CHEMICAL ENGINEERING TRANSACTIONS
VOL. 72, 2019
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Jeng Shiun Lim, Azizul Azri Mustaffa, Nur Nabila Abdul Hamid, Jiří Jaromír Klemeš

ISBN 978-88-95608-69-3; **ISSN** 2283-9216
DOI: 10.3303/CET1972009

Inherent Safety Assessment of Solvent Alternatives for Palm Oil Recovery

Syaza Izyanni Ahmad[a], Nor Alafiza Yunus[a, *], Haslenda Hashim[a], Roslina Rashid[b]

[a]Department of Chemical Engineering, School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia (UTM), Malaysia
[b]Department of Bioprocess and Polymer Engineering, School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia (UTM), Malaysia
alafiza@utm.my

Solvent extraction is a method implemented with the purpose to recover the remaining oil in spent bleaching earth. n-hexane is the most commonly used solvent in solvent extraction due to its advantages such as able to easily extract the oil and can be separated easily with low chances to form emulsions during the extraction process. Although n-hexane is a good solvent for extraction, n-hexane can easily vaporise to the surroundings due to its volatility making it a threat to human health and environment due to its high toxicity and high flammability characteristics. N-hexane should be replaced with greener solvents in term of safety and environmental impacts. This paper aims to evaluate the inherent safety of the solvents designed by the previous work involving three new solvents which are cyclohexane, 2-pentanone and isopropyl acetate and compare it with the existing solvent which is n-hexane. The inherent safety assessment of these solvent were done using the Numerical Descriptive Inherent Safety (NuDIST) technique. In this technique, scores are assigned to each solvent according to their inherent safety level in term of three parameters. The parameters involved are flammability, explosiveness and toxicity. In NuDIST, higher scores indicate higher hazard and is not preferable compared to lower scores. According to the assessment done, cyclohexane is the least hazardous solvent with CSTS of 191.53 while n-hexane is evaluated as the most hazardous solvent with CSTS of 198.32. Inherent safety assessment done between cyclohexane and n-hexane using the NuDIST method indicates cyclohexane as the inherently safer choice than n-hexane. This further supports the result produced by the previous work which indicates cyclohexane as having more promising properties as a solvent in order to extract palm oil in spent bleaching earth compared to n-hexane.

1. Introduction

Inherent safety can be defined as the concept of preventing hazards during the design stage of a process. There are four inherent safety principles that can be used in order to achieve hazard reduction or elimination in plant design (Crowl and Louvar, 2011). The first principle is intensification or also known as minimisation through usage of substance in smaller quantities in operating the plants which also reduces the inventory of hazardous materials. For example, intensification can be done through the use of small continuous reactor instead of large batch reactor or inventory reduction of hazardous raw material. The second principle is substitution. Substitution can be done by replacing hazardous materials to safer materials for hazard reduction for example to use less hazardous solvents instead of hazardous solvents. The third principle is attenuation which refers to hazardous materials operated under less hazardous materials for example to reduce operating temperature and pressure or to reduce boiling point through the use of vacuum. The fourth principle is simplification. Simplification can be done by designing equipment with the target to minimise failures. Noted examples that can be done in simplification is to design easy to use control panels, to design plants with easy and safer maintenance or to choose equipment with low failure rates.
The focus of this paper is to further discuss one inherent safety principle which is substitution of hazardous materials to safer materials. Typical examples of materials substitution are to use solvents that are less toxic,

Paper Received: 10 October 2018; Revised: 27 October 2018; Accepted: 08 November 2018

Please cite this article as: Ahmad S.I., Yunus N.A., Hashim H., Rashid R., 2019, Inherent safety assessment of solvent alternatives for palm oil recovery, Chemical Engineering Transactions, 72, 49-54 DOI:10.3303/CET1972009

to use water as a heat transfer fluid instead of hot oil as well as to use chemicals with higher flash points, boiling points, and other less hazardous properties.

Material design can be done through two methods which are experimental and computational methods (Klein et al., 1992). Experimental method is costly and time-consuming while computational method is much more preferable due to its ability to quickly design the needed material and only the promising solvents need further verification experimentally.

One notable means of substitution is material design using the Computer-aided Molecular Design (CAMD). CAMD is used to determine the identity of molecule or molecular structure formed according to the defined set of target properties and chemical building blocks (Ten et al., 2017). CAMD is suitable to be used in designing safer chemicals with suitable target properties to the intended process that will not reduce the quality of the product.

Karunanithi et al. (2006) presented a CAMD framework to design and choose solvents for crystallisation solution. The chosen solvent was then verified using the experimental verification work (Karunanithi et al., 2007). Ten et al. (2017) applied CAMD approach in designing molecules with specified target properties and advantageous safety and health characteristics. New alternative solvents to replace the commonly used solvents in the post combustion carbon capture process in power plants were also designed using the CAMD (Ahmad et al., 2018). Potential solvents designed were then evaluated for their performance in term of energy required for solvent regeneration. Khor et al. (2017) used CAMD in identifying replacement solvents with the most suitable attributes in recovering residual oil from palm pressed fibre in the palm oil mill industry. CAMD was used in designing solvents with environmental impact consideration during the extraction and recovery process (Ooi et al., 2018). This work formulates CAMD with the inclusion of molecular properties that will affect the quantitative assessment of the environmental impact of a process. Solvents produced using this approach has the ability to improve overall environmental characteristic of a process with better performance balance for a set of predefined properties.

Yunus et al. (2018) designed new solvent in order to substitute n-hexane in extracting oil from spent bleaching earth using Computer-Aided Molecular Design (CAMD). Various efforts were conducted in order to recover the remaining oil in spent bleaching earth including solvent extraction. n-hexane is the most commonly used solvent in solvent extraction. According to Yunus et al. (2018), n-hexane is able to easily extract the oil due to the polarity of the oil molecule making the oil to be easily attracted to the solvent. N-hexane can be separated easily with low chances to form emulsions during the extraction process. Although n-hexane is a good solvent for extraction, it is highly flammable as well as very toxic for human and the environment. Besides, n-hexane can easily vaporise to the surroundings due to its volatility. N-hexane should be replaced with greener solvents in term of safety and environmental impacts.

Yunus et al. (2018) found that cyclohexane has promising properties to replace n-hexane as a solvent in extracting palm oil in spent bleaching earth. Cyclohexane has less impact on human health and the environment compared to n-hexane. In addition, cyclohexane was also found to be more attractive in term of economic aspect compared to n-hexane.

This paper is an extension to the previous work done by Yunus et al. (2018) with the aim to perform inherent safety assessment to the solvent alternatives for palm oil recovery designed by Yunus et al. (2018). Inherent safety assessment on the solvent alternatives is important in order to identify the hazard level posed by the solvents in term of fire, explosion and toxic release accidents. The inherent safety assessment of solvent alternatives was done using the Numerical Descriptive Inherent Safety (NuDIST) technique (Ahmad et al., 2014) in order to observe their inherent safety level. This technique was also applied in designing chemical processes (Ahmad et al., 2013) as well as in the production of biodiesel (Ahmad et al., 2016) indicating its suitability and flexibility to be used for various types of process including solvent assessment.

2. Application of the NuDIST for inherent safety assessment of solvent

2.1 Solvent chosen for assessment

There are three solvents designed by Yunus et al. (2018) taken for inherent safety assessment which are cyclohexane, 2-pentanone and isopropyl acetate. These solvents were compared to n-hexane in term of inherent safety parameters.

2.2 Inherent safety parameters involved

There are three parameters involved in evaluating the inherent safety of the solvents using the NuDIST technique which are flammability (FL), explosiveness (EXP) and toxicity (TOX).

The flash point value of a chemical is used to determine the flammability hazards of a chemical in most inherent safety assessment technique. The flash point of a liquid is defined as the lowest temperature at which it emits enough vapor to form an ignitable mixture with air (Crowl and Louvar, 2011). Thus, liquids with lower flash points are more hazardous than liquids with higher flash points.

As for the explosiveness parameter, the tendency of chemicals to form an explosive mixture in air (also known as explosiveness) depends on the range between explosion limits (Heikkila, 1999). Below the Lower Explosion Limit (LEL), the mixture is too lean to burn while the mixture is too rich for combustion above the Upper Explosion Limit (UEL) (Crowl and Louvar, 2011). Thus, wider range between LEL and UEL indicates a higher tendency for an explosion.

One indicator that can be used in determining the toxicity of a chemical established by the American Conference of Governmental Industrial Hygienists (ACGIH) is called threshold limit values (TLVs). In this method, threshold limit values for short-term exposure limit (TLV-STEL) are used, which is more significant for an acute toxicity type of event. A lower TLV-STEL value for a chemical indicates a larger toxicity hazard compared to a chemical with a higher TLV-STEL value. In this method, a higher score represents higher hazard imposed by the chemicals as a chemical with a lower TLV-STEL value is more hazardous than a chemical with a higher TLV-STEL value.

2.3 Methodology

Figure 1 shows the methodology flowchart of this work. This work begins with data collection of data needed for inherent safety evaluation for example the flash point, upper and lower explosion limits and the TLV-STEL value for toxicity. The next step is to apply the gathered values into the logistic equations in order to produce flammability, explosiveness and toxicity score. Then, flammability, explosiveness and toxicity scores are added together to produce a single Chemical Safety Total Score (CSTS) representing each solvent. Lastly, an analysis of the scores is done in order to conclude the assessment.

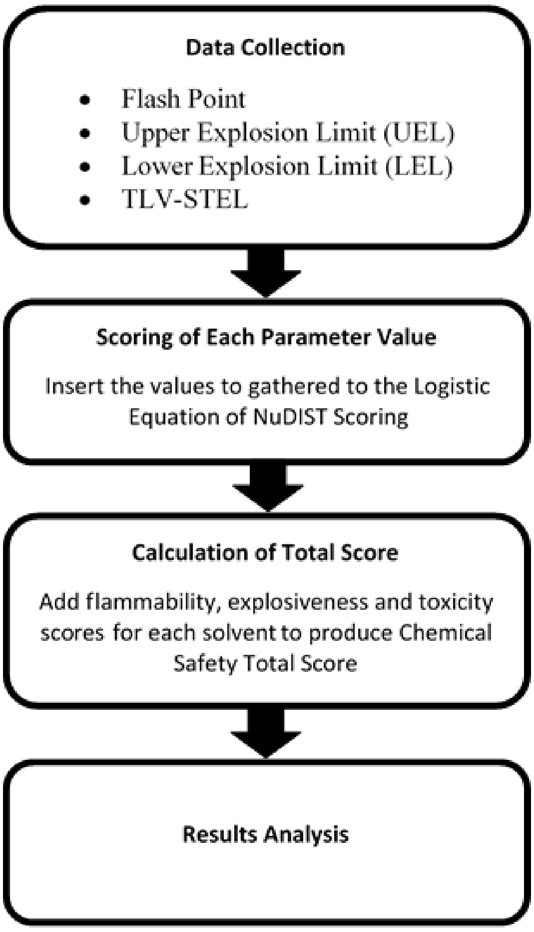

Figure 1: Methodology Flowchart

2.3.1 Data collection

There are three values that need to be gathered for each solvent in order to complete the inherent safety assessment which are flash point, upper and lower explosiveness levels and TLV-STEL values. Table 1 shows the values collected from the literatures for each solvent.

Table 1: Parameter values of each solvent

Solvent	Flash Point (°C)	Upper Explosion Limit (UEL) (%)	Lower Explosion Limit (LEL) (%)	TLV-STEL (ppm)
Cyclohexane	-18.15	8	1.3	300
2-pentanone	7.22	8.2	1.5	250
Isopropyl acetate	4.44	7.2	1.8	200
n-hexane	-21.65	7.5	1.2	150

2.3.2 Scoring of each parameter value

Parameter values tabulated in Table 1 were applied to the logistic equation of NuDIST scoring as shown in Table 2. Flash point and TLV-STEL values were simply inserted into Eq(1) and Eq(3). However, the UEL values need to be subtracted with the LEL values producing UEL-LEL values. The UEL-LEL values were then inserted into Eq(2). Detailed explanation can be found in the published works by Ahmad et al. (2014). The score produced for each parameter values are shown in Table 3.

Table 2: Logistic equation of NuDIST scoring

Parameter	Parameter Values Needed	Logistic Function	Equation No.
Flammability (SFL)	Flash Point (°C)	$S_{FL} = 100 \times (1 - \left(\frac{1}{1 + 3.03e^{-0.02x}}\right))$	(1)
Explosiveness (SEXP)	Lower and Upper Explosion Limit (%UEL-%LEL)	$S_{EXP} = 100 \times \left(\frac{1}{1 + 1096.63e^{-0.14x}}\right)$	(2)
Toxicity (STOX)	TLV-STEL (ppm)	$S_{TOX} = 100 \times (1 - \left(\frac{1}{1 + 403.4288e^{-0.012x}}\right))$	(3)

2.3.3 Calculation of total score

The scores produced for all three parameters are then added together to produce one unique score representing each solvent called the Chemical Safety Total Score (CSTS) as shown in Eq(4) where S_{FL}, S_{EXP} and S_{TOX} are the scores for flammability, explosiveness and toxicity parameters.

$$CSTS = S_{FL} + S_{EXP} + S_{TOX} \tag{4}$$

3. Results and discussion

Table 3 shows the scores produced for each parameter values. As mentioned previously, higher score indicates higher level of hazard. In term of flammability parameter, isopropyl acetate as the most hazardous solvent in term of flammability with SFL of 99.73 followed by 2-pentanone, cyclohexane and n-hexane with SFL of 99.71, 99.62 and 99.58. This indicates that, cyclohexane and n-hexane as safer in term of flammability compared to isopropyl acetate and 2-pentanone.

Isopropyl acetate is regarded as safer compared to n-hexane, cyclohexane and 2-pentanone with SEXP of 0.19, 0.22, 0.23 and 0.23. This indicates n-hexane, cyclohexane and 2-pentanone as more hazardous in term of explosiveness compared to isopropyl acetate.

As for toxicity parameter, n-hexane is the most hazardous solvent with STOX of 98.52 followed by isopropyl acetate and 2-pentanone with STOX of 97.34 and 95.26 while cyclohexane is the least hazardous with STOX of 91.68. This indicates n-hexane, isopropyl acetate and 2-pentanone as more hazardous in term of toxicity parameter.

Results tabulated in Table 3 illustrate the level of hazard posed by each solvent if either fire, explosion or toxic release accidents occur as a standalone accident. In term of standalone accidents, cyclohexane is deemed to be the least hazardous choice in toxic release hazard reduction while n-hexane and isopropyl acetate is deemed as the least hazardous in term of fire and explosion accidents.

Table 3: Scores produced for each parameter value

Solvent	Flash Point (°C)	SFL	UEL (%)	LEL (%)	UEL-LEL (%)	SEXP	TLV-STEL (ppm)	STOX
Cyclohexane	-18.15	99.62	8	1.3	6.7	0.23	300	91.68
2-pentanone	7.22	99.71	8.2	1.5	6.7	0.23	250	95.26
Isopropyl acetate	4.44	99.73	7.2	1.8	5.4	0.19	200	97.34
n-hexane	-21.65	99.58	7.5	1.2	6.3	0.22	150	98.52

However, Gupta and Edwards (2003) pointed out that any fire and explosion accidents occur are usually followed by toxic release, due to leakage as the accidents happen. The CSTS was calculated for each solvent to illustrate the combination of fire, explosion and toxic release accidents. Table 4 shows the CSTS produced for each solvent.

Table 4: CSTS score produced for each solvent

Solvent	FL Score	EXP Score	TOX Score	CSTS	Rank
Cyclohexane	99.62	0.23	91.68	191.53	1
2-pentanone	99.71	0.23	95.26	195.20	2
Isopropyl acetate	99.73	0.19	97.34	197.26	3
n-hexane	99.58	0.22	98.52	198.32	4

Rank 1 - Least Hazardous, Rank 4 - Most Hazardous

According to Table 4, cyclohexane is the least hazardous solvent with CSTS of 191.53 followed by 2-pentanone and isopropyl acetate with CSTS of 195.20 and 197.26 while n-hexane is evaluated as the most hazardous solvent with CSTS of 198.32. If a combination of fire, explosion and toxic release occur, cyclohexane is deemed as the least hazardous solvent compared to the other solvents. This further supports the results produced by Yunus et al. (2018) which indicate cyclohexane as having more promising properties as a solvent in order to extract palm oil in spent bleaching earth compared to n-hexane.

There is one limitation of this work that can be identified. This work only focused on assessing the solvents in terms of inherent safety parameters. Inherent safety assessment evaluates the solvents in term of maximum hazards inflicted by the solvents to the workers. Furthermore, inherent safety assessment mostly focused on identifying hazards that can cause accidents. As an example, flammability parameter is used to evaluate the potential of the solvents to cause fire accident while explosiveness and toxicity parameters focused in identifying the solvents' potential to cause explosion and toxic release accidents. However, it is not comprehensive in order to illustrate the risk of the solvents in term of health and environment. Thus, it is recommended for future study for the alternative solvents as well as n-hexane to be assessed in term of inherent health and environmental parameters. Inherent health assessment includes parameters such as occupational exposure limit in its evaluation. This assessment focuses on assessing the solvents in term of the riskiest situation for the workers to get maximum exposure to hazardous substances. Meanwhile, environmental assessment is also crucial in order to determine the solvents' potential in term of the largest impact to the environment if any leakage of the solvents occur especially if any of the accidents mentioned previously occur. Thus, additional assessment on health and environment impact need to be done on n-hexane and the alternative solvents for comprehensive insights on the hazard, health risk as well as environmental impacts of the solvents.

4. Conclusions

In conclusion, an inherent safety assessment was done on n-hexane and three new solvents designed in the previous work which are cyclohexane, 2-pentanone and isopropyl acetate. The inherent safety assessment was done using the Numerical Descriptive Inherent Safety (NuDIST) technique focusing on three parameters. The parameters involved are flammability, explosiveness and toxicity. According to the assessment done, cyclohexane is the least hazardous solvent with CSTS of 191.53 while n-hexane is evaluated as the most hazardous solvent with CSTS of 198.32. The inherent safety assessment done using the NuDIST further supports the argument made by the previous work which indicates cyclohexane as having more promising properties as a solvent in order to extract palm oil in spent bleaching earth compared to n-hexane. Inherent safety assessment as done in this work evaluates the solvents in term of maximum hazards inflicted by the solvents to the workers. Thus, it is recommended for future study for the alternative solvents as well as n-hexane to be assessed in term of inherent health and environmental impacts. Inclusion of inherent health assessment and environmental impact assessment with inherent safety assessment in deciding the best solvents to recover the remaining oil in spent bleaching earth will provides more insights on the maximum hazard as well as maximum exposure and environmental impacts brought by the solvents towards the workers, nearby residents as well as the environment.

Acknowledgments

The authors express gratitude to the Malaysian Ministry of Education (MOE) and Universiti Teknologi Malaysia (UTM) for facilitating throughout completing the research under the Post-Doctoral Fellowship Scheme for the project under vot no. Q.J130000.21A2.04E26.

References

Ahmad S.I., Hashim H., Hassim M.H., 2014, Numerical Descriptive Inherent Safety Technique (NuDIST) for Inherent Safety Assessment in Petrochemical Industry, Process Safety and Environmental Protection, 92, 379-389.

Ahmad S.I., Hashim H., Hassim M.H., Abdul Muis Z., 2016. Inherent Safety Assessment of Biodiesel Production: Flammability Parameter, Procedia Engineering, 148, 1177-1183.

Ahmad S.I., Hashim H., Hassim M.H., Srinivasan R., 2013, Safety Assessment Curve (SAC) for Inherent Safety Assessment in Petrochemical Industry, Chemical Engineering Transactions, 35, 1267-1272.

Ahmad M.Z., Hashim H., Mustaffa A.A., Maarof H., Yunus N. A., 2018, Design of Energy Efficient Reactive Solvents for Post Combustion CO_2 Capture using Computer Aided Approach, Journal of Cleaner Production, 176, 704-715.

Crowl D.A., Louvar J.F., 2011, Chemical Process Safety Fundamentals with Applications (3rd Ed), Pearson Education Inc., Massachussetts, USA.

Gupta J.P., Edwards D.W., 2003, A Simple Graphical Method for Measuring Inherent Safety, Hazardous Mater, 104, 15-30.

Karunanithi A.T., Achenie L.E.K., Gani R., 2006, A Computer-aided Molecular Design Framework for Crystallization Solvent Design, Chemical Engineering Science, 61, 1247-1260.

Karunanithi A.T., Acquah C., Achenie L.E.K., Sithambaram S., Suib S.L., Gani R., 2007, An Experimental Verification of Morphology of Ibuprofen Crystals from CAMD Designed Solvent, Chemical Engineering Science, 62, 3276-3281.

Kheang L.S., Foon C.S., May C.Y., Ngan M.A., 2006, A Study of Residual Oils Recovered from Spent Bleaching Earth: Their Characteristics and Applications, American Journal of Applied Sciences, 3(10), 2063-2067.

Klein J., Wu D., Gani R., 1992, Computer Aided Mixture Design with Specified Property Constraints, Computers & Chemical Engineering, 16, S229-S236.

Khor S.Y., Liam K.Y., Loh W. X., Tan, C.Y., Ng L.Y., Hassim M. H., Ng D.K.S., Chemmangattuvalappil N.G., 2017, Computer Aided Molecular Design for Alternative Sustainable Solvent to Extract Oil from Palm Pressed Fibre, Process Safety and Environmental Protection, 106, 211-223.

Ooi J., Ng D.K.S., Chemmangattuvalappil N.G., 2018, Optimal Molecular Design towards an Environmental Friendly Solvent Recovery Process, Computer and Chemical Engineering, 117, 391-409.

Ten J.Y., Hassim M.H., Ng D.K.S., Chemmangattuvalappil, N. G., 2017, A Molecular Design Methodology by the Simultaneous Optimisation of Performance, Safety and Health Aspects, Chemical Engineering Science, 159, 140-153.

Yunus N.A., Mohamad Zaki N., Wan Alwi S.R., 2018, Design of Solvents for Palm Oil Recovery using Computer-Aided Approach, Chemical Engineering Transactions, 63, 583-588.