller (TIC) dysfunction in the reactor and in the calcination (specific to the wet-chemical method) and the corrosion of pipelines and tanks.

As noted earlier, the risk assessment of nanostructured zinc oxide synthesis with the Health, Safety and Environmental (HSE) Management System was performed using the severity of impact and the probability of events. To this end, the severity of the impact of potential health and environmental hazards was determined for both the wet-chemical and hydrothermal methods through assessing the skin and respiratory exposures and by measuring the dispersed pollutant concentration in ChemSTEER.

In the wet-chemical method, the personnel involved in the process only became exposed to health hazards by inhaling ammonia vapors at mean daily doses of 0.0031 mg/kg/d from the primary tank (the mixing tank), 0.0004 mg/kg/d from the dryer and 0.0001 mg/kg/d from the calcination. In the wet-chemical process, the dispersion of ammonia as an environmental release from each of the pollution sources including the mixing tank, the dryer, and the calcination was estimated at 0.01 μg/m^3, 0.02 μg/m^3 and 0.2 μg/m^3, in respective order.

In the hydrothermal method, the health hazards that threatened the personnel included the inhalation of NOx from the reactor and potential skin contact with wastewaters. The results obtained from the ChemSTEER showed a mean daily NOx exposure dose of about 0.02 mg/kg/d and reported the mean skin exposure to wastewaters to be about 1.2 mg/kg/d. In the hydrothermal process, the concentration of NOx as an environmental pollutant was about 0.16 μg/m^3 at the reactor outlet and the potential wastewater dispersion in the environment was about 0.5 kg/d.

Tables 2 and 3 present the results obtained from modeling the skin and respiratory exposure and the pollutant dispersion into the environment from each pollution source using both the wet-chemical and hydrothermal methods.

Table 2. Skin and respiratory contacts

Method	Type of Contact	Pollution Sources	Potential Dose Rate (mg/d)	Lifetime Average Daily Dose (mg/kg/d)	Average Daily Dose (mg/kg/d)	Exposure Limit TWA (8 hours)	Acute Potential Dose (mg/kg/d)
Wet-Chemical	Respiratory	Ammonia emission from the reactor	83.1036	0.058	1.1016	25 ppm	1.1872
		Ammonia emission from the dryer	12.46	0.0087	0.1652		0.1780
		Ammonia emission from calcination	4.1551	0.0029	0.055		0.059
	Skin	-	-	-	-	-	-
Hydrothermal	Respiratory	No$_x$ emission	4.98	0.0022	0.02	5 ppm	0.56
	Skin	Wastewater	202.45	0.091	1.2	-	22.4

Table 3. Results from modeling the environmental dispersion of pollutants

Method	Pollution Sources	Media	Daily Release Rate (kg/site-day)	Annual Release Rate (kg/year-all site)	Concentration μg/m^3	Standard
Wet-Chemical	Ammonia emission from the reactor	Air	0.021	0.65	0.2	Annual of 100 μg/m^3
	Ammonia emission from the dryer	Air	0.003	0.09	0.02	
	Ammonia emission from calcinations	Air	0.001	0.03	0.01	
Hydrothermal	No$_x$ emission from the reactor	Air	0.002	0.051	0.16	Annual of 0.053 ppm (100 μg/m^3)
	Wastewater	Soil/water	0.5	10	-	-

As shown in Tables 2 and 3, in the wet-chemical method, occupational exposure through respiratory contact with each pollution source produced an average daily dose of ammonia emission below the standard occupational exposure limit of 8-hour total weighted average (the possibility of skin contact with chemicals was negligible in this method). In the hydrothermal method, too, occupational exposure through respiratory contact was below the standard 8-hour occupational exposure limit. In the wet-chemical method, ammonia dispersion into the environment through the pollution sources, and in the hydrothermal method, NOx dispersion from the reactor, were estimated to be below the environmental standards.

The safety of the processes is further discussed here.

TIC is the main control factor in wet-chemical processes that may cause damage if failing to function. In this method, the main reactor door is left open and the tank is therefore not pressurized. TIC dysfunction cannot cause explosion; however, the dispersion of ammonia into the environment increases and threatens the air quality and the general health of the personnel. Due to the pressure increase in the calcination stage, TIC dysfunction can be precarious and may lead to explosions.

In hydrothermal processes, the main safety risk is the possibility of explosion in the reactor. TIC dysfunction (the control factor in this method) can lead to reactor explosion. In this method, the door of the main reactor is kept shut and reaction occurs at 10-20 bar. TIC dysfunction thus increases the temperature and pressure and may lead to explosions. Reactor corrosion due to the synthesis of materials, the high temperature and the acidic medium is also possible.

After identifying the hazards and estimating the occupational exposure to the intended chemicals and the environmental pollutant concentrations, the health, safety and environmental risks associated with wet-chemical and hydrothermal processes were assessed. Table 4 presents the results obtained.

Table 4. Health, safety, and environmental risk assessment in wet-chemical and hydrothermal processes

Risk Assessment				Risk	HSE Parameters'	Synthesis Method
Risk Level	RPN	Probability	Sevier			
Low (Acceptable)	4C	C	4	Ammonia emission from the reactor	Health (Respiratory)	Wet-Chemical
Low (Acceptable)	4D	D	4	Ammonia emission from the dryer		
Low (Acceptable)	4D	D	4	Ammonia emission from calcination		
High (Undesirable)	2C	C	2	Ammonia storage tank		
Low (Acceptable)	4D	D	4	Ammonia emission from the reactor	Environmental Risk	
Low (Acceptable)	4D	D	4	Ammonia emission from the dryer		
Low (Acceptable)	4D	D	4	Ammonia emission from calcination		
Low (Acceptable)	4D	D	4	Ammonia storage tank		
High (Undesirable)	2D	D	2	TIC failure in the reactor	Safety	
Medium (Acceptable; Management Review)	1E	E	1	TIC dysfunction in calcination		
High (Undesirable)	3C	C	3	Corrosion in the pipeline and tank		
Low (Acceptable)	4D	D	4	NOx emission from the reactor	Respiratory contact	Hydrothermal
Low (Acceptable)	4E	E	4	Wastewater (containing sodium nitrate and solvent)	Skin Contact	
Low (Acceptable)	4D	D	4	NOx emission from the reactor	Environmental Risk	
Medium (Acceptable; Management Review)	3E	E	3	Wastewater (containing sodium nitrate and solvent)		
High (Undesirable)	2D	D	2	TIC dysfunction in the reactor and explosion	Safety	
High (Undesirable)	3C	C	3	Corrosion in the pipeline and tank		

To propose an appropriate method of nanostructured zinc oxide synthesis in accordance with the Health, Safety and Environmental (HSE) Management System, a pairwise comparison of wet-chemical and hydrothermal processes was carried out based on the acceptable risk percentage and the number of potential health, safety and environmental hazards using the Analytic Hierarchy Process in Expert Choice.

The criteria were weighted by averaging the scores obtained in structured questionnaires developed by industrial experts and scholars in environment, health and safety.

Table 5 presents the results obtained from the pairwise comparison and Table 6 examines the priority of the two processes in the synthesis of nanostructured zinc oxide in percentage.

Table 5. Pairwise comparison of the processes

	Health			Safety		Environment	
	Acceptable Health Risk	Number of Skin Hazards	Number of respiratory Hazards	Acceptable Safety Risk	Number of Safety Hazards	Acceptable Environmental Risk	Number of Environmental Hazards
Wet-Chemical	0.25	0.75	0.167	0.5	0.333	0.857	0.167
Hydrothermal	0.75	0.25	0.833	0.5	0.667	0.143	0.833

Table 6. Priority of the synthesis of nanostructured zinc oxide in accordance with the HSE management system

Method	Wet-Chemical	Hydrothermal
Priority	0.417	0.583
Rank	2	1

As shown in Table 6, the hydrothermal process has a weight percent of 0.583 and entails the lowest risk and is considered the more appropriate method of synthesis in accordance with the HSE management system compared to the wet-chemical method with the weight percent of 0.417.

Various studies have been conducted on the health, safety and environmental risks posed by chemical processes [10-12]. Kweku et al. [2] compared a number of simple health, safety and environmental risk assessment methods in relation to chemical processes at their initial development stage. Junghwan et al. [17] modified the TRIZ method of evaluating chemical process safety. Nowak and Bucheli [18] examined nanomaterial behaviors with respect to the environmental impacts of nanomaterials.

The cited studies can help improve the level of safety in chemical processes and identify nanomaterial hazards. The present study is also a step toward the improvement of nanomaterial synthesis, which has never been examined in such great detail.

The results obtained are based on an integrated approach to the health, safety and environmental risk assessment of wet-chemical and hydrothermal methods at their early stages of development. Reducing the health, safety and environmental risks associated with these processes, the potential hazards occurring in their development stages and consequently the financial costs incurred can help develop safer methods of nanomaterial synthesis at an industrial scale.

CONCLUSION

The integrated approach to HSE management system is crucial for improving the health, safety and environmental standards of nanomaterial synthesis. Since this approach reduces potential hazards, its neglecting can have adverse economic consequences. The integrated HSE management system prioritizes all hazardous industrial activities. The increasing development of nanotechnology and its uncertain health, safety and environmental consequences mandate the investigation of nanotechnologies and nanomaterial synthesis processes. To reduce industrial hazards, synthesis processes and their management should be further addressed. Achieving safer nanotechnologies requires extensive studies on the synthesis, use and disposal of nanomaterials and their byproducts. Inherently safe processes help reduce potential hazards by eliminating the use of hazardous materials and replacing harmful chemicals with safer materials and encouraging process modification and improvement [10]. The present study is distinguished from other studies in that it uses the integrated approach to HSE management system with respect to nanomaterial synthesis processes.

The results obtained revealed low to high health, safety and environmental risk levels in both the wet-chemical and hydrothermal processes of nanomaterial synthesis. In order to propose an appropriate method of nanostructured zinc oxide synthesis in accordance with the HSE management system, a pairwise comparison of the wet-chemical and hydrothermal processes was conducted based on the acceptable risk percentage and the number of potential health, safety and environmental hazards. Overall, the hydrothermal method showed a lower risk and was considered the more appropriate method in terms of compliance with the HSE management system.

Observing the HSE parameters should not be limited to the economic and technical aspects of chemical synthesis and should also be considered in the early stages of synthesis processes so as to mitigate the associated risks and promote safety in industries. Encouraging manufacturers to use safer processes and making them aware of the benefits of systematic and integrated HSE systems in synthesis processes can accelerate the achievement of this goal.

Acknowledgements. *The present study was approved by the Research Institute of Petroleum Industry (RIPI) in Tehran, Iran. The authors would like to express their gratitude to the RIPI Nanotechnology Research Center for their sincere collaboration and support.*

REFERENCES

1. M. Harbawi S. Mustapha, T. Choong, S. Abdul Rashid, S. Kadir, Z. Abdul Rashid, *Env. Sci. Tech.*, **5**, 64, (2008).
2. I. Kweku Adu, H. Sugiyama, U. Fischer, K. Hungerbuhler, *Proc. Saf. Env. Prot.* **86**, 93, (2008).
3. K. Ostertag, B. Husing, *J. Cl. Prod.*, **16**, 948, (2008).
4. http://www.ccst.us/publications/2010/2010Nano.pdf
5. S. Claudia, B. Markus, C. Qasim, D. Maria, F. Teresa, I. Stig, N. Bernd, *Toxicology*, **269**, 169, (2010).
6. S. Claudia, W. Peter, K. Harald, B. Nowack, *Env. Intel.* **37**, 1142 (2011).
7. J. Monica, G. Calster, A. Patsa, A nanotechnology legal framework, Nanotechnology environmental health and safety: Risks, regulation and management, USA: Elsevier, 2014, p. 265.
8. K. Savolainen, L. Pylkkänen, H. Norppa, G. Falck, H. Lindberg, T. Tuomi, M. Vippola, H. Alenius, K. Hämeri, J. Koivisto, D. Brouwer, D. Mark, D. Bard, M. Berges, M. Seipenbusch, *Saf. Sci.*, **48**, 963 (2010).
9. M. Hassim, M. Hurme, *Loss Prev. Proc. Ind.*, **23**, 127 (2010a).
10. M. Hassim, M. Hurme, *Loss Prev. Proc. Ind.*, **23**, 127 (2010b).
11. M. Hassim, M. Hurme, *Loss Prev. Proc. Ind.*, **23**, 127 (2010c).
12. M. Hassim, M. Hurme, *Loss Prev. Proc. Ind.*, **23**, 127 (2010d).
13. R. Rosli, A. Shariff, *Loss Prev. Proc. Ind.*, **23**, 157 (2010).
14. M. Gentile, W. Rogers, M. Mannan, Proc. Saf. Env. Prot., **81**, 444 (2003).
15. L. Zhang, Y. Jiang, Y. Ding, N. Daskalakis, L. Jeuken, M. Povey, J. Alex, D. York, *Nanopart. Res.*, **12**, 1625 (2009).
16. T. Saaty, *Serv. Sci.*, **1**, 83 (2008).
17. K. Junghwan, K. Jinkyung, L. Younghee, L. Wonsub, *Loss Prev. Proc. Ind.*, **22**, 1043, (2009).
18. B. Nowack, T. Bucheli, *Env. Pol.*, **150**, 5 (2007).