

Article

# Experimental Investigation of Methane Hydrate Induction Time in the Presence of Cassava Peel as a Hydrate Inhibitor

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**Abstract:** The oil and gas industry faces numerous problems, from the exploration to the production phase. One of the most common problems faced by the industry is the formation of gas hydrates in the pipeline during the deep-water operation. The advancement of kinetic hydrate inhibitors (KHIs) has been rapid. However, as the natural degradation of conventional KHIs, such as polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap), is challenging, there is a need to develop environmental-friendly KHIs with enhanced biodegradability to improve possible environmental risks. Thus, green inhibitors have been developed as a new class of KHIs. Research for enhancement of green hydrate inhibitors, as an alternative for existing low dosage hydrate inhibitors (LDHIs), has increased. In this paper, the effect of induction time with presence of cassava peels on the formation of methane hydrate was studied and compared with commercialized inhibitor, PVP. The performance of cassava peels as a kinetic hydrate inhibitor was investigated using high pressure micro differential scanning calorimetry ( $\mu$ -DSC). For the induction time measurement, linear cooling ramps at a constant cooling rate of 0.5 K/min were used under isobaric conditions. Aqueous solutions of 0.5 wt % and 1.0 wt % of cassava peels were prepared and the induction time of methane hydrate formation in these solutions was measured at pressure ranges from 4.0 to 10.0 MPa. One of the characteristics to be a good kinetic inhibitor is the presence of hydroxyl functional group in inhibitors, which assist to form hydrogen bonds with water molecules, thus preventing hydrates formation. Fourier transform infrared (FTIR) analysis confirms the presence of hydroxyl groups in cassava peels with wavenumber value of  $3370.68\text{ cm}^{-1}$ . Cassava peel solution is observed to delay the induction times at all pressure settings and it is better at 1.0 wt % concentration. However, at lower pressures of 4 and 6 MPa, the performance is less effective when compared to a commercial inhibitor, PVP. At high pressures of 8 and 10 MPa, it can be seen that the performance is as effective as PVP. This research paper shows that cassava peels have high potential to be developed as a gas hydrate green kinetic inhibitor that can be applied for industry usage in the future.

**Keywords:** gas hydrates; kinetic inhibitor; flow assurance; cassava peels; induction time; high pressure micro-DS

## 1. Introduction

Gas hydrates are nonstoichiometric crystalline compounds that consist of host water and guest hydrocarbon molecules, such as methane, ethane, and propane. They form through hydrogen bonds with the water molecules, enclathrating guest molecules at high pressure and low temperature [1]. The appearance of gas hydrates is similar to an ice-like crystalline solid. The water molecule traps gaseous molecules such as methane, ethane, and carbon dioxide to form hydrates [1]. It is more common

in deep water operation due to the high pressure and low temperature conditions [2]. Gas hydrates can be categorized into three structures: structure I, structure II, and structure H. The structures are based on their water molecules and the gas molecules arrangement depending on the type of natural gas trapped inside the cavity.

Hydrate studies gained importance mainly for three reasons: (i) hydrate can be used as a natural resource [1,3], (ii) hydrates can be a geohazard [4], and (iii) hydrate dissociation can contribute to global warming [5]. Gas hydrate formation in transmission pipelines is a serious economic and safety problem for the oil and gas industry. Gas hydrates are being a nuisance, especially in the flow assurance of hydrocarbons. The presence of gas hydrates reduces significantly the flow efficiency of hydrocarbon. The biggest concern related to gas hydrates is the blockages they form in pipelines, blowout preventers, and transmission lines [1]. The blockages formed by gas hydrates will reduce the flow of hydrocarbon significantly and it will eventually affect the field production. The faultiness caused by hydrates in valves and in the heat exchangers mechanism will also cost a fortune to the company to compensate for the maintenance cost.

The most challenging and intriguing question regarding hydrate concerns how hydrates form, dissociate, and inhibit with time. Precise knowledge of kinetics of gas hydrate formation and applying the reliable models to remove hydrate formation is critical. Understanding the induction time of gas hydrate formation is useful in order to focus on the development of thermodynamic inhibitors (THIs) and kinetic hydrate inhibitors (KHIs) for the oil and gas industry. Induction time is time taken for crystal nuclei to form until the appearance of a detectable volume of hydrate phase [1].

Numerous studies have been done worldwide to prevent the gas hydrate formation. Inhibitors such as THIs, KHIs, and anti-agglomerates (AAs) have been designed to prevent or delay the formation of hydrates [6–9]. The conventional methods, such as depressurization, thermal heating, chemical injection, and mechanical cleaning via pigging the plugged site, were also introduced to rectify hydrate plugging [2,10]. Some of the drawbacks of these methods involve the massive quantities of injection required, the toxicity of the injection inhibitors, induced vaporization of liquid hydrocarbons, and incompatible method for sub-sea pipelines [11]. One of the conventional ways is to heat or insulate the plugged site of the pipeline, but this increases the potential of rupturing the pipelines [12]. The introduction of a low dosage hydrate inhibitor (LDHI) such as KHI managed to reduce the usage of inhibitors, as the concentration required by LDHI to be effective is around 0.25 to 1.0 wt %. Despite the low amount of usage, KHI still suffers from limitations, such as low subcooling, limited induction time, and expensive cost [13].

Sloan's group is among the earliest to synthesize and test polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap). PVP is a water-soluble polymer made from monomer N-pyrrolidone. It is commonly used in the medical field as the binder for pharmaceuticals tablets [14]. While it is soluble in water, it is also soluble in other solvents such as methanol and glycol. The polymer possesses hydroxyl and carbonyl end groups thanks to the higher molecular weight-type products being polymerized in, normally, hydrogen peroxide as the initiator [15]. The presence of hydroxyl group in PVP allows it to be a good KHI, as it can form a hydrogen bond with the hydrate to delay the growth and nucleation [16].

Research on natural polymer from natural agriculture waste is one of interest in order to explore the potential of these natural polymers to be an effective hydrate inhibitor [17]. This research focuses on the waste product of cassava, which is the peels, to explore the potential of cassava peels as KHI. Cassava is scientifically known as *Manihot Esculenta* Crantz, is one of the major sources of carbohydrates in tropical countries, after rice and maize. Global production of cassava left the peel as abundant natural waste. These lignocellulose wastes produced during cassava processing have been found to have high potential to be an effective natural-based kinetic hydrate inhibitor (KHI). World annual cassava production has increased by approximately 100 million tons (1 ton = 1000 kg) since 2000. This is driven by demand for cassava food products in Africa and for dried cassava and starch for use in livestock feed in Asia [18]. However, the growing industry of cassava products contributes to a large

amount of waste. In Nigeria, 2.96 million metric tons of peels are produced annually and they are left to rot. The foul odors and poisonous air may be inhaled by man and animals resulting in diseases and infections [19]. Cassava starch processing produces a large number of solid wastes, which is the cassava peels, and direct discharge of these solid wastes causes environmental problems. Utilization of cassava peels as a precursor for activated carbon with a high surface area has been demonstrated by various researchers [20,21]. The effect of cassava peels to be a kinetic hydrate inhibition has not been reported previously in the literature. However, Xu has reported, in his journal paper, natural material, which is pectin, that widely exists in ripe fruits and certain vegetables, could tremendously improve induction time of methane hydrate nucleation and retard hydrate crystal growth [22]. The induction time extended ten times than the commercial hydrate inhibitor. It can solve one of the most vexing problems of the gas industry, which are hydrate blockages during transportation in the pipeline [22]. Chitosan, that was derived from shrimp cells, were used in the hydrate formation experiments in order to evaluate their performance as a kinetic inhibitor and chitosan was reported to be able to delay the onset of nucleation [23]. Cassava peels contain hydroxyl groups, whereby the hydroxyl groups are significant in the KHI working mechanism. The hydroxyl groups will form hydrogen bonds with the water molecules, thus preventing the entrapment of gas molecules. This action will delay the formation of hydrates for a certain period of time until it exceeds the residence time in the hydrate formation zone [21,24]. In this study, the induction time of hydrate formation at different concentrations of cassava peels and comparison with PVP has been investigated. The characterization of cassava peels is experimentally measured using Fourier transform infrared FTIR to confirm the presence of hydroxyls group.

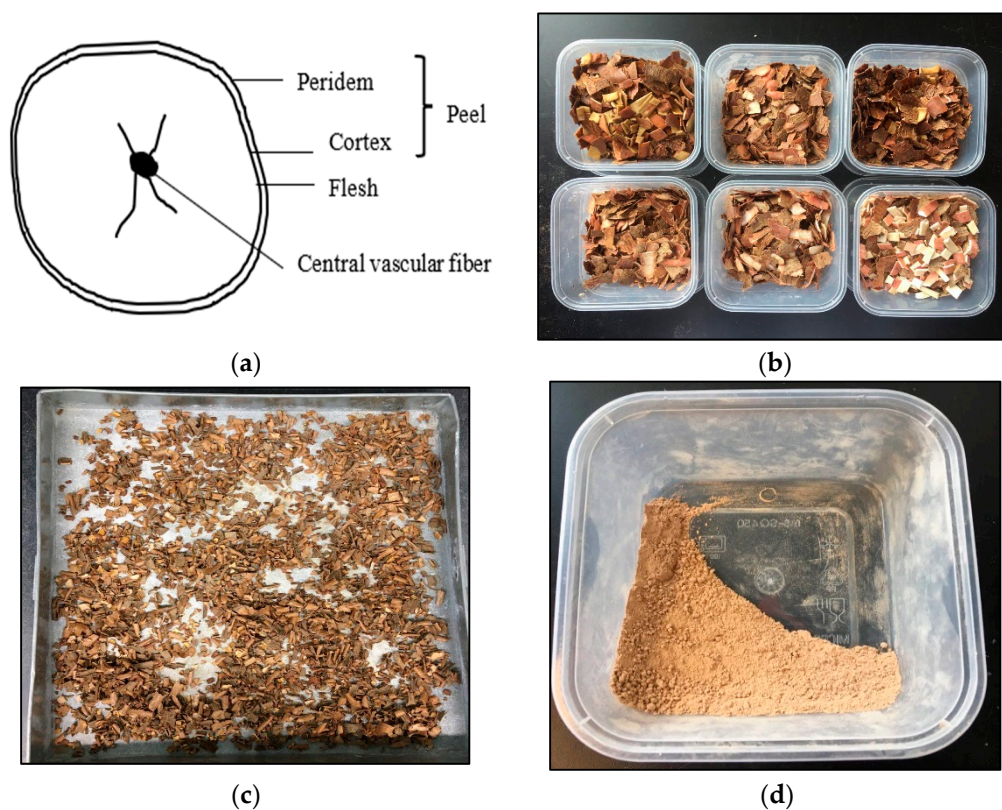
## 2. Materials and Methods

Cassava peels and PVP used in this work were purchased from a market in Malaysia and Sigma-Aldrich, respectively. Methane gas with a purity of 99.9 mol % was supplied by Air Products and mixed with deionized water to form methane hydrates. Deionized water was used to prepare inhibitor solution to the desired concentration.

### 2.1. Cassava Peels Preparation

The research focuses on using the waste product of cassava, cassava peels. There are two skin layers of cassava; cortex and periderm, as shown in Figure 1. Both layers were used for the sample preparation. Cassavas were first peeled off to obtain the cortex and periderm, as shown in Figure 2, before being washed repeatedly for cleaning purpose. The cassava peels were then soaked in deionized water for 24 h for further cleaning, and then dried in the oven at 60 °C for 24 h to remove moisture content [25], as shown in Figure 3. After drying process, cassava peels were ground using a mortar grinder before being sieved using a strainer with 100 mesh (150 µm), as observed in Figure 4. Cassava peels powder was then dissolved in deionized water and stirred continuously for 2 h using a magnetic stirrer at 200 rpm to form the solution. A solubility test was carried out to identify the optimum amount of cassava peels powder that was able to dissolve in deionized water to produce cassava peels solution using the Kainuma method [26]. First, 0.5 g of cassava peels powder was added into 10 mL deionized water and heated at 60 °C for 30 min without mixing. The sample was then centrifuged at 1600 rpm for 10 min. The undissolved solute was filtered using filter paper and weighed. The supernatant was separated (5 mL), dried, weighed, and calculated using the following solubility equation:

$$\% \text{ solubility} = \frac{\text{weight of mixture (g)} - \text{weight of solute left (g)}}{\text{weight of mixture (g)}} \times 100\%$$



**Figure 1.** (a) Cross section of cassava; (b) Cassava peels before being dried; (c) Cassava peels after being dried; (d) Powdered cassava peels.

### 2.2. Hydroxyl Group Identification Using FTIR

Cassava peels powder was analyzed using FTIR spectroscopy analysis to determine the presence of hydroxyl groups. Hydroxyl groups were significant in inhibitors as they form hydrogen bonds with water molecules, thus inhibiting growth. The basic principle behind FTIR analysis is the interpretation of absorption and reflection of infrared light when the signal is in contact with the sample. The results were represented in a plot of transmittance percentage against wave number. The range of wave numbers covered by this apparatus is between 7800 to 350  $\text{cm}^{-1}$ .

### 2.3. Morphology and Composition Identification Using SEM

Scanning electron microscopy (SEM) was conducted to identify the morphology and chemical composition of cassava peels powder. This helped in identifying the toxicity and compatibility when used in reservoir environment. The apparatus functioned through the detection of electrons that were deflected from the sample, which generated magnified images.

### 2.4. Measurement of Induction Time Using $\mu$ -DSC

The experiment was conducted using SETARAM micro differential scanning calorimeter ( $\mu$ -DSC). Methane gas and deionized water were injected into the apparatus to form hydrate. All solutions (CP and PVP) were tested at four pressure points: 4, 6, 8, and 10 MPa. The cooling rate was set to 0.5 K/min and heating rate was set to 1 K/min. The experiment was conducted in a temperature range of  $-20$  to  $20$  °C. Blank samples containing deionized water and methane gas were also tested in the  $\mu$ -DSC, to be a point of reference to compare with the inhibitor effectiveness against other solutions. The results obtained from the  $\mu$ -DSC were plotted on a graph of heat flow against time, and peaks could be observed, as shown in Figure 2; the smaller peak represents an exothermic process signifying hydrate formation while the bigger peak represents ice formation. For an endothermic process, the smaller

peak indicates hydrate dissociation and the bigger peak represents ice dissociation. The induction time of hydrate can be determined from the onset time of the first peak.

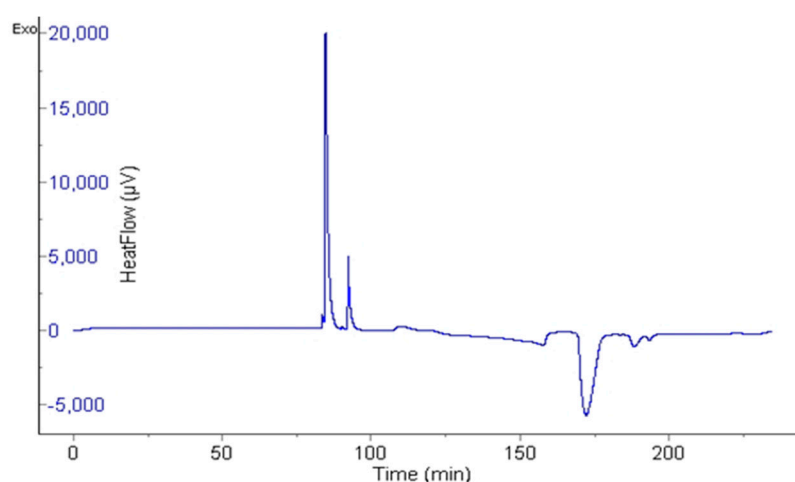


Figure 2.  $\mu$ -DSC curve for hydrate formation and dissociation.

### 3. Results and Discussion

The potential of cassava peels solution to inhibit gas hydrate was tested and compared to PVP, as it was commonly used as a commercial KHI in industry. The high presence of hydroxyl (OH) groups in cassava peels indicate the potential to be a kinetic hydrate inhibitor and thus has gained interest from various researchers. Cassava peels were tested for its inhibitory properties of methane hydrates due to its biodegradability and biocompatibility, with bottom hole fluids.

#### 3.1. Hydroxyl Group Identification Using FTIR

From FTIR analysis, the plot of transmittance percentage against wave number was obtained and interpreted. Several peaks could be found in reference to Figure 3. The presence of hydroxyl (OH) groups could be identified from the spectrum and would, generally, display a pattern resembling a long and wide trough. The wave numbers from the graph were also observed and compared to the wave numbers in infrared spectroscopy absorption, as displayed in Table 1. One of the numbers in the spectrum read  $3370.68\text{ cm}^{-1}$ , which rests in the category of intermolecular bonded hydroxyl groups with a wave number range of  $3550\text{--}3200\text{ cm}^{-1}$ . This proved the abundance of hydroxyl groups in the powdered cassava peels, which helped to form hydrogen bonds with water molecules, thus delaying and preventing the formation of gas hydrates. The starch was a polysaccharide which consists of anhydroglucose, amylose, and amylopectin. Amylose could form bonds with the hydrophobic gas molecules, while the amylopectin inhibited the hydrate from agglomerating [27].

Table 1. IR adsorption table.

Absorption	Functional Group	Compound Class
3700–3584	O–H stretching	Alcohol
3550–3200	O–H stretching	Alcohol
3500	N–H stretching	Primary amine



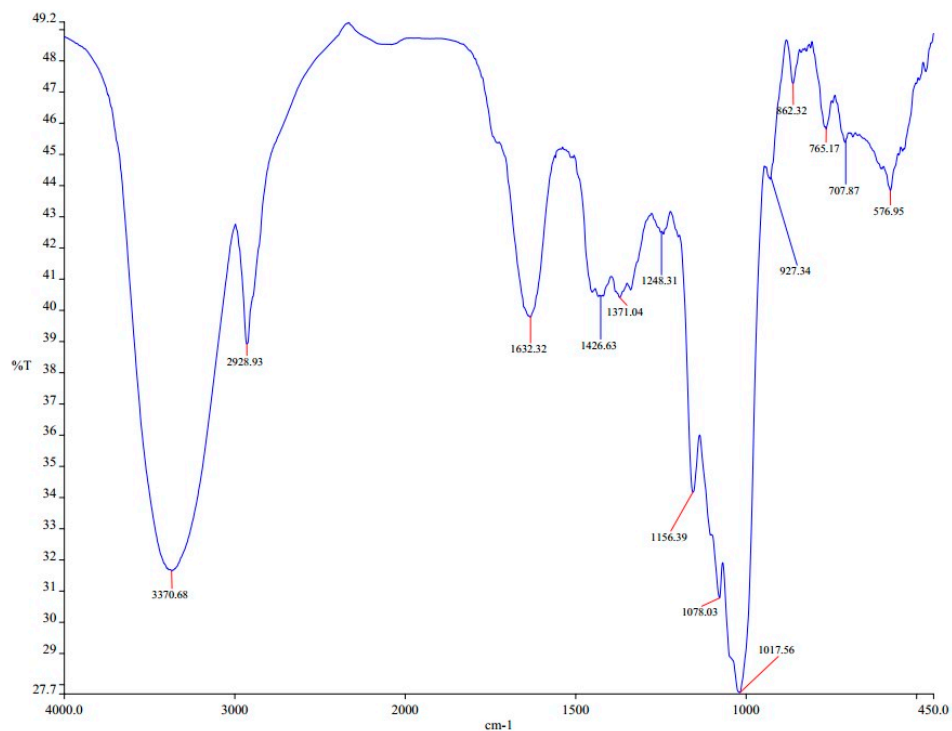


Figure 3. FTIR spectra for cassava peels.

### 3.2. Morphology and Elemental Composition Analysis Using SEM

The powdered cassava peel was run in SEM to analyze the morphology and elemental composition of the sample. Electron microscopy technique was applied to represent the topographic information of the surface and the cross-section of the membrane specimen. SEM was used to inspect the surface of a membrane for the identification of the surface characters of the membrane and also to observe the formation of fouling [28]. A scanned electron micrograph was obtained from the experiment and is shown in Figure 4. The cassava peels were found to have angular granules with a diameter in between 4–20  $\mu\text{m}$ . The angular granules can indicate the existence of compound starch granules, which means it contains hydroxyl groups [21].

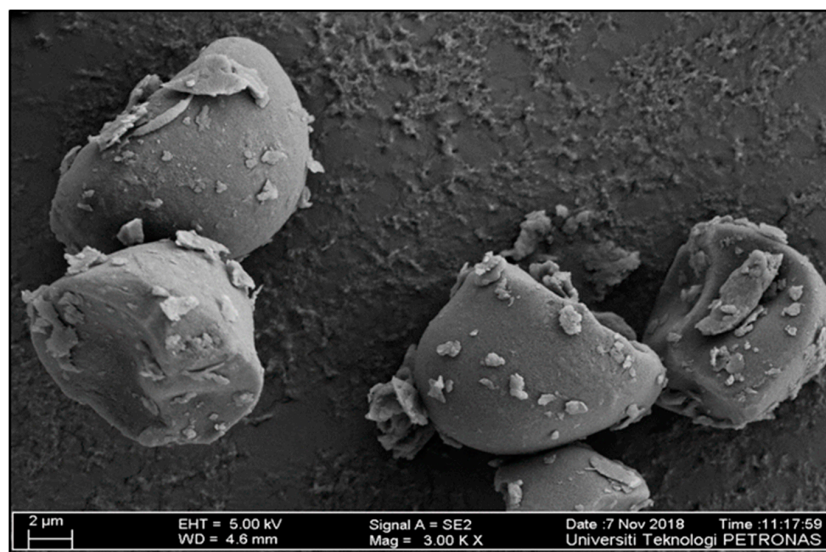
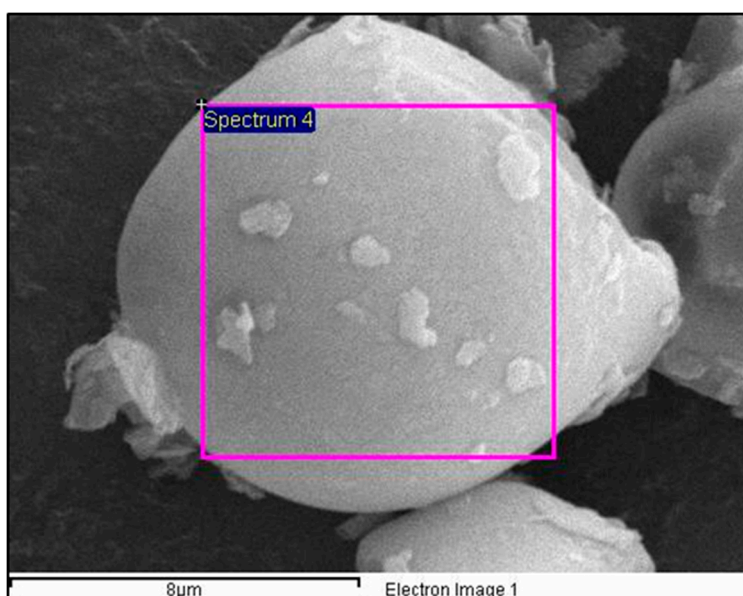


Figure 4. Scanning electron micrograph of cassava peel powder.

Energy Dispersive X-Ray (EDX) analysis was run to identify the number of elements present within the cassava peels, which can indicate their toxicity and elemental compatibility with bottom hole fluids. Figure 5 shows the area of interest to analyze the composition of cassava peels. Electron microscopy was one of the most important techniques in the characterization of the surface morphology and elemental composition of various types of membranes, to be used for numerous applications [28].



**Figure 5.** Energy Dispersive X-Ray (EDX) analysis of cassava peel.

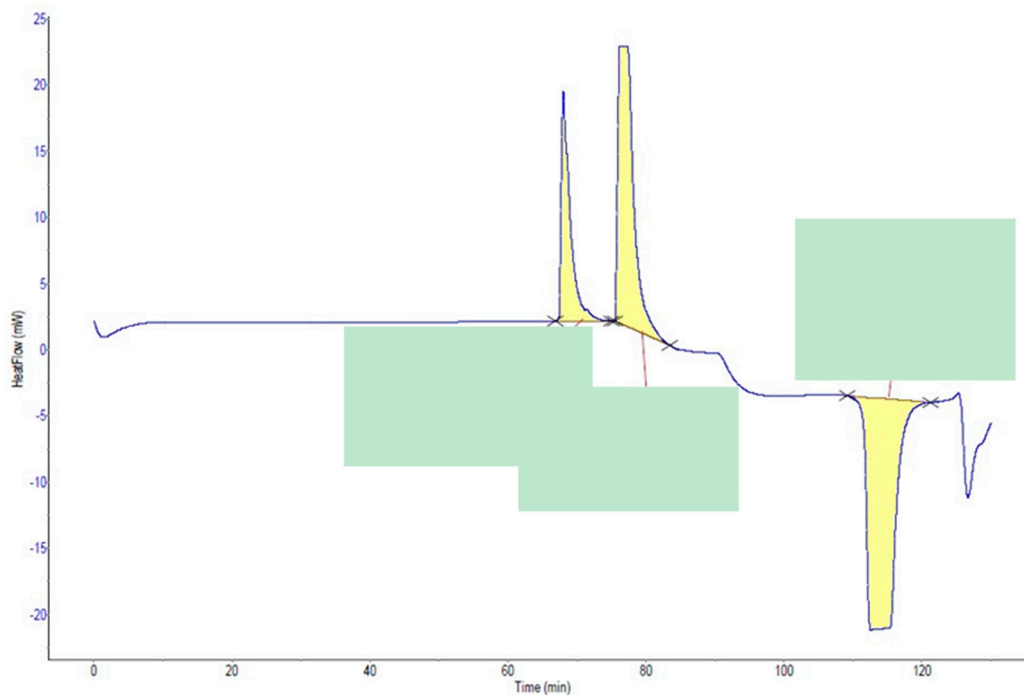
The elements, compounds, and the corresponding amounts are represented in Table 2. From the analysis, cassava peels contained 71.5 wt %  $\text{CaCO}_3$  and 28.12 wt %  $\text{SiO}_2$ . Based on the results found from EDX, the elements and compounds found in cassava peels are not toxic for the reservoir environment as they are all naturally occurring chemical compounds.

**Table 2.** Elemental composition of cassava peels.

Element	Compound	Weight (%)	Atomic (%)
C	$\text{CaCO}_3$	71.50	77.09
O	$\text{SiO}_2$	28.12	22.76
Al	$\text{Al}_2\text{O}_3$	0.10	0.05
Si	$\text{SiO}_2$	0.09	0.04
K	Potassium feldspar	0.19	0.06
Totals	-	100.00	100.00

### 3.3. Measurement of Induction Time Using $\mu$ -DSC

Figure 6 showed typical heat flow profiles from  $\mu$ -DSC for methane hydrate in the presence of 1.0 wt % cassava peel solution at 10 MPa. It was observed that two peaks appeared during the exothermic process, which denoted the appearance of methane hydrate and ice [29]. The induction time of hydrate could be found from the onset time of the first peak from thermogram results. Induction times for the different samples and pressure settings were recorded and compared using a bar chart.



**Figure 6.** Typical heat flow profile with the presence of hydrate inhibitor at 10 MPa.

Induction time was measured based on the difference in the heat flow between the sample and the reference cell as a function of time during the phase transition [30]. The induction time of methane hydrate formation was measured for each sample at a pressure range from 4 to 10 MPa. PVP solutions were formulated with different concentrations of 0.5 and 1.0 wt %. The solutions were tested at a pressure of 4, 6, 8, and 10 MPa, while injecting methane gas and deionized water to form hydrates. All samples were runs three times to calculate the average induction time. The results for the sample without inhibitor were shown in Table 3 and the results for induction time in presence of a inhibitor were tabulated in Table 4.

**Table 3.** Methane hydrate induction without inhibitor (blank sample).

Sample	Pressure (MPa)	Induction Time (min)
Without inhibitor (blank sample)	4.0	65.84
	6.0	67.92
	8.0	64.14
	10.0	32.54

**Table 4.** Methane hydrate induction time in presence of PVP and CP as inhibitor.

Pressure (MPa)	Concentration (wt %)	No of Runs	Average Induction Time for PVP (min)	Average Induction Time for CP (min)
4.0	0.5	3	120.00	82.73
4.0	1.0	3	136.00	74.54
6.0	0.5	3	76.00	70.97
6.0	1.0	3	80.40	68.92
8.0	0.5	3	70.33	65.00
8.0	1.0	3	74.22	67.55
10.0	0.5	3	68.70	65.40
10.0	1.0	3	70.52	67.46



From Figure 7, it can be seen that the induction times of methane hydrates using the cassava peels solution were longer for both 0.5 and 1.0 wt % when compared to the blank sample. This showed that cassava peels at 4 MPa could act as an inhibitor, in which the hydroxyl group compete for hydrogen bonding with the water molecules, thereby preventing the hydrate formation. It was also observed that PVP performs significantly better than cassava peels at this pressure. The induction time was used to evaluate the performance of kinetic hydrate inhibitors. It described the ability of KHIs to prolong the hydrate formation and/or crystal growth. Longer induction time indicated greater inhibition [31]. It was observed that the cassava peels effectively delay the formation hydrates by around 2 min when compared to the blank sample. However, at 6 MPa, cassava peels did not perform as effectively as the commercialized PVP for both concentrations. At an increased pressure of 8 MPa, the performance of cassava peels as an inhibitor increased as the induction time was closed to the induction time of hydrates in the presence of PVP, as shown in Figure 7. The induction time difference between the blank sample and cassava peels also improved to 3 min, showing the cassava's increased effectiveness at higher pressure. The difference between CP and PVP at 1 wt % was around 6 min. Both concentrations of cassava peel increased the induction time by an average of 5 min when compared to the blank sample. The time difference between cassava peel and PVP was only 3 min. At 10 MPa and 1 wt %, the CP solution increased induction time from 62.54 to 67.50 min (the highest increment from another comparison). As pressure was increased gradually, the performance of cassava peels solution improved to almost the same level as the PVP solution. At higher pressure, the hydroxyl group in the cassava peels bonded more readily with the water molecules, ultimately inhibiting the growth of hydrate nuclei. The results showed that a concentration of 1.0 wt % was better in inhibiting hydrate as opposed to 0.5 wt %. More concentration should be studied in order to observe the optimum concentration of cassava peels that could act as effective KHIs.

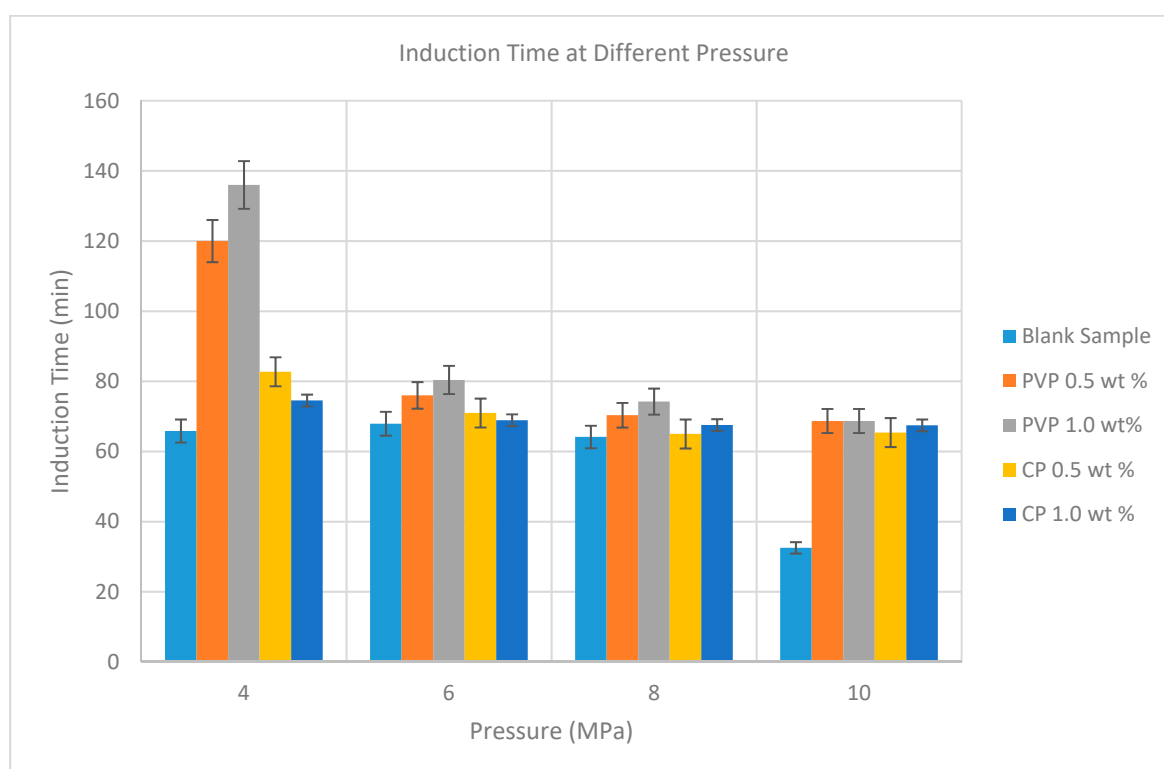


Figure 7. Induction time at different pressure.

#### 4. Conclusions

The analysis of this study found that cassava peels possess the kinetic inhibiting ability. From the FTIR analysis, it has been confirmed that hydroxyl groups are present in cassava peels. Hydroxyl groups play a significant role in kinetic hydrate inhibitors as they delay the formation of hydrates by forming hydrogen bonds with water molecules, thus disrupting the entrapment of gas molecules. According to SEM results, it can be observed that cassava peels were found to have angular granules with a diameter in between 4–20  $\mu\text{m}$ . The angular granules can indicate the existence of compound starch granules, which means it contains hydroxyl groups. Besides that, the composition of cassava peels is determined to be non-toxic and compounds can be naturally found in the earth, which means they are compatible with reservoir fluids. The use of cassava peels as a kinetic inhibitor is justified and the currently disposed of cassava peels from the cassava processing industry can now be used for a greater purpose. From induction time data from  $\mu$ -DSC results, cassava peel shows a high potential to delay methane hydrate formation at higher pressure. Cassava peel solution is observed to prolong the induction times at all pressure settings and it is better at 1.0 wt % concentration. However, at lower pressures (4 and 6 MPa), their performance is insignificant when compared to the commercial inhibitor, PVP. At high pressure of 8 and 10 MPa, it can be seen that the performance of cassava peels is as effective as PVP, which suggests that the optimum operating pressure and concentration for cassava peel is 10 MPa and 1.0 wt %, respectively.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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