CHEMICAL ENGINEERING TRANSACTIONS
VOL. 63, 2018
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Jeng Shiun Lim, Wai Shin Ho, Jiří J. Klemeš

ISBN 978-88-95608-61-7; **ISSN** 2283-9216
DOI: 10.3303/CET1863098

Design of Solvents for Palm Oil Recovery using Computer-Aided Approach

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In palm oil refinery process, bleaching earth is used in bleaching process. Used bleaching earth, also known as spent bleaching earth (SBE) is removed from the process as waste which contains some remaining oil. Many studies have been done to fully utilise the SBE before it is turned into waste. One of the known studies includes the extraction of remained palm oil from SBE. The extractions process is either using solvent or supercritical fluids processes. The commonly used solvents for extraction are hexane, ethanol and methanol. These solvents have some disadvantages, for example hexane is flammable and has low extraction yield as well as high in toxicity. New suitable solvents are needed to improve the performance in the extraction process. Through this study, new solvent for extraction of oil in SBE was obtained with the implementation of Computer Molecular Design (CAMD). Both linear and non-linear target properties were included during designing the solvent. Property models are used in order to meet the needs of the specified properties. The properties that are needed for solvent design were obtained from literature study. CAMD was used to generate possible solvent candidates. The steps involved are, first, data of solvent, SBE and palm oil was collected from the literature, then the problem definition is formulated to solve the design problem. Next, designing the solvent was performed by using CAMD based on the input data obtained and the defined problem in the previous steps. CAMD generated all the possible structures of solvents. The solvent candidates were screened based on specified target properties. Lastly, solvent performance evaluation was done by using Aspen-HYSYS simulation software in order to evaluate the performance of the five best solvent candidates that were selected after the screening process. Through this study, it is found that, cyclohexane is the best solvent to replace n-hexane as it satisfied all the target properties. Based on the simulation result, cyclohexane is capable to extract up to 90.19 % of palm oil remained in the spent bleaching earth. Meanwhile, the toxicity parameter of cyclohexane is only 2.07 mol/L which is lower than n-hexane, 3.02 mol/L. On the other hand, the boiling point of cyclohexane, 353.15 K is slightly higher than n-hexane, 340.15 K.

1. Introduction

The processes in the palm oil refining include degumming, bleaching and deodorisation. The purpose of bleaching process is to remove colour by using bleaching earth (Kheang et al., 2006). Bleaching earth will be removed as solid waste known as spent bleaching earth (SBE) after the bleaching process. SBE is usually disposed to landfills or waste dumps. Due to increasing cost of disposal and being an environmental hazard, it is desirable to recover oil, before disposing off SBE as per environmental regulations (Kheang et al., 2006).
As one of the largest producers of palm oil, Malaysian palm oil refineries produced around 120,000 metric tonnes of SBE and 36,000 tonnes of the oil is estimated can be recovered (Kheang et al., 2006). It is about 20 % to 35 % of oil can be recovered (Al-Zahrani and Daous, 2000). Many efforts had been done to recover the remaining oil in SBE before discarding it including solvent extraction. The most commonly solvent used in the solvent extraction is n-hexane. N-hexane is considered as a good solvent in the oil extraction process since it can easily extract the oil. This is due to its polarity that can easily attract the oil. N-hexane is easy to be separated and has small chances to form emulsions during the extraction process. Even though n-hexane is a

Please cite this article as: Nor Alafiza Yunus, Norlela Mohamad Zaki, Sharifah Rafidah Wan Alwi, 2018, Design of solvent for palm oil recovery using computational-aided approach, Chemical Engineering Transactions, 63, 583-588 DOI:10.3303/CET1863098

good solvent in terms of extraction, it is a highly flammable solvent, toxic to human and also the environment. High volatility characteristic of n-hexane will made n-hexane easily vaporised to the surroundings. Thus, alternative solvents should be designed to replace n-hexane with the consideration of safety, and environmental impact.

The solvent can be designed by either experimental or computational method. Experimental method is a time-consuming, and costly. Meanwhile for computational method, it can identify solvent candidates in a very quick way where only the promising solvents need further verification experimentally (Klein et al., 1992). Ahmad et al. (2015) proposed an optimal solvent design for CO_2 capture process using computer-aided approach. The approach can be implemented to design of solvent for oil recovery. The objective of this study is to design new solvent to replace n-hexane for extraction of oil from SBE using CAMD. In designing the solvent, the crucial step is to determine the target properties. CAMD has the capability in predicting, estimating and designing molecules (Ng et al., 2015). The performance of the selected solvents was then evaluated using ASPEN-HYSYS simulator.

2. Methodology

There are five steps involved in solvent design as illustrated in Figure 1 below.

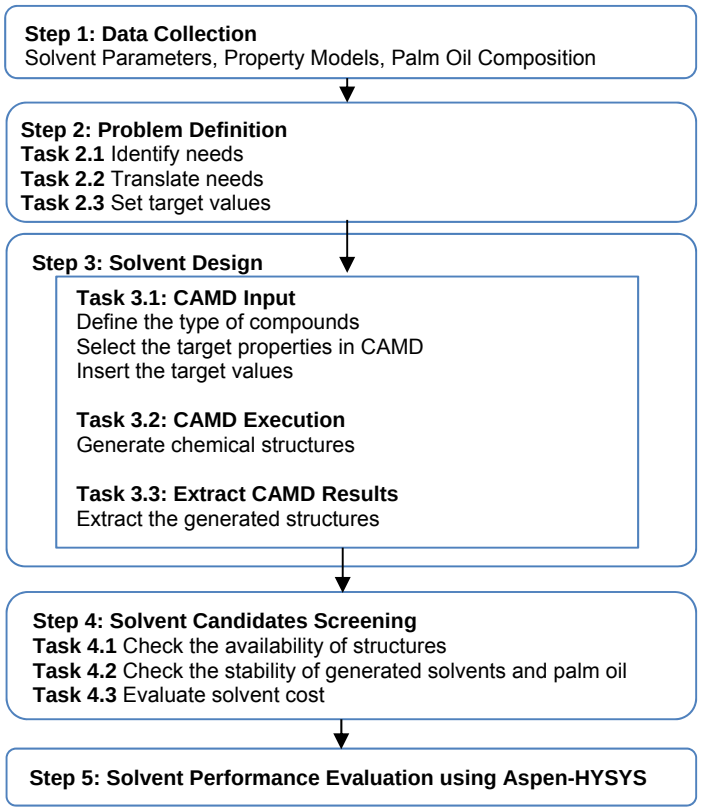

Figure 1: Solvent design steps

2.1 Step 1: Data collection

Properties of the solvents were reviewed in literature such as the boiling point, vapour pressure, toxicity parameter and solubility parameter (Gebreslassie and Diwekar, 2015). Solvent parameters which were heavily influenced in extraction process of oil from SBE are being focused on in this research. The parameters obtained were based on the current solvent that has been used which is n-hexane. Based on the models that have been specified below, linear and non-linear problems were applied to the parameters. The required property models were retrieved from database. Lethal concentration, solubility and Gibbs energy of mixing parameters were estimated using model represented in Table 1.

Based on Eq(1) that represents toxicity parameter which is based on lethal concentration, ng is the number of groups in the model, n_i is the number of groups of type i in the compound, α_i is toxicity contribution of the group i. Toxicity parameter uses group contribution method in determining the lethal concentration of each

structures. Eq(2) represents Hansen solubility parameter where δ_d is solubility parameter due to dispersion forces, δ_p is solubility parameter due to dipole forces and δ_h is solubility parameter due to hydrogen bonding. Gibbs energy of mixing is represented by Eq(3), where R is a gas constant, T is operating temperature, x_i is mol fraction of species i and γ_i is activity coefficients of species i. Negative value of Gibbs energy indicates the species is stable. In order to design solvent for extraction process, the solute properties also need to be studied. In this study, the solute is palm oil. Palm oil has three major composition of fatty acids, which are palmitic acid (43.5 %), oleic acid (39.8 %) and linoleic acid (10.2 %) (Tan et al., 2009).

Table 1: Property model for each target property

Target property	Model	Equation		Reference
Lethal concentration, LC_{50}	Group Contribution method	$-\log LC_{50} = \sum_{i=1}^{ng} n_i \alpha_i$	(1)	Martin and Young (2001)
Solubility parameter,δ	Hansen solubility parameter	$\delta = \sqrt{{\delta_d}^2 + {\delta_p}^2 + {\delta_h}^2}$	(2)	Bielicka-Daszkiewicz et al. (2010)
Stability, ΔG^{mix}	Gibbs energy of mixing	$\Delta G^{mix} = RT(\sum x_i \ln \gamma_i + \sum x_i \ln x_i)$	(3)	Smith et al. (2005)

2.2 Step 2: Problem definition

There are three tasks in the problem definition step, which are define needs, translate and set the target values for each need. The needs are categorised into three categories: performance, safety and environment. The performance of solvent is observed through the ability of solvent to extract oil from SBE and its the easiness to be separated. In term of safety, and the environment, the solvent should not be easily vaporised to the surroundings and has no health impact to human and living things. All needs are translated into target properties. The performance is measured from extraction yield, meanwhile the vaporisation rate is measured from the boiling point of chemical and health impact is translated into toxicity parameter. Then, target values are settled for all the target properties as listed in Table 2. The target values are obtained from literature and by comparison with commonly used solvents for palm oil extraction including n-hexane.

Table 2: Need, target property and target value of solvent design

Need	Target Property	Target Value	Unit
Able to extract oil from SBE	Solubility (δ)	11 ≤ Solubility (δ) ≤ 21	
Easy to separate	Boiling Point (T_b)	329 ≤ T_b ≤ 384	K
No losses to surrounding	Vapour pressure (P_v)	P_v ≤ 1	atm
Not harmful to human and living things	Lethal concentration, (LC_{50})	-log(LC_{50}) < 3.0	mol/L

2.3 Step 3: Solvent design

CAMD tool was used to generate the molecule structures. CAMD will generate all possible combination of the selected functional groups to create a chemical structure based on the specified target properties. To generate the structure, user need to specify the functional groups and the target properties. For solvent design, the common function group of alkane, alcohol, amine, ketone, aldehyde, ether and ester were selected. All the target properties listed in Table 2 were defined and the values were set in the CAMD. Since not all target properties were included in the CAMD, only boiling points and total solubility parameters were being set in the software. The chemical structures are then generated, and the results are analysed. From the results obtained, Chemical Abstract Service (CAS) registry number, Simplified Molecular-Input Line-Entry System (SMILES), total solubility parameter, boiling point as well as lethal concentration were collected from database.

2.4 Step 4: Solvent screening

The generated solvents in the previous steps were further screened. In this step, the solvent stability was evaluated based on the Gibbs energy of mixing. The unstable solvents were removed. Cost of each solvent candidate is obtained, and the solvent candidates are ranked according to the cost. The top five promising solvent candidates were chosen for the next step.

2.5 Step 5: Performance evaluation

In this step, Aspen HYSYS software was used to evaluate the performance of the five selected solvent candidates. The objective of this step is to estimate the yield of the extraction process of palm oil using each of the solvent candidates. The process is simulated based on the extraction process of palm oil in SBE as illustrated in Figure 3. The top five solvent candidates were simulated, and the results is analysed.

3. Results and discussion

Total of 39 chemical structures were generated using CAMD. The structures were extracted from CAMD for further screening process

3.1 Solvents candidates screening

Not all of the generated structures from CAMD are known chemicals. Some structure can be unknown. The generated structures were analysed using chemical database to check the CAS number and the target properties. Only 19 structures were unknown, and they were eliminated. Remaining 20 chemical structures were further screened on the stability. The designed solvents must be stable enough to withstand heat and pressure as the solvents were used for repeated heating, vaporizing and cooling process. All of the 20 solvents candidates were analysed for their stability by calculating the ΔG^{mix}. Examples of ΔG^{mix} results are shown in Figure 2a to 2c. The calculated value of ΔG^{mix} for all solvent candidates show negative values which indicates all the solvents were completely miscible with the palm oil at higher mole fraction of solvent.

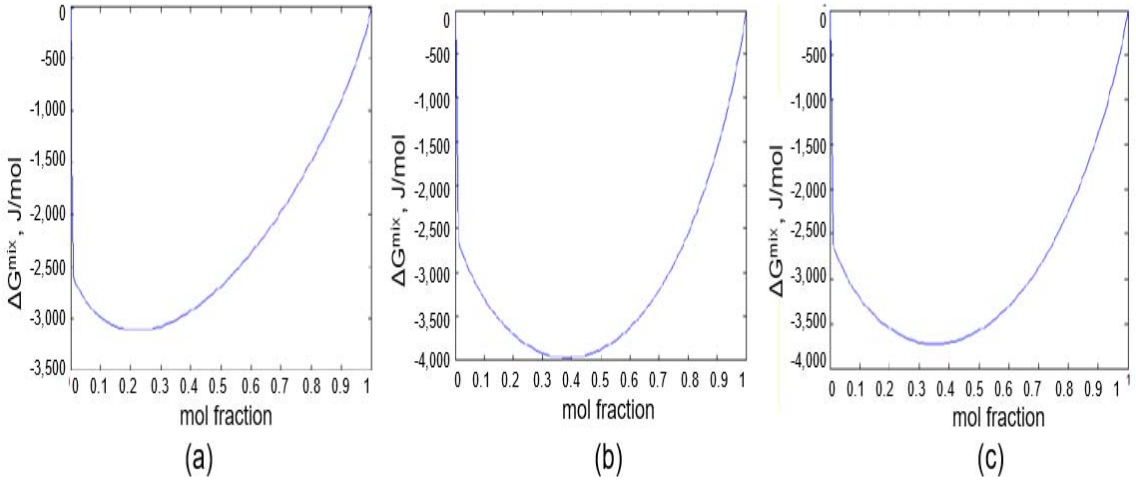

Figure 2: Gibbs energy of mixing of palm oil with (a) 3-methyltetrahydrofuran (b) 3-ethyloxetane (c) isopropyl acetate

Based on Figure 2a, it shows that the mixture was in metastable equilibrium states. This can be clearly seen at composition mole fraction of 3-methyltetrahydrofuran from 0.2 until 1.0. In this region, the mixture is said to be slightly unstable. A metastable equilibrium state is known as sensitive states. This is primarily due to caution that needs to be applied when handling mixture under metastable equilibrium (O'connell and Haile, 2005).

Figure 2b shows the mixture was in stable equilibrium states. Stable equilibrium states occur at global minimum point where small disturbance did not affect the mixture. This was mainly because the mixture is in highly stable states. From Figure 2b, it shows the mixture was in slightly equivalence state which is at 0.4 mole fraction of 3-ethyloxetane that contributes to the stability itself. Figure 2c shows the mixture was in stable equilibrium states. However, the mixture is less stable compared to mixture in Figure 2a. This is because the mixture of isopropyl acetate and palm oil were at the local minimum point. The mixture is said to be in the metastable and stable equilibrium states since both types of equilibrium are exhibited in the mixture. It can be concluded that the mixture is slightly stable compared to the mixture of 3-methyltetrahydrofuran and less stable than mixture of 3-ethyloxetane with palm oil.

It is noticed that all graphs show downward curve without any phase split as there is no fluctuation shown in the graph. The stability of solvents is very crucial in determining the best promising solvent so that the solvents will not be affected by any disturbance.

The designated solvent must not only exhibit a great performance in extracting palm oil from SBE, but it also must be economical and low cost. Cost is used as the final selection criterion since there are many candidates that meet the specified target properties. The costs of all the solvent candidates were obtained from literature study as well as from worldwide chemical suppliers for instance Alibaba.com, Labchem Sdn. Bhd., Sigma-Aldrich, Synquest Laboratories, and Richest Group Limited. The solvent candidates were ranked in ascending order based on the cost as shown in Table 3.

Table 3: Solvents candidates

No	Chemical Name	Boiling point, T_b (K)	Total Solubility parameter, δ (Mpa$^{1/2}$)	-log(LC_{50}) (mol/L)	Cost (RM/L)
1	Cyclohexane	353.12	17.88	2.07	3.95
2	2-isopropoxybutane	373.04	14.73	2.22	8.43
3	2-isopropoxypropane	340.42	14.88	1.86	10.28
4	2-pentanone	378.40	19.10	2.88	64.51
5	2-methyl-2-butanol	373.15	19.62	1.84	72.21
6	3-methyltetrahydrofuran	349.35	18.41	2.85	98.40
7	Isopropyl acetate	353.12	17.88	2.96	121.90
8	3-methyl-1-butanamine	377.17	18.80	2.82	416.25
9	3-methylbutan-2-one	352.76	18.41	1.33	487.30
10	3,3-dimethyl-2-butanone	374.62	17.15	2.64	730.95

3.2 Solvent performance evaluation

In this step, only the top five solvents candidates from Table 3 were selected for performance evaluation. The solvent performance was evaluated based on the performance of extraction of oil in the spent bleaching earth. Based on literature study, the initial palm oil content in SBE is set at 30 % (Al-Zahrani and Daous, 2000). The extraction operating conditions are set at 1 atm and specific boiling point temperature for each solvent. Based on Figure 3 which shows the Process Flow Diagram (PFD) of the extraction process based on the palm oil refining process in Malaysia, the extraction process of palm oil from spent bleaching earth took place at operation unit S-101 which is known as oil separator. Solvent candidates are added in the oil separator unit and they undergo separation process before spent bleaching earth is separated at the bottom part of the oil separator unit. All five selected solvent candidates were evaluated based on the extraction of palm oil yield using Aspen-HYSYS simulation. Results of the simulation are shown in Table 4.

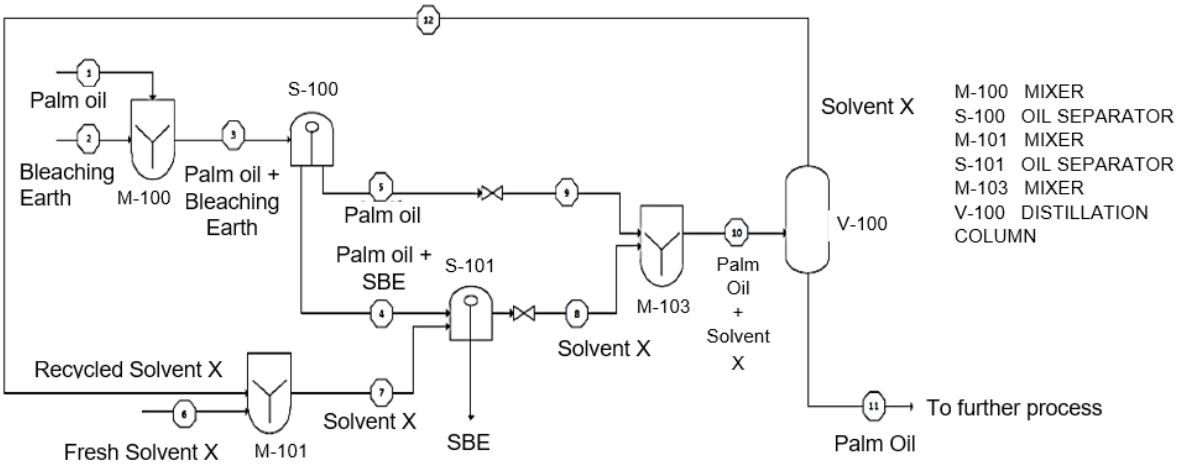

Figure 3: Process flow diagram of extraction of palm oil

Based on Table 4, it clearly shows that cyclohexane has the greatest ability in extraction of palm oil in spent bleaching earth since it possesses highest percentage of extracted oil which is 90.19 % followed by 2-pentanone with 90.06 % of extracted oil. Other solvents, 2-methyl-2-butanol, 2-isopropoxypropane and 2-isopropoxybutane can extract about 89.94 %, 89.09 % and 88.40 %. All the solvent candidates had better performance as compared to n-hexane, which can extract 80.50 % of oil in spent bleaching earth. Table 4 shows the comparison of cyclohexane and n-hexane properties.

Based on Table 4, cyclohexane has slightly higher boiling point compared to n-hexane. Solvent with higher boiling point can reduce the losses to the surrounding due to vaporisation. Volatility can be directly be determined by the boiling point of the solvent where the relationship of both parameters is directly proportional. Vaporisation rate of cyclohexane is lower. It shows that cyclohexane possesses higher resistance from vaporising to the surrounding. It may require higher energy in the extraction process.
The results also compared the difference in solubility parameter, $\Delta\delta$ of solvent and palm oil. Low value of $\Delta\delta$ means that the solvent has solubility parameter that is close to palm oil which indicates that the mixture is soluble. Since cyclohexane has lower $\Delta\delta$ than n-hexane it has good miscibility with palm oil as compared to n-hexane. The lethal concentration of cyclohexane was much lower than n-hexane. The toxicity level exposure to human and environment can be minimised

Table 4: Properties comparison of n-hexane and top five solvent candidates

Solvent	Boiling point (K)	$\Delta\delta$ ($MPa^{1/2}$)	Lethal concentration (mol/L)	Cost (RM/L)	Extracted palm oil from SBE (%)
Cyclohexane	353.12	2.12	2.07	3.95	90.19
2-pentanone	378.40	19.10	2.88	64.51	90.06
2-methyl-2-butanol	373.15	19.62	1.84	72.21	89.94
2-isopropoxypropane	340.42	14.88	1.86	10.28	89.09
2-isopropoxybutane	373.04	14.73	2.22	8.43	88.40
N-hexane	340.00	3.16	3.02	24.00	80.50

4. Conclusion

In conclusion, an optimal solvent has been designed by using CAMD to replace n-hexane, a commonly used solvent in oil extraction from SBE, by specifying the target properties of the targeted solvent. As the results, 20 feasible solvents were generated, and 5 solvents' performances were evaluated. Cyclohexane shows good performance with promising properties as a solvent to extract palm oil in SBE. It has less impact on the environmental as well as to human health. It is also discovered that cyclohexane is an economic solvent based on the current price. The actual properties of the selected solvent and the extraction performance should be further verified experimentally in the future work.

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