Polysaccharides from *Tamarindus indica* L. as natural kinetic hydrates inhibitor at high subcooling environment

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Received: 28 October 2021 / Accepted: 20 February 2022 / Published online: 11 March 2022 © The Author(s) 2022

Abstract

In an offshore system, hydrocarbon fluids are produced at deeper depths in the oceans, and extended pipelines delivering fluids over long distances are common. Subsequently, these practices increase the tendency of unprocessed water-containing hydrocarbon fluid to be exposed to lower temperatures and higher pressures conditions where hydrate formation is favourable. One of the solutions to resolve this problem is by introducing hydrate inhibitors preferably low dosage hydrate inhibitors (LDHIs). The more versatile LDHIs; Kinetic Hydrate Inhibitors (KHIs) could further be optimised in cost and its biodegradation properties. The current study used an ionic, neutral, hydrophilic, mucoadhesive and highly branched *Tamarindus indica* L. polysaccharide (TSP). TSP as a new natural kinetic hydrate inhibitor due to its high methoxyl content. In this study, the polysaccharides were extracted using water-based extraction method which resulted in 61.3% yield. The performance of TSP in delaying the clathrate hydrates formation was evaluated based on the induction time recorded from the thermogram generated by a high pressure micro-differential scanning calorimeter device (HP-μDSC) at pressure of 5 MPa with subcooling degree of 17.3 °C. Three TSP concentrations (0.10 wt%, 0.25 wt%, and 0.50 wt%) were tested to determine the optimal concentration used to increase the delay time at the prescribed conditions while comparing it to a condition when there is no addition of TSP. The outcomes shows that TSP is able to delay hydrates formation at high degree of subcooling. The TSP works well at low concentration at high degree of subcooling while remain relatively economical and biodegradable.

Keywords Kinetic hydrates inhibitor · Biopolymer · Tamarind seed polysaccharides · High degree of subcooling · Induction time

Introduction

In general, hydrate inhibitors can be categorised into two categories: low dosage hydrate inhibitors (LDHIs) and thermodynamic hydrate inhibitors (THIs). In a recent case, LDHIs such as kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs) are widely used to control gas hydrate formation due to its lower cost and better performance relatively to THIs. In fact, the application of THIs has become difficult to manage due to its high injection volumes requirement especially in offshore and remote region (Fu et al. 2001; Shahnazar et al. 2018). Contrarily, LDHIs used lower concentrations, often around 0.3–0.5 mass % as compared to the conventional THIs that used 10–60 mass % (Arjmandi et al. 2005; Shahnazar et al. 2018). The inhibitory mechanisms of the two main groups of hydrates inhibitors stated before can be differentiated. Firstly, THIs inhibit by shifting the phase boundary of the hydrate through injecting high concentration of chemical inhibitors such as methanol (MeOH) and monoethylene Glycol (MEG). These inhibitors create an intramolecular interaction energy, disrupting the thermodynamic equilibrium line between water and gas molecules (Harooni and Ali 2017). However, THIs require significant volume of MeOH or MEG to achieve effective dosage for inhibition compared to LDHIs (Carroll 2020).
resulting in increased environmental pollution, storage and safety difficulties, as well as being less cost-effective at higher water cuts (Fu et al. 2001; Shahnazar et al. 2018).

As a result, KHI, a polymer-based chemical, has emerged as a practical alternative to THI because it only requires a small dose in the multiphase to effectively inhibit hydrates. KHI is composed of water-soluble polymers that interfere with the development properties of the hydrate-prone region and delay hydrate nucleation within the timeframe of water residence (Erfani et al. 2013). It has a high absorbance to the polar surfaces of hydrate crystals (water molecules), which inhibits water molecules from interacting with gas molecules by forming new hydrogen bond with the KHIs. The most representable commercial KHIs are Poly (N-vinyl pyrrolidone) (PVP), poly (N-vinylcaprolactam) (PVCap), and N-methyl-N-vinylacetamide (Xu et al. 2016). The subcooling restrictions and time constraints on regulating hydrate formation are its limitations (Ke and Kelland 2016; Kelland et al. 2000; Shahnazar et al. 2018). Commonly, KHIs is generally implemented in the industry since it is considerably less expensive than THIs. However, there is a potential for further development. In consideration of commercial KHIs possessing low biodegradation properties, many researchers are looking for potential biodegradable polymers that can maintain or produce better inhibition properties to substitute the current KHIs (Kelland 2018; Xu et al. 2016). Proposal of new sources of natural polymer as innovative kinetic hydrate inhibitor should be investigated and tested. Amongst this natural polymer are green hydrate inhibitors which comes from biocomponent of organic sources.

Green hydrates inhibitors have recently been presented as a new inhibitor that can dramatically cut the overall OPEX cost of hydrocarbon production while also reducing the environmental impact of chemical pollution. According to current studies, antifreeze proteins (AFP) or antifreeze glycoproteins (AFGP) are one of the patented green inhibitors (Xu et al. 2010). In 2010, the use of AFP was reported to be successful in inhibiting propane hydrates. In terms of delaying the nucleation process, AFP derived from fish outperformed the best commercial KHI polymers as Kelland (2018) informed researchers that the best readily biodegradable polymers studied has shown a poorer KHI performance than the benchmark PVCap.

The suggested polysaccharides can be obtained from organic waste and statistically, using Malaysia as an example, the projected waste generation rates for Malaysia for 2010–2020 is about 4.3% per annum where the largest contributor for solid waste comes from organic waste (include agriculture waste) that would be approximately 45% (Agamuthu and Victor 2011). If industries could utilise those high amounts of waste for other application, reduction of waste would be significant. These efforts are parallel with extended producer responsibility (EPR) which are becoming more popular globally (Sakai et al. 2011). It is in the industries best interest to find greener alternative to not only for reducing waste but to reduce pollution. Additionally, this effort also overlaps with creating a Circular Economy (CE) which is the development model that aims to reduce negative output from human activities by applying the “3 R’s”; Reduce, Reuse, and Recycle (Icibaci 2019; Scarpellini et al. 2019). Developing a CE would help to develop the industries and company sustainability plan, re-using waste as a material for production thus reduce production cost and be another source of income (Muafi 2021; Vargas-Hernández and López 2021). Hence, developing KHIs from waste produced from agriculture could impact significantly on a company social, economic and environmental standing dependant on the agriculture product.

The optimal place for injection depends on the gas hydrate formation stages and the LDHIs used. Gas hydrate formation process can be summarised in three main stages. It begins with gas dissolution (unstable) through hydrate nucleation (metastable) to agglomeration (stable) stage. Gas hydrate is formed when the two mains’ elements, gas molecules are entrapped in water molecules that have formed a quasi-cavity by hydrogen bonding. These cavities combine to form labile clusters which agglomerate until the hydrate nuclei reaches its critical radius becoming a stable crystal (Tang et al. 2010). The KHIs are introduced in between the nucleation and agglomeration stage to interrupt the hydrates formation.

Attribute of the pectin extracted from citrus fruits as well as studies of its application as a natural kinetic hydrate inhibitor has been studied by a number of researchers (Rezzoug et al. 2008; Sayah et al. 2014; Xu et al. 2016) allowing researchers to investigate the correct properties. In
Comparison to traditional KHI, pectin inhibitor is projected to have a strong biodegradation characteristic. Different doses of pectin inhibitor and PVCap inhibitor were examined by assessing the induction time of methane hydrate formation using the crystal growth inhibition (CGI) technique. Study showed that modest dose of pectin inhibitor can lengthen the induction period up to 50 h, whereas PVCap only has an induction period of 10.6 h. It remains to be considerably effective (10 times better performance) after the pectin dosage was reduced by 66% of PVCap dosage (Xu et al. 2016).

The high efficiency was attributed to the presence of a large number of oxygen and hydroxyl active groups, which rapidly formed hydrogen bonds with water molecules, reducing water activity in the formation of hydrates even further. As illustrated in Fig. 1, the functional groups in pectin structure suggests it might be a suitable KHI.

The functional groups of tamarind seed polysaccharides were investigated in this study. Tamarind (Tamarind indica L.) Seed Polysaccharides (TSP) is a natural branching polysaccharide polymer in which polysaccharides make up 65% of the seed (Kaur et al. 2012). It is a mucoidhesive, ionic, neutral, hydrophilic, highly branched polysaccharide with a cellulose-like backbone and about 80% xylose and galactoxylose substitution at the glucan chain (Jana et al. 2013). TSP is composed of monomers that are made up of glucose, galactose, and xylose sugars in the ratio 2.80:2.25:1.00 (Goyal et al. 2007; Nayak et al. 2018). TSP has become a viable option for commercial pectin in Japan due to its excellent gel strength and heat stability, as well as its high methoxyl content (6.8–8.37%) (Yuguchi et al. 2004). Based on its water retention capacity or ability to absorb water, TSP was discovered to have a high swelling index. Tamarind xyloglucan possesses similar characteristic as most polysaccharides that it is still water-soluble even though its individual chains are not fully hydrated due to β (1 → 4) cellulose backbone promotes inter-chain interactions. However, a balanced hydrophobic and hydrophilic character has allowed it to form a colloidal dispersion in water solution (Picout et al. 2003). The physiochemical structure of TSP is illustrated in Fig. 2. Similar functional groups as pectin can be identified in TSP. Therefore, it is strongly believed that it has a potential as a natural kinetic hydrate inhibitor.

Nucleation of a hydrate phase is the main event used to measure the inhibition performance of KHI. It can be further classified into homogeneous nucleation or heterogeneous nucleation. A homogeneous nucleation is known as an ideal situation where a critical radius is created directly from the parent nucleus (Davies et al. 2009; Khurana et al. 2017) which is nearly impossible to occur in an offshore pipeline condition. Meanwhile, the heterogeneous nucleation is encountered in multiple phase transitions in the presence of existing impurities. To evaluate the inhibition performance of KHI, induction time of hydrate nucleation phase is the key element that is used to differentiate between a good and a bad KHI. The induction time is the period where the hydrate starts to experience cooling phase until the first appearance of hydrate crystals (Xu et al. 2016). However, the hydrate nucleation process is very stochastic in nature. Many researchers find it difficult to validate the induction time of KHI performance from laboratory experiment due to the large variations in experimental results for the proposed mechanism. Thus, statistical approach is employed to ensure the nucleation experiment undergoes multiple repetitions in order to generate reliable data base for nucleation tendency of a system. Traditional laboratory experiments proposed to evaluate the performance of KHI include flow loops, rocking-cells and high-pressure autoclaves tests (Mcnamee 2011). These methods require longer run time to achieve more viable data. As a result, the high-pressure micro-differential scanning calorimeter (HP-DSC) has established as a device for investigating the effect of hydrate nucleation on

Fig. 1 Pectin structural group (Vos 2008)
KHI performance that involves a significantly smaller sample volume (~1 mL or less) and has a reliable and accurate hydrate onset point detection (Ke and Kelland 2016). This paper aims to analyse the induction time of TSP inhibitor based on the thermogram generated by HP-μDSC device.

**Methods**

Tamarind (*Tamarind indica* L.) seed polysaccharides were carefully chosen from the local food product and the extraction procedures employed in this experiment is a combination of chemical extraction methods proposed by Chawanoraseset et al. (2016) and Kumar et al. (2011). The nucleation time are determined by using the HP-μDSC device after further analysis.

**Preparation and chemical properties of Tamarind (*Tamarind indica* L.) seed powder**

The seeds were washed up with distilled water after the pulse tissues were removed by hand. The seeds were then dried for 30 min at 100 °C before being left to cool to room temperature. To separate the brown skins, the seeds were lightly blended in a blender for 1–2 min. The kernel seeds without the brown peels were turn into powdered form with a blender. The powder was sieved to have a consistent size. The sieved TSP powder (20 g) was defatted by using hexane solvent and the defatted seed powder was collected.

TSP is made up of monomers that are made up of glucose, galactose, and xylose sugars in the ratio 2.80:2.25:1.00, respectively (Goyal et al. 2007; Nayak et al. 2018). TSP, a galactoxyloglucan with exceptional gel strength and heat stability as well as a high methoxyl content (6.8–8.37%), can be used in place of commercial pectin. Tamarind xyloglucan has a similar property to other polysaccharides in that it is still water soluble even when its individual chains are not fully hydrated, but it has been able to form a colloidal dispersion in aqueous solution due to a balanced hydrophobic and hydrophilic properties (Picout et al. 2003; Yamatoya et al. 2020).

**Tamarind seed polysaccharides (TSP) extraction**

Initially, 20 g of TSP powder was soaked for 24 h in 800 mL of distilled water. To ensure the release of mucilage into the distilled water, the mixture was cooked for 1 h at 100 °C and then set aside for 2 h. To remove all of the foreign materials, the solution was centrifuged at 6000 rpm for 20 min. The supernatant was separated from the rest of the mixture. For mucilage precipitation, an equal amount of acetone was added to the supernatant. The precipitate was collected using a stainless filter and dried for 4 h at 50 °C in an oven. The dried polymer was kept in a desiccator until it was needed again. The dry polymer was mixed with distilled water to make polysaccharides inhibitors at various concentrations. For its performance, TSP inhibitors were tested at concentrations of 0.10 wt%, 0.25 wt%, and 0.50 wt%.
Degree of methyl esterification (DME) of TSP

From the average spectra from the FTIR results, the DME = A1740/(A1740 + A1630) was calculated using a previously established method, where absorbance at 1630 cm\(^{-1}\) refers to the COO group and absorbance at 1740 cm\(^{-1}\) corresponds to the carbonyl group from both COOH and COOCH\(_3\), respectively (Chatjigakis et al. 1998; Gribaa et al. 2013; Manrique and Lajolo 2002). The A1630 value was calculated by taking the average of the A1628 and A1632 values. The Y-axis of the FTIR finding would be converted into absorbance from transmittance with the following equation:

\[
\text{Absorbance}(A) = \log \frac{1}{\text{Transmittance}(T)}
\]

This determination would help us in characterising the extracted TSP. For 50% and above DME, it would be considered as a high methoxylated polysaccharides (HMP) while below 50% are considered low methoxylated polysaccharides (LMP).

Water solubility determination and Fourier-transform infrared spectroscopy (FTIR) testing

Polysaccharides are economical and easy to obtain, but they are typically insoluble in water or have a high viscosity after dissolving in water, making them difficult to inject into a pipeline during use. It must either increase its water solubility or develop a new injection procedure (Wang et al. 2019). The solubility is related to the hydrophilic and hydrophobic chain present in the polymer. A hydrophilic dominant polymer would allow better solubilisation which indirectly relate to its inhibition mechanisms through adsorption. Hence, the solubility of TSP is important for it allows the TSP to mix with the multiphase fluid composing mainly of water and hydrocarbon. Therefore, the dried polysaccharides were subjected to a solubility test using distilled water as the solvent in two separate conditions: room temperature water and boiling water. Another test also conducted to identify and validate the presence of hydroxyl groups (OH) found in the natural polymer. Both the tamarind seeds powder before and after extraction FTIR results were documented. The result will be then compared to past FTIR results on polysaccharides.

HP-\(\mu\)DSC nucleation time determination

The thermal analysis of methane hydrate production was carried out in this work using a high pressure micro-differential scanning calorimeter (HP-\(\mu\)DSC) from Setaram Sensys Evo Tg-DSC 7. Heat flow thermograms and temperature vs. time were plotted. Onset and offset temperature of hydrate nucleation can also be determined. Hastelloy Cells S60/55999 were utilised to make a pair of gas-tight high-pressure cells. These cells can endure up to 40 MPa of pressure and are highly resistant to corrosive substances. The cell has a volume of 0.33 mL. This device’s operational temperature ranges from −45 to 120 °C, with a scanning rate of 0.001–2 °C/min.

When the voltage is delivered, two electrodes are linked to a Peltier element (semiconductor) to create a temperature difference. This application enables a small-scale medium-to-medium heat transfer procedure without the use of refrigerant fluid. In atmospheric pressure, cell gauge pressure is measured using a pressure gauge with an accuracy of ± 0.1 MPa. During the experiment, nitrogen gas is released to protect the HP cells against moisture condensation at low temperatures. The peak area was identified, the noise was normalised, and the offset temperature was detected using CalistoTM software. The peak identified will allow researchers to determine the induction time or the hydrates nucleation time. TSP concentrations evaluated in this study were 0 wt%, 0.10 wt%, 0.25 wt%, and 0.50 wt% thus total sample were 16 samples (including blank sample); each concentration has four samples. The hydrates nucleation was detected when the positive heat flow was observed. The time was averaged, and the induction can be deduced following these equations:

\[
\text{Nucleation time} = \text{Peak Onset Time} - \text{Equilibrium Time}
\]

where equilibrium time is:

\[
\text{Equilibrium Time} = (\text{Initial Temperature} - \text{Equilibrium Temperature}) \times (\text{Cooling Rate})
\]

The nucleation time of all the peaks were accounted for and averaged to obtain an average nucleation time for each run.

\[
\text{Average nucleation time} = (\text{NT}_1 + \text{NT}_2 + \cdots + \text{NT}_n)/n
\]

where NT refers to the nucleation time.

Experimental design

The experiment was done to identify if TSP can inhibit hydrate formation as a KHIs. The expected results from this experiment should be based on the induction time measurement calculated from the thermogram created by the calorimeter device. The induction time is defined as the time between the start of the cooling phase of methane hydrates
and the first appearance of the hydrates. Using McCain (1990) findings, the expected equilibrium temperature at the fix pressure of 5 MPa (725.189–725 psia) are approximately 6.1 °C (42.98 °F) thus the subcooling is 17 °C which is higher than the current commercial KHIs application which approximately at 10–12 °C subcooling (Del Villano et al. 2008). The equilibrium temperature will then be used to calculate the nucleation time as shown in Eq. (1) (Fig. 3).

In this experiment, a pressure of 5 MPa is proposed as a constant variable for the isothermal method that is used to measure the induction time (Ke and Kelland 2016). The pressure of 5 MPa was chosen since the methane hydrates will undoubtedly crystallise at this pressure. The crystallisation process of methane hydrates may be too fast for the calorimeter device to catch the heat flow if a greater pressure is utilised for this experiment. Concentration of polysaccharides at 0.10 wt%, 0.25 wt%, and 0.50 wt% will be compared to study varied concentration effects of inhibition performance on methane hydrates when the pressure is kept constant. Using a scanning rate of 1.2 °C/min, the methane gas will begin to cool from 22 to 10 °C, and then continue to drop from 10 to −11 °C with a scanning rate of 0.5 °C/min.

To guarantee complete hydrate crystallisation, the isothermal mode is used at −11 °C for around 15 h for the isothermal method allowing time for clear peak to form. The dissociation of the hydrates will be continued by heating at the same scanning rate (0.5 °C/min) until the temperature reaches 22 °C once more. Furthermore, for methane hydrates stimulation, it is strongly advised to employ a lower scanning rate during the heating and cooling procedure. This is because a lower scanning rate often equates to a higher level of accuracy. If the scanning rate is reduced, the thermogram will have a better resolution. To acquire more reliable results, a scanning rate as low as 0.5 °C/min is suggested in this experiment. The polysaccharide experiment results will be based on the induction time of methane hydrate formation utilizing a pure water system as a reference.

Result and discussion

TSP extraction yield

The brown peels from the kernel seeds were used to separate the tamarind seeds, which were then ground in a blender. For polysaccharides extraction, 20 g of powder was collected and purified in 800 mL of distilled water. The polysaccharides were subsequently precipitated with acetone as described by Chawananorasest et al. (2016) and Kumar et al. (2011), and the percentage yield was estimated using the dry weight obtained from TSP. The percentage yield of TSP recovered by this approach was 61.3% (w/w), which is higher than the 50% expected in the plan (Table 1). Based on the dried polymer developed in this experiment, the physical properties of polysaccharides were evaluated with the naked eye. It was a dried polymer that was white in colour and irregular in shape. The recovered polysaccharides were found to be odourless, hard, rough in texture, and brittle (Figs. 4 and 5).

TSP Degree of methyl esterification (DME) results

After converting the transmittance into absorbance, in Table 2; the DME is calculated which categorised TSP as a possible high methoxylated polymer. This suggests that the storage requirement is low temperature environment without

Table 1  TSP extraction results—(from the experiment conducted during this study)

| Dry weight (g) | Supernatant (mL) | Dried TSP (g) | Yield (%) |
|---------------|-----------------|---------------|-----------|
| 20            | 450             | 12.26         | 61.3      |
Water solubility test results

As polysaccharides usually have low solubility, the dried TSP were subjected to a solubility test using distilled water as the solvent in two separate conditions: room temperature water and boiling water. The dried polymer appears to be sparingly soluble in room temperature water but quickly solubilise in boiling water according to the investigation. The result indicates that TSP require solubilisation with boiling water to effectively inject into hydrate prone location. Solubilisation of TSP is closely related to KHI performance since efficient KHIs depends on the adsorption affinity of KHIs. Therefore, TSP efficiency can further improve by grafted by hydrophilic group improvement or the use of microcapsule technology to encapsulate.

Table 2 TSP degree of methyl esterification—(from the experiment conducted during this study)

| State                  | A1740 | A1630 | DME = A1740/(A1740 + A1630) |
|------------------------|-------|-------|-----------------------------|
| Before TSP extraction  | − 1.55| − 1.54| 0.50                        |
| After TSP extraction   | − 1.76| − 1.74| 0.50                        |
peaks at 1079.70 cm\(^{-1}\) and 1084.14 cm\(^{-1}\), respectively. The secondary OH bending was confirmed by peaks at 667.73 cm\(^{-1}\) and 759.48 cm\(^{-1}\), respectively (Figs. 6 and 7).

Based on the Table 3, it can be summarised that the extracted TSP has similar FTIR result comparative to other polysaccharides. When compared with Premalatha et al. (2017) results, an experiment that have include FTIR analysis of Tamarind, it shows similar results. The difference is acceptable and within expectation (below 5% differences) even when compared to other polysaccharides source.

**HP-\(\mu\)DSC results**

In this section, the heat flow and the nucleation time was recorded to help determine the presence of hydrate formation and evaluate the performance of TSP. Based on Xiao et al. (2010) suggestion, a maximum heat flow less than 10 mW symbolised hydrates formation whereas a maximum heat flow larger than 20 mW represented ice formation in their studies in ionic liquid inhibitor. As can be seen in the following graph, the heat flow did not exceed 10 mW, indicating that hydrate rather than ice was formed. This graph also illustrates the stochastic behaviour during hydrate formation; hence, multiple runs is conducted to ensure the induction time compared between concentrations are acceptable. However, in term of determining the hydrate formation occurring, it is enough by observing the peak as suggested by Xiao et al. (2010) (Fig. 8).

In Table 4, the data tabulated has shown that concentration at 0.25 wt% and above have significant increase in induction time whereas at 0.1 wt% has reduced induction time. This suggest that at 0.1 wt%, TSP acts more as a hydrate promoter than an inhibitor while 0.25 wt% and 0.5 wt% acts an inhibitor. A box-plot graph was constructed to

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**Fig. 6** IR-Spectrum of tamarin seed powder before extraction—(from the experiment conducted during this study)

**Fig. 7** IR-Spectrum of TSP extract—(from the experiment conducted during this study)
visualise the performance of TSP at varied concentration. At all the concentration, there shows inhibitory capability as the induction time increases significantly but 0.1 wt% has consistently shown that it behaves more as a promoter as most of its nucleation time is faster than at 0 wt%. The median and average results also fall below the median and

| FTIR Wavelength | Assignment |
|-----------------|------------|
| O–H            |
| CH₃            |
| C=O, aldehyde absorption |
| C–O–C cyclic ether groups stretching |

**Table 3** Comparison of FTIR wavelength (Chen et al. 2015; Kamil et al. 2014; Premalatha et al. 2017)

| FTIR Wavelength | Assignment |
|-----------------|------------|
| O–H            |
| CH₃            |
| C=O, aldehyde absorption |
| C–O–C cyclic ether groups stretching |

**Fig. 8** Heat flow graph of TSP in distilled water—(from the experiment conducted during this study)

**Table 4** Induction time of the tested concentration—(from the experiment conducted during this study)

| TSP concentration (wt%) | Time to reach equilibrium temperature (min) | Time (min) | Time (min) | Time (min) | Average induction time (Nucleation Time) | Difference in induction relative to 0 wt% |
|-------------------------|---------------------------------------------|------------|------------|------------|------------------------------------------|-----------------------------------------|
| 0                       | 10.56                                       | 68.85      | 161.32     | 70.41      | 123.56                                   | 106.035                                 |
| 0.10                    | 31.44                                       | 49.44      | 67.44      | 250.44     | 99.690                                   | − 6.345                                 |
| 0.25                    | 28.44                                       | 73.44      | 307.44     | 421.44     | 207.690                                  | 101.655                                 |
| 0.50                    | 35.94                                       | 284.94     | 319.44     | 481.44     | 280.440                                  | 174.405                                 |
average of the pure water (0 wt%) where TSP was not added. In terms of performance, 0.5 wt% has the best performance as it has a higher median and average induction time. Moving forward, excluding 0.1 wt% as a viable concentration, in terms of potential, TSP has a higher potential to have higher induction time (Fig. 9).

However, the minimum induction time remains to be similar for each concentration but due to the increase performance from increasing the TSP concentration, the range of induction time also increase thus increasing the level of uncertainties despite knowing their mean. This also suggests that TSP is economical as it requires lesser concentration. Further reducing logistical and storage issues in regard to hydrate prevention practice.

**Conclusion**

The findings on the performance TSP were investigated. The extracted TSP exceed initial expectation of 50%, in this research, researcher manage to extract 61.3% of TSP. Polysaccharides have high potential to inhibit hydrates by delaying the induction time longer with a lower concentration relatively, giving it an economic edge compared to the conventional kinetic inhibitor. TSP appears to be sparingly soluble in room temperature water but quickly solubilise in boiling water. This information helps operator to solubilise the polymer into higher temperature fluid when injecting, as the purpose is to prevent hydrate formation, the additional high temperature of fluid injected would contribute to the hydrate prevention. In term of effective TSP concentration, it is recommended to used 0.25 wt% and above to reliably mitigate hydrate formation.

The findings also confirm that organic sources that are considered waste have other applications. If proper infrastructure is in place globally. The waste generated from organic waste could be substantially reduce. In regard to TSP, the finding will hopefully open up discussion to other organic sources that have high waste generation i.e., Mango seed that are a major part of a mango fruit that are not utilised thus thrown away could be used for hydrate inhibition or other application. From another perspective, developing products or utilisation of waste as material for other application also fits with initiatives and policies that are becoming trending namely Circular Economy (CE) and Extended Producer Responsibility (EPR). Adding to this, company adopting this approach would gain competitive edge from cost reduction and partially becoming self-sustaining.

These findings showed the upper limit of the inhibition ability of TSP as the condition of the fluid is static which differ from on-site environment where the fluid is often in dynamic flow condition. Hence, experimentation that imitate the dynamic condition would give a more accurate representation of TSP ability as a KHIs. Comparative studies should also be done by future researchers to compare between other natural KHIs and agriculture sources. TSP may be a contender as the extracted polysaccharides from TSP has high waste to polysaccharides conversion rate (50–60%). Although these findings introduce *Tamarindus indica* L. as a new natural kinetic hydrate inhibitor, additional
comprehensive experimentation could be conducted to further solidified TSP as a viable KHI alternative.

Acknowledgements The authors would like to acknowledge Centralized Analytical Laboratory, Universiti Teknologi PETRONAS for the technical assistance with HP-μDSC.

Funding This research was funded by YAYASN UNIVERSITI TEKNOLOGI PETRONAS (YUTP), Grant numbers: 015-LC0160 and 015-LC0230.

Declarations

Conflict of interest The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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