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Design of Surfactant for Water in Diesel Emulsion Fuel for Designing Eco-Friendly Fuel

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Diesel engines are known as one of the biggest contributors to environmental problems caused by exhaust emissions and are the reasons for health hazardous. Nitrogen oxides (NO_x) and particulate matters (PM) are the main pollutants from diesel engines. This problem attracts much interest regarding the development of eco-friendly fuels for the enhancement of the environment and human health. The use of water in diesel emulsion fuel with proper surfactants as a stable system can be proposed as an alternative to solve the problem. Selection of the appropriate surfactants is a very crucial task to obtain stable emulsion. Trial and error approach through experimental work is the conventional method to find the suitable surfactant as emulsifier for water in diesel emulsion. It is typically time consuming, costly and difficult to obtain the optimal target properties. The objective of this study is to design appropriate surfactants that can be used as emulsifiers for the formulation of water in diesel emulsions fuel using product design approach. There are four steps involved in this research. Step 1 is the problem definition. The surfactant problem is defined where the product attributes and needs are identified and translated to physico-chemical properties as the target properties and the target value of the target properties are set. There are four properties chosen as the target properties, which are surface tension, hydrophilic-lipophilic balance, critical micelle concentration and cloud point. Step 2 is the identification of pure component property. The property model for pure component is identified. Step 3 is designing the surfactants. In this step, the non-ionic surfactant database is screened and the chemical that does not fulfil the target properties will be eliminated. Step 4 is the selection of the surfactant. All the candidates fulfilled the target properties set in step 1. The price of the chemical will be used as criteria to choose the potential candidates. From 197 chemicals' candidates from the chemical database library, two candidates are suggested as the potential surfactants for water in diesel emulsion fuel. These chemicals are propylene glycol stearate and polyoxyethylene (2) stearyl ether. These two chemicals had fulfilled all the target values of the target properties. The price of these chemicals are 16 times cheaper than the most common surfactant used for water in diesel emulsion fuel, which is SPAN 80.

1. Introduction

Diesel fuel used in compression ignition engines contributes to environmental pollutions due to the released of carbon dioxide (CO_2), carbon monoxide (CO), particulate matter and nitrogen oxides (NO_x) to the atmosphere. One of the alternatives to reduce the emissions and to improve the combustion process with better engine performance without modification of the engine, is by using water in diesel emulsion as a fuel (Abu Zaid, 2004). Most of the research done through the experimental approach is to identify the impact of water in diesel fuel to the combustion process, engine efficiency and exhaust emissions. The use of water in diesel emulsion as alternative fuels has been reported as the effective approach that can reduce the engine smoke level and the Nitrogen oxide level without any engine modifications (Novikov et al., 1996). A research done by Nadeem et al. (2006) demonstrated that the water in diesel emulsion can reduce the greenhouse gases without affecting the engine's performance. At the same time, micro-explosion phenomena occur due to the presence of water, which contributes to the increasing volatility of the fuel. This can improve the combustion efficiency (Hasannuddin et

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al., 2015). The presence of water contributes to the reduction of exhaust temperature and improved the combustion efficiency and lead to the reduction of NO_x, CO, particulate matter and unburned hydrocarbon (Alahmer, 2010). According to Guzmán et al. (2015), water in diesel emulsion can reduce 10 % and 40 % of particulate matter and NO_x.

The use of emulsion as alternative fuel requires significant observation on the stability of the emulsion. Instability emulsion fuel can deteriorate the diesel engine. It is important to find the suitable surfactant that can form stable water in diesel emulsion (Mohammed et al., 2014). As oil and water are immiscible with each other, a surfactant is used to prepare the emulsion (Lin and Wang, 2003). Emulsifier, or known as surfactant, has two parts. One part has affinity for water and the other part has affinity for oil. The surfactant forms a thin interfacial film between the two liquids to decrease the water surface tension and minimise the contact, coalescence and aggregation of the internal dispersed phase (Chen and Tao, 2005). Selection of the suitable surfactant is the main criteria for emulsions to stay stable over a wide temperature span and for a specific time. The surfactants must burn readily without soot formation and should not contain sulphur and nitrogen. They should contain only carbon, hydrogen and oxygen and they should preferably not have aromatic rings in their structure (Dantas Neto et al., 2011). According to Dantas Neto et al. (2013), the main factors that influenced a stable emulsion are the nature of surfactant and the ratio of surfactant mixture. Properties such as the critical micelle concentration (CMC), the Krafft temperature (TK), the cloud point (CP), the surface tension (σ), the hydrophilic-lipophilic balance (HLB) and the phase inversion temperature (PIT) are fundamental to predict the effects of the addition of surfactants in solution (Tadros, 2013).

Sorbitan monooleate, or known as SPAN 80, is the common surfactant used to form water in diesel emulsion fuel. Many research had been done to identify the performance of water in diesel emulsion as alternatives fuel by using SPAN 80 as surfactant. This is because SPAN 80 performs well as a surfactant and can form a stable emulsion fuel. Research done by El-Din et al. (2013) mentioned that the emulsion can stable up to a month by using SPAN 80. Current research found that the formulation of WiDE fuel with SPAN 80 can form a stable emulsion up to 3 months (El-Din et al., 2017). The price of the SPAN 80 is very expensive. The price of SPAN 80 from Alibaba's website is USD 42 to 49 per kg. The aim of this study is design the surfactant that has properties similar or approachable to the SPAN 80 at a cheaper price.

2. Methodology

For this case study, computer aided molecular design (CAMD) approach is used to select the suitable surfactant to form water in diesel emulsion fuel. There are four main steps involved in the designing of the non-ionic surfactant for water in diesel emulsion fuel, which are problem definition, identification of property models for pure component, design of surfactant and final selection, as shown in Figure 1. This methodology is adapted and modified from Ng et al. (2007). For this research, non-ionic surfactant database library is developed manually by collecting the chemical name and the experimental data of HLB value of the chemical. The non-ionic surfactant database consists of 197 non-ionic surfactants obtained from the research done by (Guo et al., 2006) is used as initial database for screening process in Step 3. Generally, the target properties of the chemicals are collected from the literature. If the value is not available, the pure component property models will be used to predict the value of the properties.

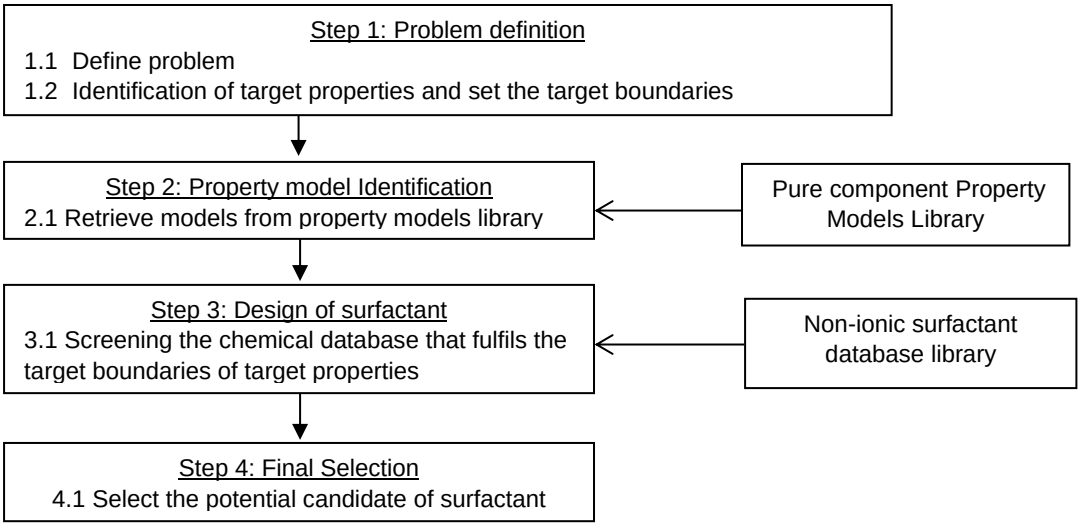

Figure 1: Framework for design of potential non-ionic surfactants for water in diesel emulsion fuel

2.1 Step 1 – Problem definition

Step 1 is the problem definition. Problem definition is the identification of the consumer needs for specific products, and of relating these needs to a set of desired target properties. The surfactant problem is defined where the product attributes and needs are identified and translated to physico-chemical properties as target properties and the target boundaries of the target properties are set. The target properties and target boundaries are selected from the literature. Selections of the target properties are based on the property of surfactant that gives impact to the WiDE fuel and to form a stable emulsion.
For this case study, the main target is to find potential chemicals that have thermo physical properties similar or approachable to SPAN 80 at cheaper price and to be used as surfactant for water in diesel emulsion fuel. In this case study, four properties are identified as important target properties to form water in oil emulsion. The properties involved are critical micelle concentration, cloud point, surface tension and hydrophilic lipophilic balance. Table 1 shows the detail explanation about the target properties and target boundaries of the potential candidate of surfactant.

Table 1: The target properties and target boundaries for design of surfactant for water in diesel emulsion fuel

No	Target Properties	Unit	Description	Min	Max	References for target boundaries
1	Critical Micelle Concentration (CMC)	mN/m	Indicate the point at which monolayer adsorption of surfactant molecule at the interface is complete.	3.22	6.60	Span 80
2	Cloud point (CP)	°C	Cloud point temperatures are an excellent means of screening candidate surfactants, as stable emulsified formulated products can be obtained only below the cloud point of the surfactant system (Michele et al., 2014)	10	-	ASTM D5773
3	Surface tension (σ)	mN/m	Measure of the wetting ability of a compound and it is a very important property for surfactants.	29.05	60.75	Span 80
4	Hydrophilic - lipophilic balance (HLB)	-	The most common method to correlate the surfactant structure with the effectiveness of the surfactant as emulsifiers. - HLB values between 3 to 6 indicates the formation of a water-in-oil emulsion (Tadros, 2013)	3	6	Tadros, 2013

Selection of the target properties is important task to identify and choose the suitable surfactant that will affect the stability of the emulsion. For the selection of surfactant for emulsion, there are four important target properties involved. The target properties for selection candidates as surfactants are Hydrophilic-Lipophilic Balance (HLB), Critical Micelle Concentration (CMC), cloud point and surface tension (Michele et al., 2014). Each target property has specific function as described in the Table 1.
The next step is to set the lower and upper bound of the target properties or called as target boundaries. The range of lower and upper bound can be found from literature based on the problem definition. In this study, the target boundaries are decided based on the property of SPAN 80 and by considering the value of property that is suitable for surfactant to form water in oil emulsion. This step is very important to ensure that the designed surfactant can form a stable emulsion. As an example, the target boundaries for HLB in Table 1 is 3 to 6. This value set as boundaries because the value of HLB to form water in oil emulsion fuel must be within 3 to 6. The HLB of 8 to 18 will form oil in water emulsion.

2.2 Step 2 – Identification of pure component property model

Step 2 is the identification of the pure component property model. Pure component property model is the mathematical model for estimation of physical and chemical properties for single or pure chemical. The required property models of the four target properties are retrieved form the pure component property models' library.

Property Models library consist of the models for pure component of the target properties as shown in Table 2. The established pure component property models to predict the property of pure component are identified from the literature. There is a need to verify the property models from literature on its suitability for this study. If the model is not suitable or not available, it can be either modified or to developed new model.

Table 2: Property models library for pure component

No	Property	Property models	Equation		Reference
1	Critical Micelle Concentration (CMC)	Extended group contribution method	$-\log(\mathrm{CMC})_{\mathrm{pred}} = \sum_i N_i C_i + \sum_j M_j D_j + \sum_k O_k E_k$	(1)	Michele et al, (2013)
2	Cloud point	Group contribution method	$\mathrm{CP}^2 = \sum_i N_i C_i + \sum_j M_j D_j + \sum_k O_k E_k$	(2)	Michele et al, (2014)
3	Surface tension (σ)	Group contribution method	$F(\sigma) = \sum_i N_i C_i + w\sum_j M_j D_j + z\sum_k O_k E_k$	(3)	Conte et al., (2008)
4	Hydrophilic - lipophilic balance (HLB)	Group contribution method (Davies' method)	$\mathrm{HLB} = 7 + \sum(\text{hydrophilic group members}) + \sum(\text{lipophilic group members})$	(4)	Guo et al., (2006)

The property models for target properties are very important to predict the accurate value of the target property for the pure component if the value of the property for the chemical is not available in the literature. Table 2 shows the property models in the pure component property models library to design the potential non-ionic surfactant for water in diesel emulsion fuel. The property model's library consists of the prediction model for critical micelle concentration, surface tension, hydrophilic-lipophilic balance and cloud point. These property models are obtained from literature. All the property models, Eq(1) – Eq(4) are derived from the group contribution method.

2.3 Step 3 – Design of surfactant

Step 3 is the design of the surfactant. Non-ionic surfactant database library will be the input for screening the surfactants. The database of chemical is screened by using the target properties, which are hydrophilic-lipophilic balance, critical micelle concentration, cloud point and surface tension. Chemicals that are not fulfilled the target boundaries will be eliminated.

2.4 Step 4 – Final Selection

Step 4 is the selection of the surfactant based on the surfactant cost. At this point, all the potential candidates are fulfilling the target properties set in step 1. To choose the best surfactant, the price of the chemical will be used as criteria. From this methodology, candidates of surfactant with a cheaper price will be selected

3. Discussion

3.1 Design of surfactants

The chemical database contains 197 non-ionic surfactants is used as initial database for selection of potential candidates of surfactant. The first property used for screening the candidates of non-ionic surfactants is hydrophilic-Lipophilic Balance. Only 19 candidates had fulfilled the target value of the HLB value. The experimental data of cloud point, Critical Micelle concentration and surface tension for all 19 candidates are collected or searched from literature. Only the missing data of the property value will be predicted using the models identified in Step 2.

In this study, surface tension for 19 chemicals is predicted using Eq(3). The values of cloud point and critical micelle concentration of the candidates are predicted using Eq(2) and Eq(1). The candidates are screened based on the cloud point properties.

As a result, 13 out of 19 candidates are eliminated because the value of their cloud point is lower than the target value that has been set in Step 1. The critical micelle concentration of the six remaining candidates is screened, and only one candidate is eliminated. All candidates satisfied the surface tension target values. The final five

candidates which had fulfilled all the target boundaries set remained. These five candidates will be evaluated in the final step before being chosen as the potential surfactants. The summary of this step is shown in Table 3, where the selected candidates were being matched against the targeted property namely the hydrophilic-lipophilic balance, cloud point, critical micelle concentration and surface tension. The table presented the number of candidates selected, eliminated and remained after being matched against the targeted property.

Table 3: Number of candidates screened and eliminated at each target property

No	Target property	Number of candidate	Number of eliminated candidate	Number of remaining candidate
1	Hydrophilic -lipophilic balance (HLB)	197	178	19
2	Cloud point (CP)	19	13	6
3	Critical Micelle Concentration (CMC)	6	1	5
4	Surface tension (σ)	5	0	5

3.2 Final Selection

From 197 candidates of non-ionic surfactants in chemical database library, five potential candidates had fulfilled all the target properties required in step 1. The final selection step is to select the best potential candidates by considering their price. For the final step, the price of the potential candidates is compared to the price of SPAN 80, which is USD 42 to 49 per kg. The price of the potential candidates is listed in Table 4. The price of the SPAN 80 and potential candidates is obtained from the Alibaba website.

Table 4: The properties and price of the potential surfactants and SPAN 80

No	Chemical	CAS No	HLB	Cloud point (°C)	-log CMC (mN/m)	Surface tension (mN/m)	Price (USD) (Alibaba.com, 2017)
1	Polyoxyethylene (2) lauryl ether	3055-93-4	6	10.03	4.366	38.18	103,600 / kg
2	Propylene glycol myristate	29059-24-3	3.9	49.86	4.21	33.6	291 / kg
3	Propylene glycol stearate	1323-39-3	3.4	35.85	5.946	33.6	1 - 2.9 / kg
4	Polyoxyethylene(2) stearyl ether	16057-43-5	4.9	14.5	6.5	33	2.8 - 3.5 / kg
5	Polyoxyethylene (2) cetyl ether	9004-95-9	5.7	164.86	6.34	33	10 - 100 / kg
6	SPAN 80(as reference)	1338-43-8	4.3	25	4.912	44.9	42 – 49 / kg

From Table 4, two chemicals are eliminated from the list, which are polyoxyethylene (2) lauryl ether and propylene glycol myristate, due to their higher price compared to SPAN 80. Polyoxyethylene (2) cetyl ether is eliminated since the price of the chemical is almost the same with the SPAN 80. Propylene glycol stearate and polyoxyethylene (2) stearyl ether are the two candidates that will be proposed as potential surfactants due to the price of the chemicals that are approximately 16 times cheaper than the SPAN 80. The properties of these chemicals are suitable to be proposed as non-ionic surfactant for water in diesel emulsion.

4. Conclusion

Using computer-aided molecular design approach to find potential surfactant for water in diesel emulsion fuel can be time and cost saving as compared to experimental method. This research found two potential non-ionic surfactants, which are propylene glycol stearate and polyoxyethylene (2) stearyl ether, as potential surfactants that have properties approachable to SPAN 80 but at cheaper price. These potential surfactants can be proposed for further research to identify the performance of these candidates as surfactant for water in diesel emulsion fuel.

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