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# Risk assessment in the Nanofluid stabilization process and optimization of process parameters by HAZOP methodology

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## ABSTRACT

In this article, a risk assessment of the Nanofluid stabilization process was made in order to optimize the process parameters using the HAZOP methodology. The results showed that the main parameters for the HAZOP risk assessment are as follows: the weight fraction of the surfactant, the temperature when the surfactant is used, the pressure and the speed of the fluid in the homogenizer, the PH solution, the time and the power of ultrasound, the temperature of the stabilization process, the volume fraction of nanoparticles, the size of the nanoparticles, the side surface to the volume of Nano particles, zeta potentials, Nanofluid concentrations. The results of the risk number calculations before control actions showed that after control actions, all risk numbers decreased 50% and more, so this decrease was significant. This decrease showed that all control actions were appropriate and effective.

KEYWORDS: Nanofluids; Risks evaluation; Process; Stabilization; HAZOP.

# Evaluación del riesgo en el proceso de estabilización de Nanofluidos y optimización de parámetros del proceso por la metodología HAZOP

## RESUMEN

En este artículo se hizo una evaluación del riesgo del proceso de estabilización de Nanofluidos a fin de optimizar los parámetros del proceso mediante la metodología HAZOP. Los resultados mostraron que los principales parámetros para la evaluación de riesgos HAZOP son los siguientes: la fracción en peso del surfactante, la temperatura cuando se usa el surfactante, la presión y la velocidad del fluido en el homogeneizador, la solución de PH, el tiempo y la potencia de ultrasonidos, la temperatura del proceso de estabilización, la fracción de volumen de nanopartículas, el tamaño de las nanopartículas, la superficie lateral al volumen de Nano partículas, potenciales zeta, concentraciones de Nanofluidos. Los resultados de los cálculos de números de riesgo antes de las acciones de control mostraron que después de las acciones de control, todos los números de riesgo disminuyeron 50% y más, por lo que esta disminución fue significativa. Esta disminución mostró que todas las acciones de control fueron apropiadas y efectivas.

PALABRAS CLAVE: Nanofluidos; Evaluación de riesgos; Proceso; Estabilización; HAZOP.

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## Introduction

The suspension of solid particles in liquids is widely known to contribute to industrial liquid systems, such as heat transfer fluids, lubricant fluids, and magnetic fluids. Among these technologies, nanofluids as engineering materials consisting of nanometer-sized additives and base fluids have attracted interest because of their broad applications in heat transfer, cooling of microchips, drug delivery, and enhanced oil recovery. The method for the preparation of stable Nano fluids is a key concern for extending the application of Nano fluids (Mingwei Zhao et al., 2018). Due to the high demand for nanoparticle-based materials, two manufacturing approaches have developed over the years. The first is the top-down approach and involves reducing the size of bulk materials by physical or chemical processes. The final particle size, shape and surface structure are all dependent on the processing technique used. Furthermore, during the top-down approach surface imperfections are produced and ultimately influence the physicochemical properties of the manufactured nanoparticles. The second is the bottom-up approach and involves the assembly of individual atoms, molecules and smaller particles. Both approaches use a wide variety of physical and chemical manufacturing processes, which have evolved to produce nanoparticles with different sizes, shapes and compositions. Particle size, size distribution, shape and physicochemical properties are all influenced by process parameters. These parameters include initial reagent concentrations, temperature and reaction mixture pH. Moreover, during synthesis there are interactions taking place between precursor ions, reducing agents and the adsorption kinetics of the stabilizing agent. The competing parameters ultimately dictate the properties of the manufactured nanoparticles (Wisut Chamsa-ard, 2017).

Manoj Chopkar et al., (2006) studied Synthesis and characterization of nanofluid for advanced heat transfer applications. Nanofluid was prepared by dispersing about 0.2–2.0 vol.% nanocrystalline $Al_{70}Cu_{30}$ particles in ethylene glycol. The size/microstructure of the nanoparticles were characterized by X-ray diffraction and transmission electron microscopy, and the thermal conductivity of the nanofluid was measured using a modified thermal comparator. An improvement of up to two times in conductivity was recorded.

M. J. Kao et al., (2007) studied Copper-oxide brake nanofluid manufactured using arc-submerged nanoparticle synthesis system. This study revealed that a homemade machine can produce the CBN (copper-oxide brake nanofluid) which higher boiling point to reduce the occurrence of vapor-lock, higher viscosity and higher conductivity thus showing superior performance of copper brake nanofluid.

Tran X. Phuoc et al., (2007) studied Synthesis of Ag-deionized water nanofluids using multi-beam laser ablation in liquids. measurements of the thermal conductivity and viscosity of the produced samples showed that the thermal conductivity increased about 3–5% and the viscosity increased 3.7% above the base fluid viscosity even with the particle volume concentration as low as 0.01 %.

Ho Chang et al., (2008) studied Fabrication of $Al_2O_3$ nanofluid by a plasma arc nanoparticles synthesis system. The absorption properties of the $Al_2O_3$ nanofluid were analyzed using UV–Vis spectrophotometer. Moreover, the fuel calorific test showed that the combustion efficiency of 92 octane unleaded gas was greater when the weight concentration of the $Al_2O_3$ nanofluids was 3% .

S. Ananda Kumar et al., (2009) studied Synthesis and characterization of copper nanofluid by a novel one-step method. This study presented a novel one-step method for the preparation of stable, non-agglomerated copper nanofluids by reducing copper sulphate pentahydrate with sodium hypophosphite as reducing agent in ethylene glycol as base fluid by means of conventional heating. It was an in situ, one-step method which gave high yield of product with less time consumption. The characterization of the nanofluid was done by particle size analyzer, X-ray diffraction topography, UV–vis analysis and Fourier transform infrared spectroscopy (FT-IR) followed by the study of thermal conductivity of nanofluid by the transient hot wire method.

Xiaohao Wei et al., (2009) studied Synthesis and thermal conductivity of $Cu_2O$ nanofluids. Suspensions of cuprous-oxide ($Cu_2O$) nanoparticles in water, and experimentally studied the effect of reactant molar concentration and nanofluid temperature on the thermal conductivity. Substantial conductivity enhancement up to 24% was achievable with the synthesized nanofluids. The nanoparticle shape was variable by adjusting some synthesis parameters. The thermal conductivity showed both sensitivity and nonlinearity to the reactant molar concentration and the nanofluid temperature.

Xiaohao Wei et al., (2010) studied the chemical solution method to synthesize $CuS/Cu_2S$ nanofluids and experimentally measured their thermal conductivity. The measured thermal conductivity showed that the presence of nanoparticles can either upgrade or downgrade fluid conductivity, a phenomenon predicted by the recent thermal-wave theory of nanofluids.

S. Suresh et al., (2011) studied $Al_2O_3$–Cu hybrid particles synthesized by hydrogen reduction technique from the powder mixture of $Al_2O_3$ and CuO in 90:10 weight proportions obtained from a chemical route synthesis. The experimental results showed that both thermal conductivity and viscosity of the prepared hybrid nanofluids increased with the nanoparticles volume concentration. The thermal conductivity and viscosity of nanofluids had been measured and it had been found that the viscosity increase was substantially higher than the increase in thermal conductivity.

Meher Wan et al., (2012) studied an effortless and fast novel route proposed to synthesize Polyaniline nanofibers and nanofluids of Polyaniline nanofibers in DI-water were obtained with conventional two step method. The effect of particle loading (0.08%, 0.16%, and 0.24% in volume) was also observed on the thermal conductivities of synthesized nanofluids. Thermal conduction performance in nanofluids was increased appreciably due to higher crystallinity and morphological uniformity of reinforced nanofibers.

M. Nabeel Rashin et al., (2013) studied Synthesis and viscosity of novel ecofriendly ZnO–coconut oil nanofluid. Novel nanofluid of zinc oxide in coconut oil has been synthesized in various concentrations through ultrasonically assisted two step method. The experimental viscosities of nanofluids were compared with the theoretical values obtained through Einstein, Batchelor and Wang models. A small deviation was observed which may arise due to the difference in the morphology, chemical composition and interactions. New empirical relations were proposed for predicting the viscosity of coconut oil based ZnO nanofluid at various temperatures and concentrations.

Yuvaraj Haldorai et al., (2014) studied a facile and residue free synthesis of copper oxide (CuO) nanospindles by the thermal decomposition of a 3D precursor complex, copper benzoate dihydrazinate at 100 °C. The enhancement of the thermal conductivity of ethylene glycol (EG) in the presence of CuO nanospindles was examined. No surfactant was used as a dispersant. The volume fraction of CuO nanospindles suspended in EG was less than 5 vol%. The thermal conductivity of the CuO nanofluids increased with increasing particle loading.

M. Leena & S. Srinivasan (2015) studied Synthesis and ultrasonic investigations of titanium oxide nanofluids. Titanium oxide ($TiO_2$) nanoparticles (NPs) were synthesized by means of sol–gel method. Crystalline nature of synthesized $TiO_2$ NPs was confirmed by the X-ray powder diffractometry (XRD). It was observed that ultrasonic velocity was made visible on linearity with particle concentration and the results were discussed.

Gayatri Paul et al., (2016) studied Synthesis, characterization and studies on magneto-viscous properties of magnetite dispersed water based nanofluids. The observed increase in yield stress (calculated by fitting the Herschel and Bulkley model) with the applied magnetic field and concentration of dispersed nanoparticles confirmed the formation of large aggregates that restricted or prohibited the flow characteristics of the otherwise Newtonian magnetic nanofluid. The hysteresis observed during the application and withdrawal of magnetic field suggested that the chain or column like structures fail to relax within the allowed measurement time interval.

Sadegh Aberoumand et al., (2017) studied Experimental study on synthesis, stability, thermal conductivity and viscosity of Cu–engine oil nanofluid. The viscosity range for higher weight concentration nanofluid was observed from 235 cP to 35 cP in the applied temperature range. Finally, thermal conductivity and viscosity enhancements of 49% and 37% were observed for 1% weight fraction of utilized nanofluids.

Samarshi Chakraborty et al., (2018) synthesized Cu-Al Layered Double Hydroxide nanofluid at different molar ratios of Cu and Al by using co-precipitation technique and utilized this as a coolant in a pressure atomized spray to achieve high cooling rates in the temperature range of 900–600 °C for a 6 mm thick steel plate. With respect to concentration optimization, the maximum cooling rate of 168.6 °C/s was attained at a concentration of 160 ppm which was 26% higher than what was achieved by normal water spray. Results obtained from the spray cooling experiments were further verified by the thermal conductivity analysis where highest enhancement of 15.17% was also observed at 160 ppm nanofluid concentration.

Aravinth Raj Arivalagan et al., (2019) studied Synthesis and characterization of Ag and Al doped ZnO dispersed nanofluids for heat transfer applications. It was observed that the addition of small amount of Al and Ag doped ZnO nanoparticles to the ethylene glycol-water mixture increased the thermal conductivity of the base fluid. The 50% EG-%50 Water mixture showed highest thermal conductivity enhancement of 37% compared to other base fluids when 1% Al and Ag doped ZnO nanoparticles were dispersed.

Shankar Amalraj et al., (2019) studied Synthesis and characterization of $Al_2O_3$ and CuO nanoparticles into nanofluids for solar panel applications. As a result, the cooling efficiency of both CuO and $Al_2O_3$ were found as 18.2%, which was higher than the conventional one. The obtained efficiency value also compared with the reported data. This showed that CuO and $Al_2O_3$ will be a promising candidate with a base fluid of water for solar panel applications.

The HAZOP method is the most comprehensive and effective safety evaluation to identify potential hazards of chemical installations. The HAZOP starts from the design intent of the unit. And it was applied to analyze the possible deviation of process state parameters in production operation and operation control as well as the possible causes and consequences of parameter deviation during the device running. Then not only is it definite that what the main dangers and hazards of a device or system are but also measures can be taken against the consequences of change. HAZOP is a technology developed by Imperial Chemical Industries. The HAZOP is a systematic and structural analysis method, which is on the risk and operability of chemical engineering process from an expert group of experienced professionals. The advantage of the method is that it can study the whole engineering process systematically and comprehensively, thus ensuring the safe operation of the production process (Ting-Ting Gao & San-Ming Wang, (2018).

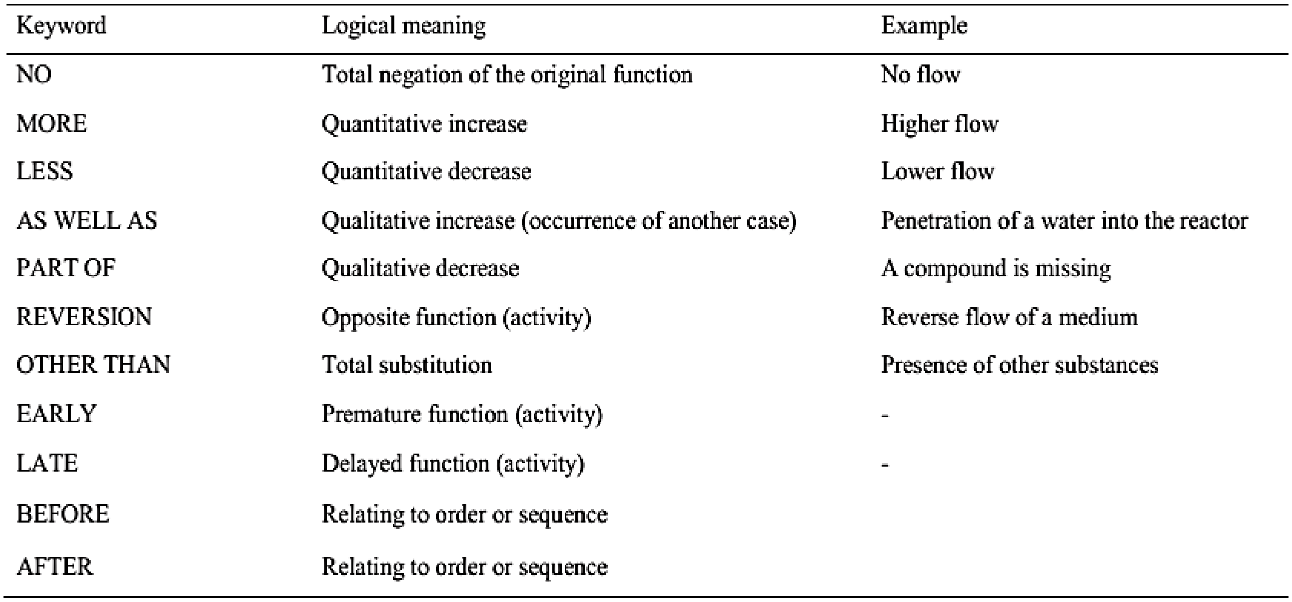
In this applicable study, for the first time, it was investigated process risk assessment of stabilization processes of nanofluids for process parameters optimization by HAZOP methodology.

## 1. Methodology

### HAZOP

Step 1 is knowing keywords in processes.

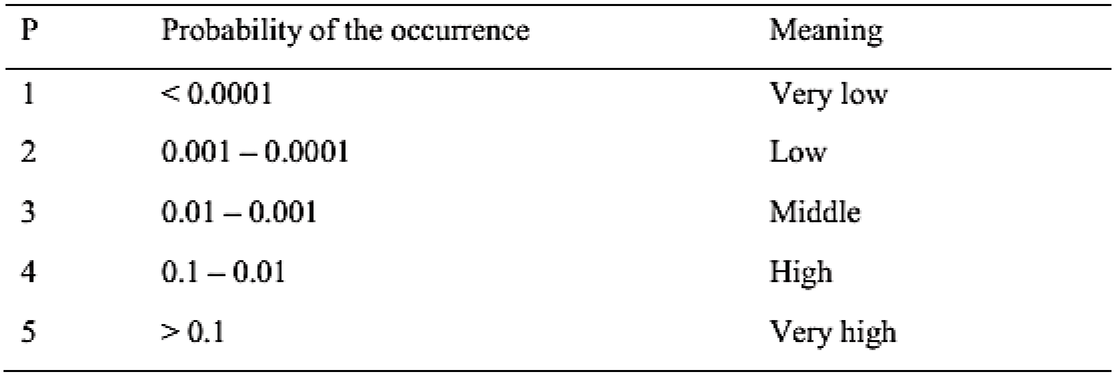
Table 1. Meaning of deviations in processes (L. Kotek, M. Tabas, 2012).



| Keyword | Logical meaning | Example |
|---|---|---|
| NO | Total negation of the original function | No flow |
| MORE | Quantitative increase | Higher flow |
| LESS | Quantitative decrease | Lower flow |
| AS WELL AS | Qualitative increase (occurrence of another case) | Penetration of a water into the reactor |
| PART OF | Qualitative decrease | A compound is missing |
| REVERSION | Opposite function (activity) | Reverse flow of a medium |
| OTHER THAN | Total substitution | Presence of other substances |
| EARLY | Premature function (activity) | - |
| LATE | Delayed function (activity) | - |
| BEFORE | Relating to order or sequence | |
| AFTER | Relating to order or sequence | |

Step 2 is identifying probability of occurrence in processes.

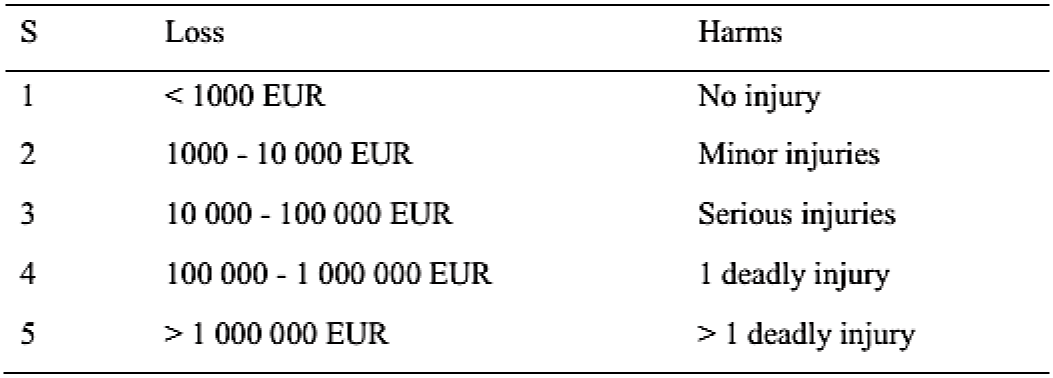
Table 2. Probability of the occurrence (L. Kotek, M. Tabas, 2012).



| P | Probability of the occurrence | Meaning |
|---|---|---|
| 1 | < 0.0001 | Very low |
| 2 | 0.001 – 0.0001 | Low |
| 3 | 0.01 – 0.001 | Middle |
| 4 | 0.1 – 0.01 | High |
| 5 | > 0.1 | Very high |

Step 3 is identifying numerical values of severities of consequences.

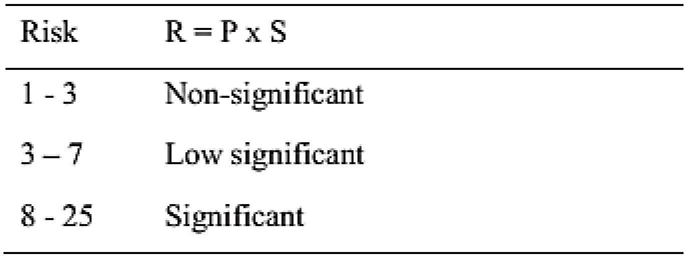
Table 3. Severity of consequence (L. Kotek, M. Tabas, 2012).



| S | Loss | Harms |
|---|---|---|
| 1 | < 1000 EUR | No injury |
| 2 | 1000 - 10 000 EUR | Minor injuries |
| 3 | 10 000 - 100 000 EUR | Serious injuries |
| 4 | 100 000 - 1 000 000 EUR | 1 deadly injury |
| 5 | > 1 000 000 EUR | > 1 deadly injury |

Step 4 is calculating and identifying risk levels.

Table 4. Risk number and its meaning (L. Kotek, M. Tabas, 2012).



| Risk | R = P x S |
|---|---|
| 1 - 3 | Non-significant |
| 3 – 7 | Low significant |
| 8 - 25 | Significant |

## 2. Results and discussions

Table 5. Risk assessment of processes of stabilization of Nano fluids by HAZOP method

| Risk assessment by HAZOP / Stabilization of Nano fluids | | | | | | | |
|---|---|---|---|---|---|---|---|
| Number | KEY WORD | DEVIATION | CAUSES | EFFECTS | Risk1=S*P | Control Actions | Risk2=S*P |
| 1 | less | Low weight fraction of the surfactant added to the Nano fluid | Trial and error until the optimum amount of surfactant is reached | The coating required to generate electrostatic repulsion and van der Waals gravity compensation | =3*3=9 | Control of surfactant concentration added to Nano fluid at optimum amount | =3*1=3 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | is not created and as a result the required stability in nano fluid is not achieved and the thermal conductivity of nano fluid will be low. | | | |
| 2 | more | High weight fraction of the surfactant added to the Nano fluid | Trial and error until the optimum amount of surfactant is reached | The ratio of thermal conductivity coefficient of the Nano fluid to the base fluid decreases | =3*3=9 | Control of surfactant concentration added to Nano fluid at optimum amount | =3*1=3 |
| 3 | more | Increasing temperature (greater that 60°C) when using surfactant | High heating process | The bond between the nanoparticles and the surfactant may be damaged and the Nano fluid may lose its stability | =2*2=4 | Set the temperature to below 60°C | =2*1=2 |
| 4 | less | Very low amount of PH | Adding too much acid to the process | The result is that the absolute value of zeta potential is low, which makes the colloidal particles less stable and results in lower thermal conductivity | =2*3=6 | Setting PH to optimum amount | =2*1=2 |
| 5 | more | Very high amount of PH | Adding too much base to the process | The result is that the absolute value of zeta potential is low, which makes the colloidal particles less stable and results in lower thermal conductivity | =2*3=6 | Setting PH to optimum amount | =2*1=3 |
| 6 | more | Too increasing fluid pressure and velocity in homogenizer | Applying homogenizer with special design | The result is cavitation (bubble production) in | - | Positive risk (An opportunity to achieve | - |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | the fluid and the high energy resulting from this phenomenon breaks down the clusters and ultimately increases the stability of the Nano fluid and increases its thermal conductivity. | | desirable for process goals) | |
| 7 | more | increasing the ultra-sonication time and power | Setting ultrasonic device parameters to high amounts | having more dispersed and stable Nano fluids and leads to having higher thermal conductivity | - | Positive risk (An opportunity to achieve desirable for process goals) | - |
| 8 | more | increasing the ultra-sonication time and power | Setting ultrasonic device parameters to high amounts | In some special Nano fluids, leads Low stability of Nano fluids and to having lower thermal conductivity | =2*2=4 | Use of optimum amount of sonication power and time | =2*1=2 |
| 9 | more | Increasing stabilization process temperature normally | Heating of medium | Increasing thermal distributive coefficient and thermal conductivity | - | Positive risk-no demand of control action | - |
| 10 | less | Decreasing stabilization process temperature | Cooling of medium | Decreasing thermal distributive coefficient and thermal conductivity | =3*3=9 | Increasing temperature to an optimum amount | =3*1=3 |
| 11 | more | Increasing volume fraction of Nano particles normally | - | Increasing thermal conductivity | - | Positive risk-no demand of control action | - |
| 12 | less | Deceasing volume fraction of Nano particles | - | Decreasing thermal conductivity | =3*3=9 | Setting volume fraction of Nano particles to an optimum value | =3*1=3 |
| 13 | less | Deceasing Nano particles sizes | - | Increasing stabilization and thermal conductivity coefficient | - | Positive risk-no demand of control action | - |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 14 | more | Increasing Nano particles sizes | - | Decreasing stabilization and thermal conductivity coefficient | =3*3=9 | Being smaller of Nano particle sizes | =3*1=3 |
| 15 | less | Decreasing of side surface to volume of Nano particles | - | Decreasing heat transfer rate | =3*3=9 | Use of Nano particles with high ratio of side surface to volume | =3*1=3 |
| 16 | more | Increasing side surface to volume of Nano particles | - | Increasing heat transfer rate | - | Positive risk-no demand of control action | - |
| 17 | more | zeta potentials between 40 and 60 mV | - | Stable Nano fluid | - | Positive risk-no demand of control action | - |
| 18 | more | zeta potentials greater than 60 mV | - | excellent stability of Nano fluid | - | Positive risk-no demand of control action | - |
| 19 | less | low zeta potentials | - | nanoparticle clustering and sedimentation | =3*3=9 | Significant increase in zeta potential | =3*1=3 |
| 20 | less | Application of fillers at low concentrations in Nano fluids | - | The nanoparticles will have many Brownian motions at high temperatures resulting in an increase in the effective conductivity. | - | Positive risk-no demand of control action | - |
| 21 | more | Application of fillers at high concentrations in Nano fluids | - | Nanoparticles tend to accumulate at high temperatures. | =3*3=9 | Use of fillers at low concentrations | =3*1=3 |

It was identified 21 deviations in process parameters. Nine of these process parameters deviations caused to positive risks. These types of risks hadn't needed any preventive control actions. Because the consequences of these risk was high stability and high thermal conductivity of Nano fluids. But for 12 remain risks, these types of risks needed to control and corrective actions. Figure 1 shows the risk numbers before control actions. Figure 2 shows risk numbers after applying control actions. Also Figure 3 shows percent of risk number decrease (%).

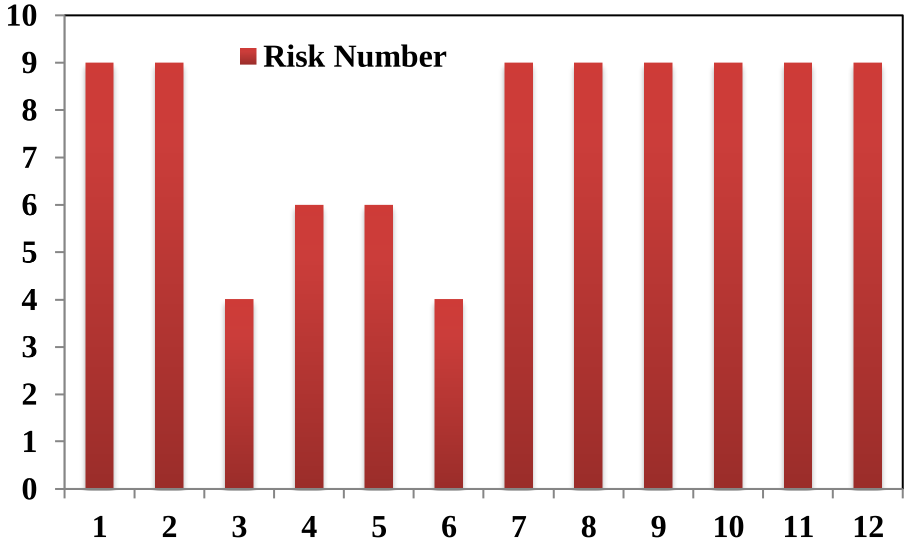


Figure 1: Risk numbers before control actions

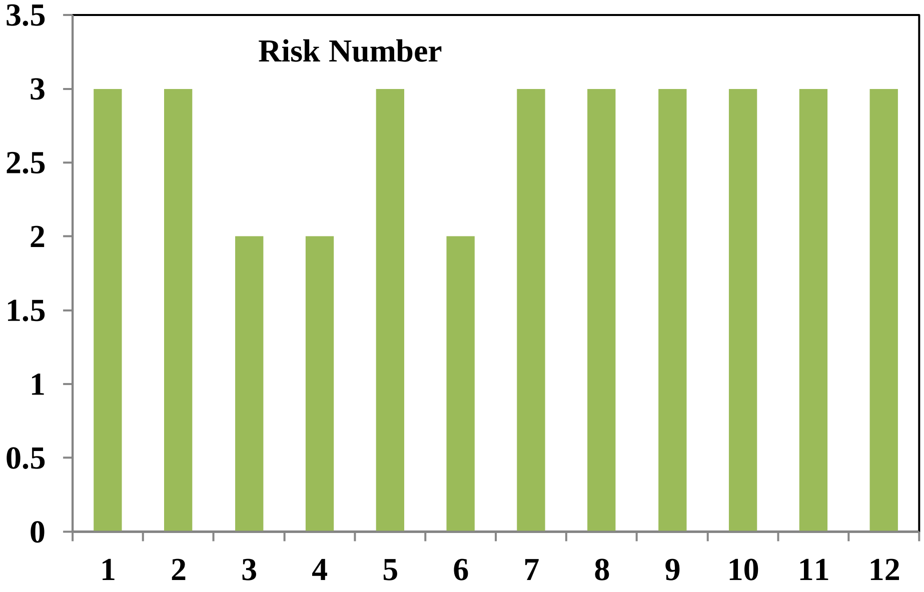


Figure 2: Risk numbers after control actions

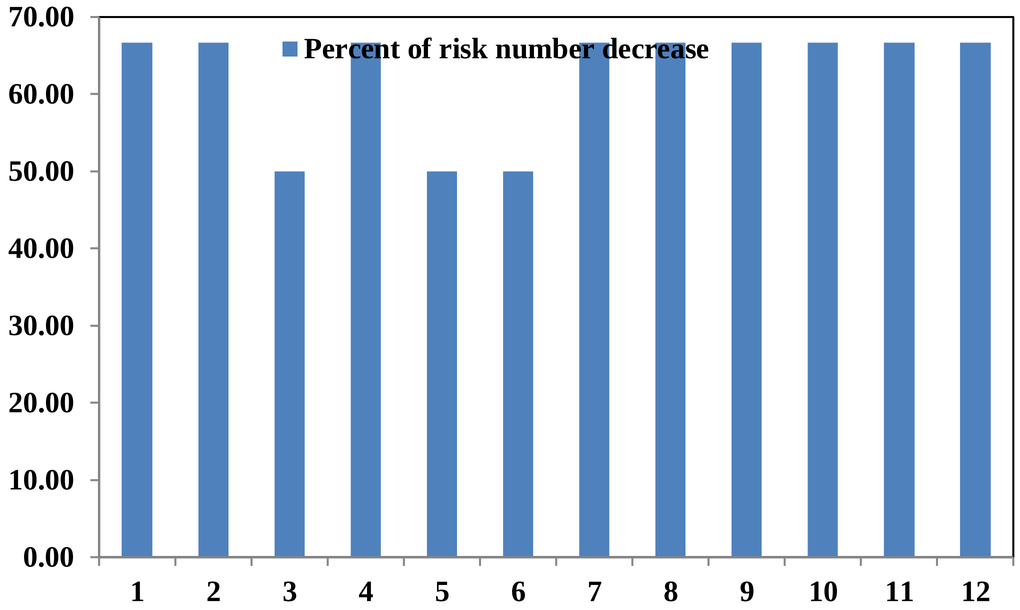


Figure 3: Percent of risk number decrease (%)

According to fig 1, eight number of risks was significant and four of them was low significant. After applying control actions, risk numbers decreased (fig 2). After decreasing risk numbers, level of them was non-significant (fig 2). Fig 3 shows the percent of decrease of risk numbers. This fig shows that decrease of risk numbers was completely significant. This means that suggested process control and preventive actions was effective for risk assessment of Nano fluids stabilization processes.

## Conclusions

This investigation showed that chemical engineering scientific concepts are a powerful tool for risk assessment by HAZOP method. It was showed that a good process design can be effective and important as a basis in control actions in HAZOP method. This excellent process design is related to appropriate adjust of process parameters such as temperature, PH and also application of nanoparticles with desired observed features.

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