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Characterization of the effectiveness of a hydrocarbon liquid solidifier

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ABSTRACT

Solidifiers are dry, granular hydrophobic polymers that form physical bonds with hydrocarbons by molecular interactions (hydrogen bonding, London forces), and are used to immobilize hydrocarbon spill propagation and dispersion. CIAgent© is a non-toxic, proprietary polymer blend listed as an "Oil Solidifier" on the EPA's National Contingency Plan Product Schedule for use on hydrocarbon spills in the navigable waterways of United States. CIAgent solidifies the liquid hydrocarbons through a rapid transformation into a cohesive rubber-like inert mass upon contact and retains the liquid for easier removal and disposal. The objective of this paper is to determine the effectiveness of the solidifier with a variety of hydrocarbon liquids that could be encountered in an oil spill scenario. The effectiveness of the solidifier was characterized in terms of the application rate, temperature change, solubility parameters and solidification time for a variety of hydrocarbon liquids (e. g., gasoline, diesel fuel, crude oil) that could be encountered by measuring the heat of solidification using a solution calorimeter. A thermogram was obtained and the heat of solidification was calculated using the temperature difference upon solidification. The temperature change and the degree of swelling in the solidifier were used to determine the solubility parameter of the solidifier (6.77 Hildebrands). The heat of solidification value was used to determine the ease and speed of the solidification of the hydrocarbon liquids. Solidification times ranged from 40 to 120 s for the liquids tested. The average application ratio in weight of solidifier to weight of hydrocarbon ranged was 3.35.

1. Introduction

Due to an ever-increasing number of spills into navigable waters and on land, a need exists for cleanup technologies that can recover oil from the oil-impacted environments to reduce adverse contaminations and long-term environmental impacts. Many agencies, including the U.S. Coast Guard, ASTM, and Canadian General Standards Board, have been actively engaged in developing standards for initial and long term oil spill remediation technologies. Use of solidifiers for oil spill remediation and cleanup has been investigated since the 1970's (Dahl et al., 1996; Goldstein et al., 1974). A solidifier is a dry granular hydrophobic material made up of polymers that transforms oil into a cohesive solidified mass with a minimal volumetric increase (El-Nemr, 2006). If enough high molecular weight polymer is utilized, the oil can be turned into a rubber-like substance. Firmly solidified material can be removed from the soil or water, leaving behind no trace of oil or sheen (PERF, 1994). Minimal documented use of solidifiers exists due to lack of practical application methods and testing under various conditions and environments (Walker and Kucklick, 1995). The interest in controlling and remediating oil spills, both environmentally and financially, has necessitated the detailed testing of solidifier materials for application to spills.

The effectiveness of a solidifier is defined as the amount required to solidify hydrocarbons under standard conditions. Some of the factors that influence the effectiveness include the type of solidifier used, the amount applied, and the solidification time. Laboratory effectiveness testing has been developed for solidifiers (Fingas and Stoodley, 1990). Solidifiers with average pick-up ratios of 10 percent by weight are available (PERF, 1992). Solidifiers make the treated hydrocarbon lighter thus improving the removal efficiency. It was also found that the amount of solidifier needed in an actual spill was larger than the amount used in laboratory testing (Fingas and Fieldhouse, 1993). The final consistency, effects of temperature, and effects of solidification time were determined for different solidifier-hydrocarbon ratios (Cardello, 1996). Walker and Michel, (1993) found that for some solidifiers, the weight of the product to hydrocarbon required to solidify a sweet crude oil was generally between 13 and 44 percent over a 30 min period. A commercial solidifier, Nochar A 650, solidified hydrocarbons into a solid with rubber like consistency that retained its shape and could be removed by mechanical means (Delaune et al., 1999). Seven pure polymers or cross-linked

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chemicals were tested with diesel fuel. Findings conclude that the gelled fuel continued to solidify over time with the ratio of solidification proportional to the mass of agent added (Rea, 1991). Crude oil samples were tested with 23 different solidifiers for their viscosity of the solidified product and the speed of the reaction (Ghalambor, 1996). He concluded that the effectiveness may depend on the level of oil asphaltenes, paraffin wax content, and sulfur content. Exxon tested the application of solidifier to oil until no visible oil remained on water surface. Most of the products solidified the oil into a firm mat; however, none of the solidifiers formed a firm solid mat with all the oils tested (Dahl et al., 1996). A new silicone solidifier was tested with light crude oil and the ratio needed to solidify was found to be 1:7, agent to oil. The solidified oil was found to contain about 85 percent by weight of the total mass (Pelletier and Sirion, 1999). Rosales and Suidan (2010) tested the effectiveness of the solidifier using a GC/MS and UV-VIS spectrophotometer. The solidifiers worked best with crude oil when the solidifier-oil ratio was 1:4. The solidification process was not selective in terms of the oil components.

Solubility parameters (δ_1 – solvent; δ_2 – polymer) have been found to aid in the selection of solvents and to predict the compatibility of polymers. They have also been applied to the study of polymer solubility and swelling, biological materials, barrier properties of polymers and surfaces (Hansen, 2000). The solubility parameter indicates the relative solvency behavior of a specific solvent. The basic assumption in the solubility parameter concept is that a correlation exists between the cohesive energy density and mutual solubility. Liquids with similar solubility parameters will be miscible, and the polymers will dissolve in solvents whose solubility parameters are similar. In cross-linked polymers the basic principle is "like seeds like" and the individual parts of the polymer chain can solvate to give a swollen gel. Maximum swelling would take place when the value of δ_2 is equal to δ_1 and the interaction parameter χ is at its minimum (Rodriguez, 2003). The energy of vaporization is a direct measure of the total cohesive energy holding the liquid's molecules together. The Hildebrand solubility parameter is defined as the square root of cohesive energy density (Hildebrand and Scott, 1962).

CIAgent is listed as an oil spill solidifier in the EPA's National Contingency Plan Product Schedule, to be used on oil spills in the navigable waterways of the United States. This proprietary polymer blend is designed specifically to solidify the hydrocarbon liquids into a removable mass with minimal volumetric increase and retains the liquid for easier removal. The dry, granular material immobilizes the hydrocarbon-based liquid spills by coagulating and physically bonding with the liquid. The solidifier enables rapid containment with applicability on both land and water; the solidifier is non-toxic, non-hazardous, non-carcinogenic and non-leaching. When CIAgent contacts a hydrocarbon liquid, the liquid associates in the molecular network of the solidifier forming a cohesive rubber-like mass that can be easily removed in most clean up situations. The physical attraction between the CIAgent and the hydrocarbon is attributed to hydrogen bonding and London forces. The solidifier does not allow the captured liquid to escape, thus minimizing any residue or contamination. In addition, no water is captured in the process of solidifying the petroleum-based spill. CIAgent© is extremely stable and the toxicity of the material encapsulated is reduced considerably. The application rate, pick-up ratio, and speed of solidification varies with the viscosity of the liquid, type of hydrocarbon, the hydrocarbon volatility, and temperature. In order to solidify a hydrocarbon, a ratio of 1–4 (CIAgent to hydrocarbon liquid) is required. The solidifier material can be used as an intermediate in a downstream process such as asphalt modification, plastic and rubber production, and adhesive additives. The solidified material can also be disposed in a landfill as per the EPA regulations (CIAgent Solutions).

No consolidated studies have been published comparing the effectiveness of solidifiers on various petroleum oils and their application for spills. The objective of this paper is to determine the effectiveness of the solidifier with a variety of hydrocarbon liquids that could be encountered in an oil spill scenario. The heat released/absorbed during solidification is measured using a solution calorimeter. The ease of solidification between the solidifier and the test hydrocarbon liquid could be inferred from the heat of solidification values (Ghalambor, 1996). The effectiveness is defined in terms and temperature change, application rate, solidification time, and solubility parameters.

2. Experimental procedure

A Parr Instrument Solution Calorimeter (Model No. 6755) was used to characterize solidifier effectiveness with a variety of hydrocarbons. All measurements were made at room temperature and atmospheric pressure. A bench scale study was conducted to evaluate the optimum ratio of the solidifier to the hydrocarbon liquids. The same ratio was used under the same test conditions in the solution calorimeter to find the heat of solidification during the process. The experimental apparatus consisted of a glass Dewar in which the solidifier was loaded volumetrically. The hydrocarbon liquids were placed in a sealed glass rotating cell. Both the reactants are allowed to reach an initial thermal equilibrium. The reaction was started by depressing the push rod and emptying the contents of the cell into the Dewar flask; the system was allowed to attain a post-period equilibrium.

Each test in a solution calorimeter was divided into three distinct time periods: (1) a pre-period during which the solidifier and the hydrocarbon liquids were allowed to come to an initial thermal equilibrium; (2) a solidification period during which the reactants are combined and an enthalpy change occurs in the system; and (3) a post-period during which the reactants are allowed to attain a post period equilibrium. A temperature versus time plot showing the three distinct time periods was obtained from the calorimeter for various combinations of the solidifier and the hydrocarbon liquids, and the results were analyzed to obtain the heat of solidification. The excess solidifier was weighed to determine the required solidifier mass, m. The ΔT_c was calculated from the difference in the pre-period (T_i) and post-period (T_f) temperature as given by the Eq. (1) (Cazes, 2005)

$$\Delta T_c = T_f - T_i \tag{1}$$

To determine a more accurate net corrected temperature change (ΔT_c) it was necessary to interpolate a point on the thermogram at which the temperature reached 63 percent of its rise. This point was chosen because it represents two time constants of maximal temperature change and therefore allows for better mathematical characterization of the thermogram. The energy change Q (calories), was calculated by the product of the net corrected temperature change, ΔT_c (°C) and the energy equivalent of the calorimeter, e (calories per °C), calculated using a standardizing procedure.

$$Q = e\Delta T_c \tag{2}$$

The change in heat of solidification at the mean solidification temperature, ΔH_T, expressed in calories per gram was obtained from the energy change, Q and the solidifier mass, m. (Cazes, 2005).

$$\Delta H_T = -\frac{Q}{m} \tag{3}$$

The release and absorption of heat during the solidification process has implication as to how the solidifier applications should be conducted in oil spill scenarios.

For polymer solutions, the heat of solidification is the energy change involved in forming one contact between the solvent and solute units. From the temperature difference, the change in heat of solidification was calculated. Using the Hildebrand's regular solution theory, the value the solubility parameter of the solidifier was calculated using the equation

$$\frac{\Delta H_m}{V} = \varphi_1\varphi_2(\delta_1 - \delta_2)^2 \tag{4}$$

where ϕ_1 is the volume fractions of solvent, ϕ_2 is the volume fractions of solidifier, δ_1 is the solubility parameter of the solvent and δ_2 is the

solubility parameter of the solidifier. The solubility parameter values of the solvents are obtained from Hansen (2000).

3. Results and discussion

An optimum ratio of solidifier to hydrocarbon was evaluated in a bench scale study by determining the ratio with the highest removal of hydrocarbon liquids. A solidifier/hydrocarbon ration of 1:4 was used in the solution calorimeter to determine the heat of solidification. Sixteen hydrocarbons were tested, including gasoline, crude oil, diesel, mineral oil, aviation fuels, and motor oil.

Solidifier temperature change occurs when the solidifier associates with the hydrocarbon. Figure 1 shows a temperature versus time plot for gasoline. The solidifier and gasoline were allowed to attain a pre-period equilibrium and brought close by depressing the push rod of the calorimeter. When solidification began, the temperature of the hydrocarbon dropped and then reached a post-period thermal equilibrium with its surroundings. The drop in temperature is calibrated from the difference in pre-period and post-period solidification temperatures. The drop in temperature is then correlated to the heat of solidification. This value indicates the speed of the reaction and the integrity of the byproduct.

Both endothermic and exothermic responses were observed during the measurements in the solution calorimeter. The polymer molecules and hydrocarbon liquids reconfigure to form closer physical bonds, requiring energy from the surrounding, resulting in a reduction in temperature (endothermic response) as shown in Figure 2. Mineral oil, gasoline, crudes and biodiesel also exhibited an endothermic response. Crude oil and gasoline have a greater association with the polymer and exhibit a greater temperature change. An exothermic response was observed when the solidifier was tested with solvents like diesel,

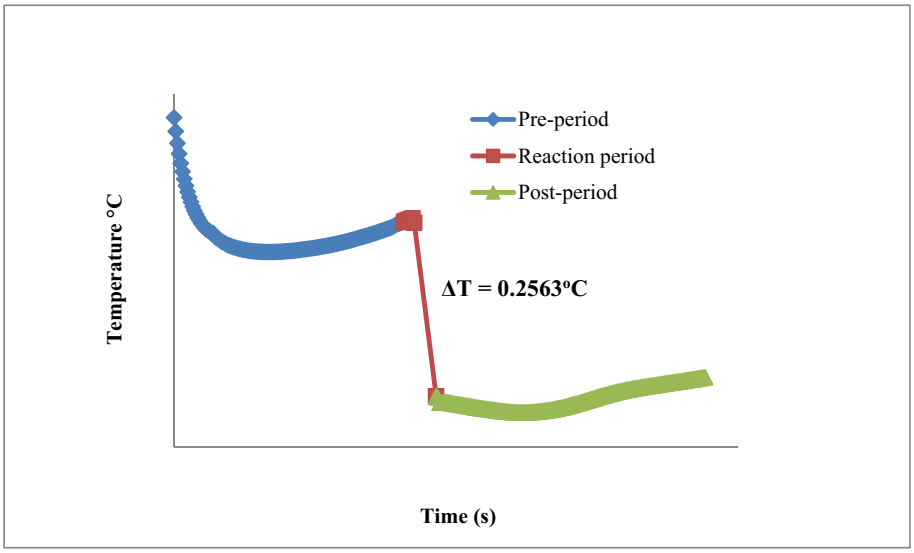

Figure 1. Temperature versus time for gasoline.

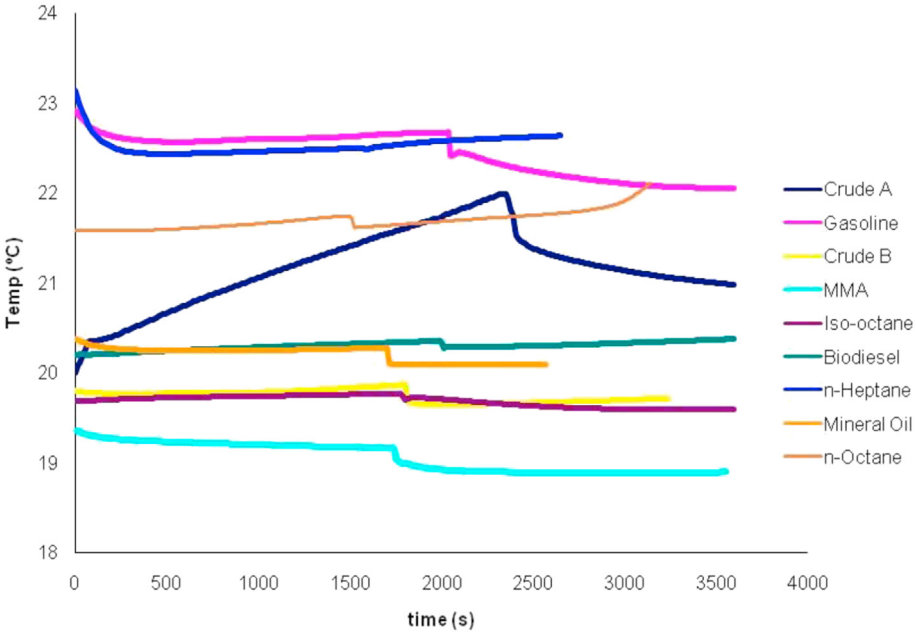

Figure 2. Temperature versus time for endothermic responses.

kerosene, motor oil, JP-4, JP-5, and JP-8. In these hydrocarbon liquids, the polymer molecules are freed from solid associations, thereby releasing energy. The energy from this relaxation exceeds the energy needed for the polymer and solvent to associate, resulting in a slight exothermicity that is observed in Figure 3. Most of the hydrocarbons, like JP-4, JP-5 and JP-8, are hydrocarbon blends with higher density. It should be noted that no chemical reaction occurs between the hydrocarbon and the solidifier.

Figures 4 and 5 illustrate the temperature change and change in heat of solidification values for the various hydrocarbons tested. The change in temperature was calculated from the calibrated pre-period and post-period values. The ΔT was the greatest for crude oils, gasoline, MMA and mineral oil. The change in heat of solidification indicates the ease with which the solidifier solidifies the hydrocarbon liquids. Higher values of the ΔH_s indicate a faster solidification and a better integrity of the solidified product. The integrity of the solidified product plays an important role in removal and disposal methods. Even though the solidifier showed both positive and negative ΔH_s responses, it was able to solidify all tested hydrocarbons (see Figure 6).

Application rates are used to assess the performance of the solidifier. The solidifier was applied to the hydrocarbon liquids until no visible hydrocarbon remained on the water surface. Application ratio is given by the grams of hydrocarbon per grams of the solidifier.

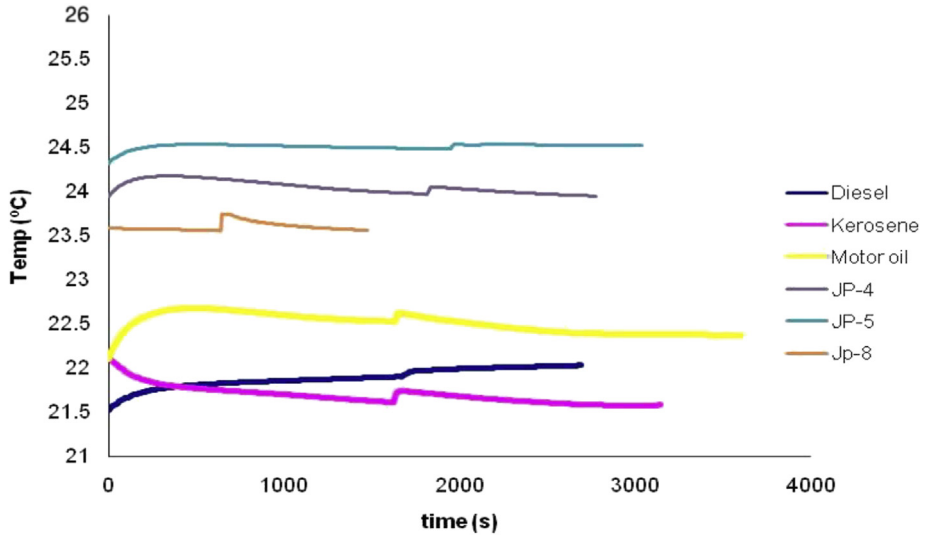

Figure 3. Temperature-time for exothermic response.

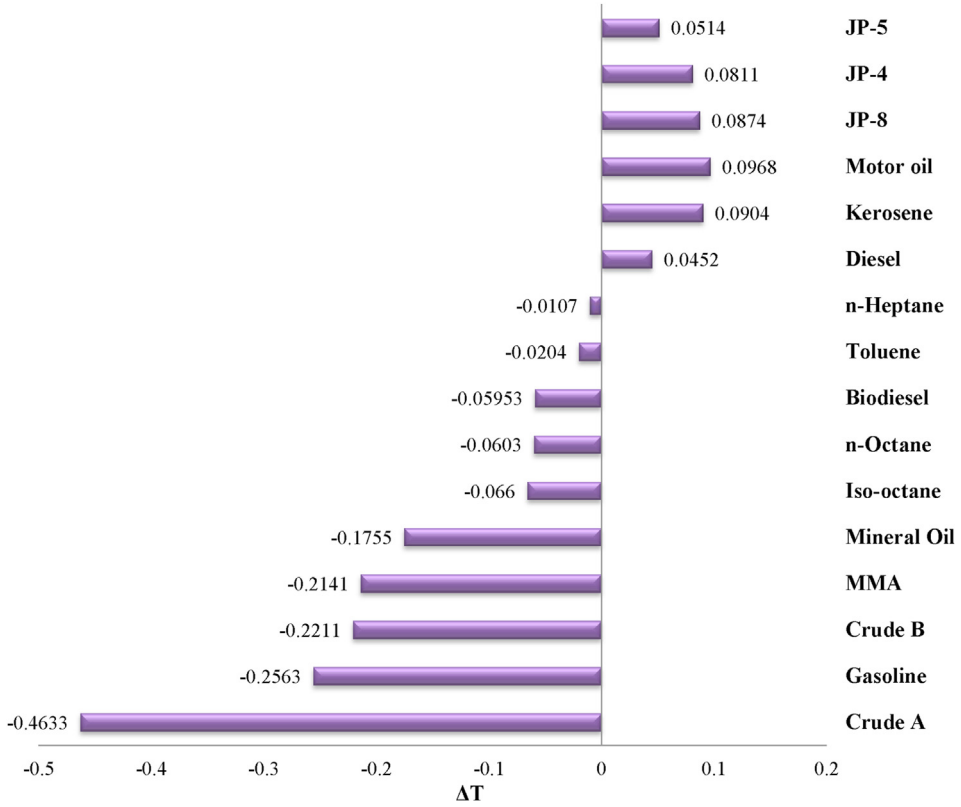

Figure 4. Temperature change for the hydrocarbon liquids.

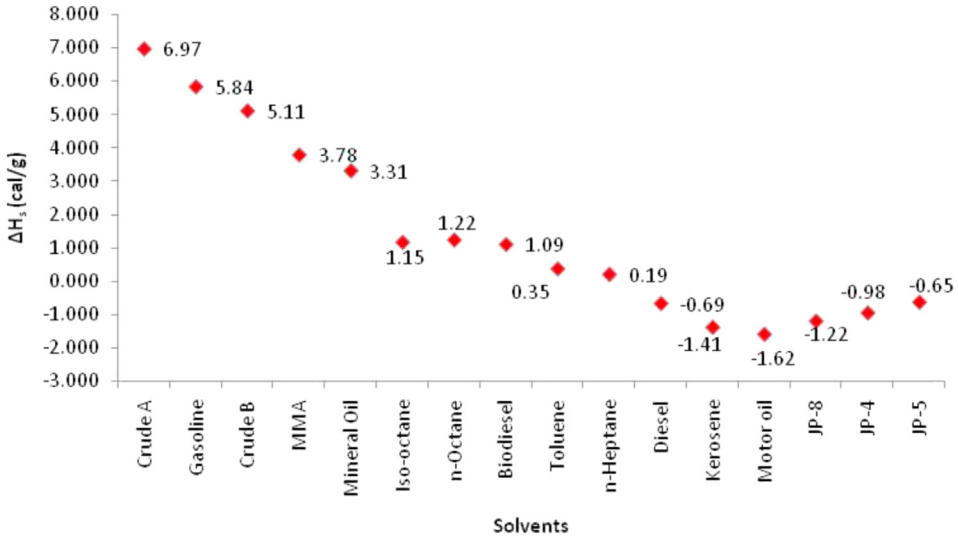

Figure 5. Heat of solidification for hydrocarbon liquids.

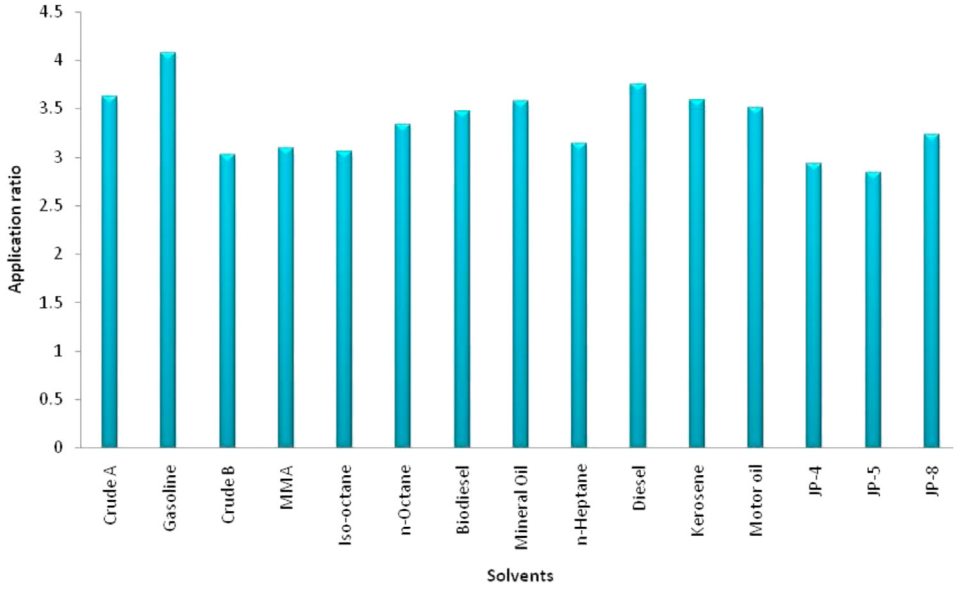

Figure 6. Application ratio of the solidifier.

The average application ratio was found to be 3.35 g of hydrocarbon per gram of solidifier on a laboratory basis. The application rate was 30.2 percent by weight of the hydrocarbon liquid to be recovered, falling within the range of recommended application rates (10–50 percent). Higher application rates may be used in practice as solidification is affected by the viscosity of the hydrocarbon liquid, temperature and the amount of volatiles present. The application rate does have implications on the amount of solidifier that has to be applied in case of an oil spill scenario.

The solidifier effectiveness also depends on the solidification time. CIAgent solidifies the hydrocarbon liquids in less than two minutes, as shown in the Figure 7; solidification increased with time. Time for complete solidification was between 1-2 h, making the solidified product firmer. Faster solidification boosts the performance of the barrier properties of the solidifier.

Solubility parameters were calculated using Eq. (4). Figure 8 shows the calculated solubility parameter of CIAgent with the various solvents tested. The solubility parameter of CIAgent was found to be 6.774 ± 0.39 Hildebrands with a 95 percent confidence interval. The coefficient of variation was 0.0576 indicating that the data is consistent. Hence CIAgent should be able to solidify hydrocarbon liquids with solubility parameters between 5 to 10 Hildebrands.

The solidifier was allowed to swell in a series of solvents of known solubility parameter. After the swelling was complete, each sample was reweighed and the weights and the specific volumes of polymer and solvent were used to calculate the swelling ratio, which is the ratio of the swollen volume to the dry volume. This is expressed by the following equation (Hamurcu, 1993)

$$Q = 1 + \left(\frac{W_2}{W_1 - 1}\right)\frac{\rho_2}{\rho_1} \tag{5}$$

where Q = the equilibrium swelling ratio; W_1 = weight of the network before swelling; W_2 = weight of the network after swelling; ρ_1 = density of the solvent; and ρ_2 = density of the polymer.

The highest degree of swelling was obtained by using the best solvent for the polymer. From Figure 9, it was estimated that the highest degree of swelling is obtained for gasoline with a swelling ratio of 6.785 in the solidifier, which is taken as Q_{max} and used to calculate the solubility parameter from the swelling measurements.

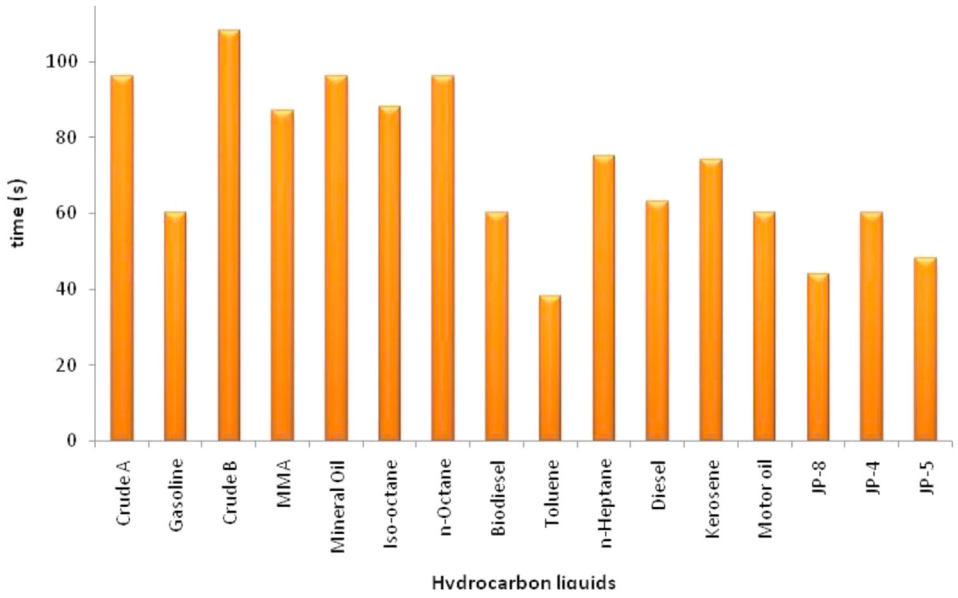

Figure 7. Solidification time of CIAgent with the hydrocarbon liquids.

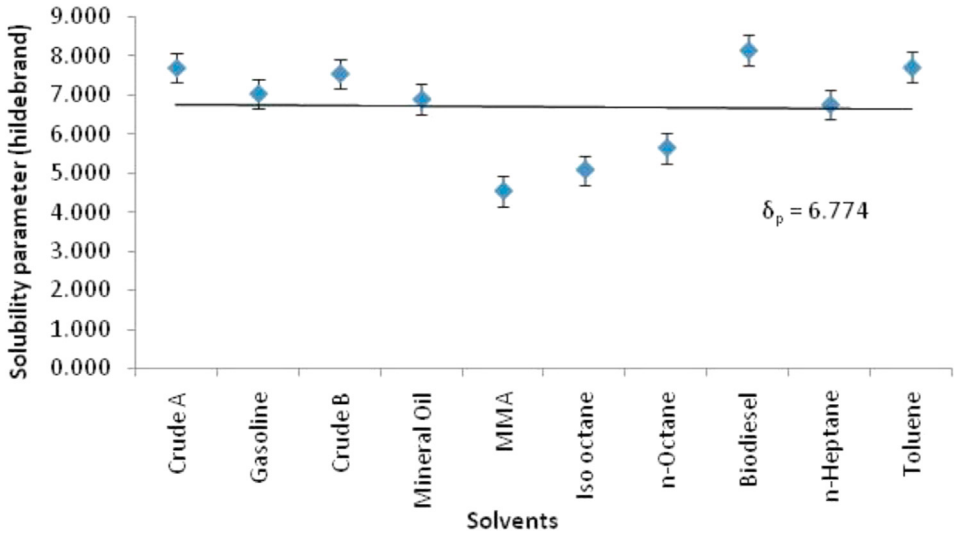

Figure 8. Solubility parameter determination of CIAgent©.

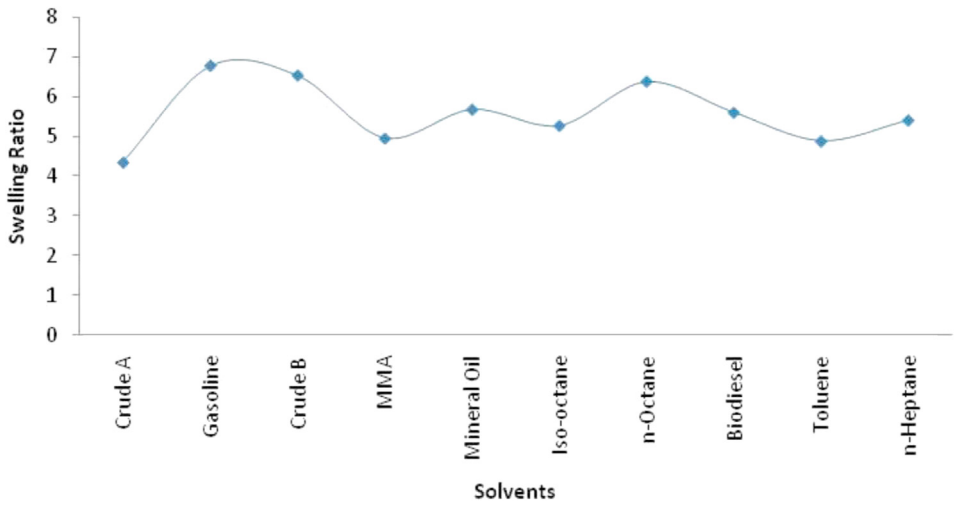

Figure 9. Swelling ratio of the solvents in CIAgent©.

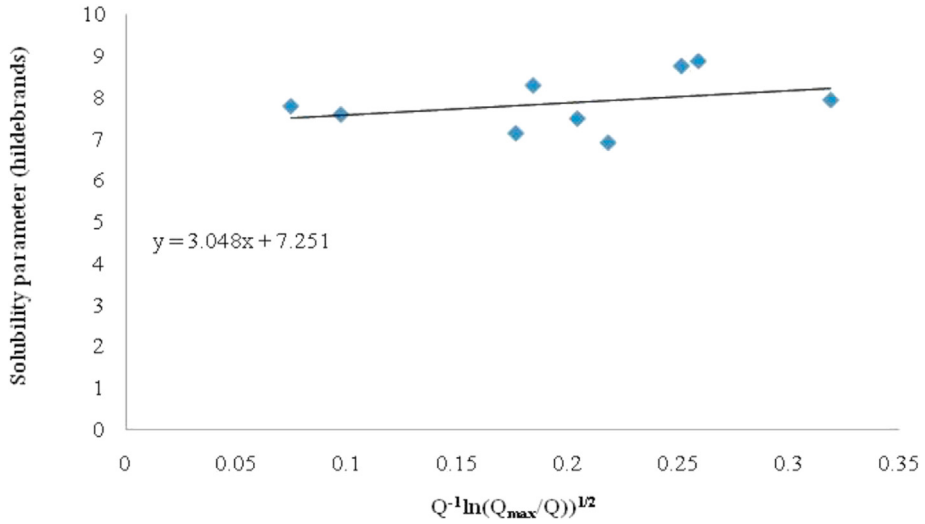

Figure 10. Solubility parameter determination from swelling measurements.

A method based on the evaluation of maximum swelling in a series of solvents of known solubility parameters was used. The solubility of a solidifier in any solvent depends on the square of the difference between their solubility parameter values. This value should be as small as possible for good solubility of a solidifier in any solvent. The following relation was used for this purpose (Gee, 1943; Gee, 1946):

$$\frac{Q}{Q_{max}} = \exp[-aQ(\delta_1 - \delta_2)]^2 \quad (6)$$

This equation is rearranged as

$$\left[\frac{1}{Q}\ln\left(\frac{Q}{Q_{max}}\right)\right]^{0.5} = \alpha^{0.5}\left(\delta_1 - \delta_2\right) \quad (7)$$

A plot of $\left[\frac{1}{Q}\ln\left(\frac{Q}{Q_{max}}\right)\right]^{0.5}$ versus the solubility parameters of the hydrocarbon liquids will produce a linear relationship where $\alpha^{1/2}$ and δ_2 can be calculated from the slope and the intercept. Figure 10 illustrates the plot of left hand side of Eq. (7) versus the solubility parameter of the various solvents used. From the plot, the solubility parameter was found to be 7.251 Hildebrands and the value of $\alpha = 0.108$ cm^3/cal using regression analysis. Flory predicted solubility parameters only for those that have a positive heat of solidification; hence no determination of solubility parameter and interaction parameter was attempted for hydrocarbons with a negative heat of solidification.

4. Conclusions

The effectiveness of CIAgent was characterized with a variety of hydrocarbon liquids that could be encountered in an oil spill scenario based on the temperature change, weight ratio of the solidifier to hydrocarbon liquids, solidification time and solubility parameters. A thermogram was obtained from the solution calorimeter and the heat of solidification was determined. These values indicate the speed of solidification and the integrity of the solidified product. A high integrity solidified product is preferred as it is more stable and less likely to break down during pick up and disposal. Crude oil and gasoline were found to have the highest heat of solidification with CIAgent. The average application ratio of solidifier to the hydrocarbon liquids was 3.34 g of hydrocarbon per gram of solidifier (in laboratory). The application rate was 30 percent by weight of the hydrocarbon liquid to be recovered, within the recommended range. The initial association of solidifier with the hydrocarbon liquids was found to be less than 2 min for most of the hydrocarbons tested. Solidification of the hydrocarbon liquids increased with time. Complete solidification was achieved between 1-2 h. The final consistency of the solidified product was rubber-like for most of the hydrocarbon liquids tested. The solubility parameter was determined by two methods using the heat of solidification and swelling ratio. From the heats of solidification values obtained using a solution calorimeter, the solubility parameter of CIAgent was calculated to be 6.776 ± 0.39 Hildebrands with a 95% confidence interval. The solubility parameter was also calculated from the swelling measurements. It was found that CIAgent had the maximum swelling in gasoline. From the plots, the solubility parameter of the solidifier was found to be 7.251 Hildebrands. The solidifier should be able to solidify hydrocarbon liquids whose solubility parameter range between 5 and 10 Hildebrands. The results presented in this work will provide insight and direction for the use of polymeric solidifiers for industrial clean-up efforts, as well as direction for development of new solidifying materials with applications targeted to specific materials.

Declarations

Author contribution statement

Jola J. Solomon: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Alan M. Hanley: Analyzed and interpreted the data; Wrote the paper.

Thomas R. Hanley: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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