



## Full Length Article

## Delayed volatiles release phenomenon at higher temperature in TGA via sample encapsulation technique



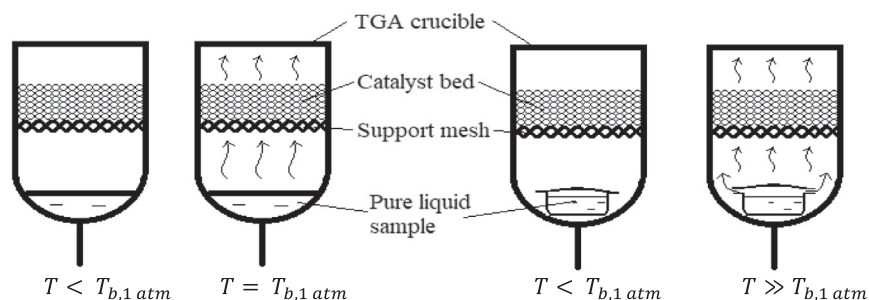
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Thermogravimetric analysis (TGA) for solid-gas reactions is well formalized and of ubiquitous use. However, the use of volatile samples in TGA often results in pre-loss of volatile sample by evaporation prior to reaching the specified thermal conditions of analysis. Therefore, sample encapsulation method was proposed as an innovative technique to address this issue. This technique was shown to provide a continuous and delayed release of vaporized samples over the range of elevated temperature through the progressive loosening of the hermetic seal of metal capsule. This effect can be enhanced by using capsule with higher material hardness and smaller surface area for sample evaporation. Application of this method in catalytic phenol reduction has shown an increase in benzene yield from 19.2 mol% to 46.5 mol% when phenol is encapsulated by tin cylinder. Based on these findings, delayed volatiles release phenomenon may lead to further opportunities in the area of thermochemical kinetics study for fuel processing such as gasification, carbonization, reforming or petrochemical reactions that involve catalyst activation at high temperature and use of volatile samples such as fuel model compounds in TGA setup.

## 1. Introduction

Thermogravimetry (TG) or thermogravimetric analysis (TGA) is a

method used to measure mass change of a sample as a function of time or temperature while subjecting the sample in a controlled atmosphere and temperature program. By observing the precise mass change of

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sample, various reactions occurring within the sample such as decomposition, crystallization, combustion, reduction, oxidation, vaporization, desorption and adsorption can be investigated rigorously [1]. Solid-gas reaction is one of the important fields covered in TGA in which pure samples or sample mixtures were often analyzed for their thermochemical reactivity or stability. As such, the current state of the art generally involves the use of thermal volatilization analysis (TVA) which requires TGA to measure physical changes such as weight, temperature, etc. and evolved gas analysis (EGA) or evolved gas detection (EGD) to measure chemical changes in the reaction system [2]. EGA and EGD instrumentations may consist of mass spectroscopy (MS), gas chromatography (GC) or infrared spectroscopy (IR), depending on the chemical properties—molecular weight, structural conformation, composition, etc.—of the evolved volatiles to be analyzed [3]. The use of volatile samples for solid-gas reaction remains a challenge in this field as the volatilization effect of these samples at lower temperatures may lead to issues such as substantial loss of sample prior to analysis and inaccurate account of the thermal stability and reactivity of sample.

The flow of gaseous sample through catalyst bed at a targeted temperature in catalytic gas-solid reaction is important as reaction temperature is an important parameter in affecting reaction kinetics [4–6]. Significant pre-volatilization of volatile samples may thus pose difficulties in attaining kinetics data across various isotherms [7]. Several existing techniques were well established in other previous works to mitigate this problem such as pulsed thermal analysis [8–11] and the use of reactive gas streams in TG system [1,12]. PTA technique involves the injection of a specified quantity of gaseous reactant through the carrier gas stream which passes over the solid sample in TG crucible for gas-solid reactions [13,14]. This technique has the advantage that reaction occurs at a well-controlled temperature and reactant amount by ensuring the solid sample reaches to the desired temperature prior to the injection of known amount of gaseous reactant [9,11]. However, this technique does not offer the feature of continuous flow of gaseous reactant through solid sample during non-isothermal reaction. The continuous feed of gaseous reactant can be accomplished through the simultaneous flow of reactive and inert gas streams into TG environment. However, the extent of reactant flux through the reaction zone was noted to be affected by crucible dimensions, hydrodynamics and direction of reactant flow in TG environment [12,15]. This effect is undesirable, causing the reaction kinetics analysis to have mass transfer limitations.

In view of these challenges, sample encapsulation technique was proposed as an innovative method in this work. This method involves the physical confinement of sample within a metal capsule or pan covered with lid which is then being crimped at the edges to form hermetically sealed capsule. As temperature increases during TGA, the increasing sample volatilization rate will result in a greater accumulation of vapor pressure within the sealed capsule. As such, the progressive loosening of hermetic seals over a range of elevated pressure will provide a continuous and delayed release of volatile samples over a range of higher temperature. With this technique, the continuous feed of gaseous reactant directly through the reaction zone of catalyst bed could be achieved at the defined temperatures and without the influence of crucible geometry and hydrodynamics of purge gas flow. The extension of this method in TGA by encapsulation of volatile samples such as fuel model compounds may lead to further opportunities in the area of thermochemical kinetics for fuel processing such as gasification, carbonization, reforming or petrochemical reactions that involve catalyst activation at high temperature and use of volatile samples.

In differential scanning calorimetry (DSC), metal capsule containing sample and empty capsule as reference were used to analyze physical or chemical phenomena of sample occurring within the capsule such as phase transitions, oxidation, reduction, decomposition, etc. [16–18]. Based on the determination of heat flux between sample and reference, quantitative parameters of these endothermic or exothermic processes can be determined [19,20]. However, in this TGA study, the chemical

and physical phenomena of sample occurring within the sealed pan were not the main aspects of study. Rather, the metal capsules in this TGA study served as sealed containers to physically isolate the volatile sample from the purge gas environment and the other solid reactants present in TGA crucible. As such, pure liquid samples were used in this analysis to ensure boiling is the only physical phenomenon that would occur. Likewise, chemical and physical phenomena of sample are only analyzed when the evolved gas from capsule comes in contact with other solid reactants within TGA crucible. The focus of this work is on the effectiveness of metal capsules in retaining the vaporized sample and releasing it at higher temperature. The application of this proposed delayed volatile release via sample encapsulation in enhancing catalytic gas-solid reactions was also examined in this work using catalytic phenol reduction.

## 2. Theory

### 2.1. Thermodynamics of vaporization

Vaporization is the phase transition of a substance from liquid to vapor phase which can be achieved through evaporation and boiling. Generally, both processes are endothermic because heat is absorbed by molecules in both instances to transit from liquid phase into gaseous phase which is of higher energy state. However, evaporation and boiling thermodynamics are very different. Evaporation is a surface phenomenon which involves vaporization of liquid from liquid surface into gaseous phase at temperatures below boiling point while boiling is a bulk phenomenon which involves the vaporization of liquid from the entire liquid phase into gaseous phase at boiling point [21].

Evaporation is a vapor-liquid exchange process which involves the accumulation of escaped molecules at the vapor above the liquid. When the vapor phase is saturated, evaporation reaches to a thermodynamic equilibrium state. The pressure exerted by this saturated vapor phase is known as saturation vapor pressure which can be determined using Clausius-Clapeyron relation (Eq. (1)) or Antoine equation (Eq. (2)) [22].

$$\frac{d \ln p}{dT} = \frac{\Delta_{\text{vap}} H^{\circ}}{RT^2} \quad (1)$$

$$\log p = A - \frac{B}{C + T} \quad (2)$$

where  $p$  is saturation vapor pressure (mmHg for Eq. (2)),  $T$  is temperature of liquid (K for Eq. (1) and °C for Eq. (2)),  $\Delta_{\text{vap}} H^{\circ}$  is standard latent heat of vaporization of liquid,  $R$  is ideal gas constant and  $A$ ,  $B$  and  $C$  are component-specific constants. Based on these equations, saturation vapor pressure increases with the increase in liquid temperature as more molecules acquire sufficient kinetic energy to escape from liquid surface into gaseous phase. Further increase in temperature will cause the saturation vapor pressure of liquid to further increase until it becomes equal with the ambient pressure. At this temperature, boiling of liquid would occur in which heat is absorbed to overcome the intermolecular attraction force of molecules within liquid phase to form bulk gaseous phase.

### 2.2. Release of vaporized volatiles at higher temperatures

When volatile liquids are being left unperturbed in an open system, a significant amount of liquid can be vaporized easily at room temperature in the absence of heating due to their high volatilities and evaporation rates. Thus, when volatiles are being heated steadily to achieve their boiling states, a portion of volatile liquid may have been pre-vaporized thus creating an undesirable issue of volatile sample escape at early stage during thermogravimetric analysis. Based on Clausius-Clapeyron relation, it is thermodynamically possible to increase the boiling point of liquid sample by increasing the surrounding

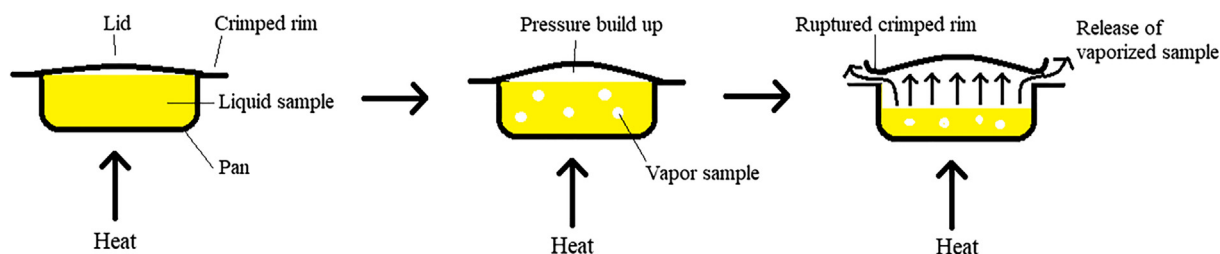


Fig. 1. Delayed release of vaporized sample via encapsulation.

pressure. Pressurization of system may be useful in delaying the boiling process of liquid sample and shifting the evaporation equilibrium towards the liquid phase. However, specifications of conventional TGAs usually allow only thermal processes to be done at atmospheric or low pressures. For thermal analysis involving pressurization, high pressure thermogravimetric analysis equipment (HP-TGA) is required instead and is usually of higher cost and rarity [23,24]. Likewise, the increase in boiling point of liquid sample via pressurization of system is not effective based on two reasons: 1.) Large pressure increase is needed to produce small increase in boiling point, 2.) Larger pressure increase is required for the same interval of boiling point increase at higher temperatures. For instance, the saturation pressures of water at 100, 120 and 140 °C are 101.42, 198.67 and 361.53 kPa respectively [25]. Thus, system pressurization for vaporization of volatiles at higher temperature in TGA analysis may not be effective due to its higher cost, rarity and risk.

In this study, encapsulation of liquid sample by hermetically sealed metal pan was proposed as an innovative method for the release of vaporized volatiles at higher temperatures and without pressurization of surroundings during TG analysis (Fig. 1). The encapsulation involves the placement of liquid sample in a cylindrical pan which is then covered by a lid. The rims of both pan and lid are crimped together to form a sealed closure using a capsule sealing tool. This setup would physically confine the liquid sample to a closed system which prevents or minimizes the escape of evaporated sample. When the encapsulated sample is being heated, pressure build-up occurs due to the thermal expansion of trapped air layer and the increasing vapor pressure of liquid sample at higher temperature. In addition, the increase in internal pressure of capsule also causes the liquid sample to boil at higher temperature, thus remaining as liquid for a longer period of time. The internal pressure will progressively increase causing the crimped rim of capsule to rupture. The ruptured rim would then function as the outlet for the release of vaporized sample in a continuous flow.

The delayed volatiles release phenomenon at higher temperature in TGA via sample encapsulation technique as proposed in this study may lead to new opportunities of analyzing catalytic gas-solid reactions in TGA. For instance, consider an experimental setup of a typical catalytic gas-solid reaction in a TGA crucible which involves the passing of vaporized samples through a suspended catalyst bed at an elevated temperature (Fig. 2). If the liquid sample is exposed to the internal environment of TGA furnace, the sample would vaporize at its atmospheric boiling point ( $T_{b,atm}$ ) and pass through the catalyst bed at this temperature. In heterogeneous catalytic study, catalyst activation at high temperature under a stream of air,  $H_2$ ,  $O_2$ , etc., is necessary to achieve the desired oxidation states of active sites, better dispersion of active sites, improved morphology and replenishment of surface and lattice species within the catalyst structure for better catalytic activity [26–31]. With the use of volatile reactant, the vaporized sample may pass through the catalyst bed prior to its activation temperature. Thus, by physically confining the sample in capsule, it can release and allow the vaporized sample to pass through the catalyst bed at a higher temperature, i.e. catalyst activation temperature.

### 3. Experimental

#### 3.1. Materials

Phenol and guaiacol were purchased from Sigma-Aldrich and used as received without any purification. Purified nitrogen gas was purchased from Linde Malaysia Sdn. Bhd. Three types of Perkin-Elmer metal capsules were obtained which are tin pan, aluminium pan (Al pan) and tin cylindrical capsules. Table 1 shows the dimensions of capsules. The TGA crucible (Fig. 2) as required for the setup was the 3.4 mL  $Al_2O_3$  crucible by NETZSCH. Dry impregnated Ag/ $TiO_2$  was used as the phenol reduction catalyst as part of the application study. The catalyst has silver loading of 9.13 wt%, specific surface area of 8.69  $m^2/g$ , average pore diameter of 9.53 nm, average  $TiO_2$  particle size of 113.13 nm, acid site density of 0.2576 mmol/g and  $H_2$  uptake amount of 0.1129 mmol/g as determined by ICP-OES, BET, TEM,  $NH_3$ -TPD and  $H_2$ -TPD techniques.

#### 3.2. Sample encapsulation technique

A micropipette of 0.1  $\mu L$  precision was used to place liquid sample into metal capsule. The dispensed volume of liquid sample by micropipette corresponds exactly to the capacity volume of metal capsules to avoid liquid spillage. Corresponding lids were used to cover the top of the filled capsules. The rims of the capsule and lid were crimped firmly using pan crimper to form hermetic seal (Fig. 3). As for the filled tin cylindrical capsules, its top end was pressed together without a lid instead to form the sealed closure. The weight of encapsulated liquid sample was determined based on the difference in weight of empty capsule with lid and weight of hermetically sealed capsule containing liquid sample [32]. All weighing procedures were repeated for three times and the measurement errors were less than 4%. In order to examine the integrity of hermetic seals, the encapsulated sample was placed in TGA setup for 15 min under 20 mL/min  $N_2$  flow without any heating. The encapsulated samples are ensured to have good seal integrity to prevent liquid leakage or loss prior to volatilization test.

#### 3.3. Volatilization of encapsulated sample

Volatilization of encapsulated liquid samples was tested in a TGA-FTIR (Thermogravimetric-Fourier Transform Infrared Spectroscopy) coupling system. Each test consisted of the volatilization of a liquid sample that is encapsulated with a particular metal capsule. The encapsulated liquid sample was placed in the TGA  $Al_2O_3$  crucible of NETZSCH STA 443 Jupiter thermogravimetric analyzer. In each test, the sample was heated from 25 °C to 400 °C at a designated heating rate under 20 mL/min  $N_2$  purge flow. Effect of heating rate on volatilization was studied by performing the experiments at heating rates of 30, 40 and 50 K/min. Effect of sample boiling point was also investigated through the Al pan encapsulated phenol and guaiacol vaporizations at 50 K/min. Effect of metal capsule material and geometry was also studied by observing phenol vaporization at 50 K/min with different metal capsules such as tin cylinder, tin pan and aluminum pan (Fig. 3). Phenol vaporization at 50 K/min was also done without sample

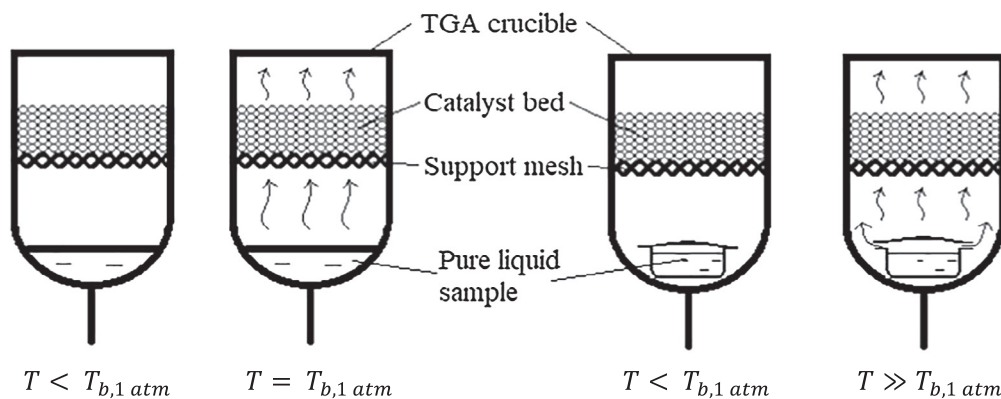


Fig. 2. Schematics of sample encapsulation concept for catalytic gas-solid reaction with standard sample (left) and encapsulated sample (right) in TGA where  $T$  is sample temperature and  $T_{b,1atm}$  is atmospheric boiling point of sample.

Table 1

Dimensions of metal capsules.

| Capsule type  | O.D. <sup>a</sup><br>(mm) | I.D. <sup>b</sup><br>(mm) | H <sub>o</sub> <sup>c</sup> (mm) | H <sub>i</sub> <sup>d</sup> (mm) | A/V <sup>e</sup><br>(mm <sup>-1</sup> ) |
|---------------|---------------------------|---------------------------|----------------------------------|----------------------------------|---|
| Tin pan       | 4.30                      | 4.20                      | 2.00                             | 1.10                             | 0.909                                   |
| Aluminium pan | 5.90                      | 5.40                      | 2.30                             | 1.40                             | 0.714                                   |
| Tin cylinder  | 2.80                      | 2.50                      | 7.00                             | 5.80                             | 0.172                                   |

<sup>a</sup> Outer diameter.

<sup>b</sup> Inner diameter.

<sup>c</sup> Outer height.

<sup>d</sup> Inner height.

<sup>e</sup> Surface area to volume of sample ratio.



Fig. 3. Hermetically sealed capsules containing liquid samples: Tin cylinder (left), Tin pan (middle), Aluminum pan (right).

encapsulation as blank test.

During heating, a 20 mL/min  $N_2$  flow was supplied in TGA to purge vaporized volatile samples into FTIR system via a 53-cm transfer line. Transfer line was maintained at 230 °C to prevent condensation of evolved vapor samples. In-situ evolved gas analysis was performed by Bruker TENSOR 27 FT-IR spectrometer to identify and quantify the vaporized samples at a particular time interval. Scans were taken at resolution of 4  $cm^{-1}$  to give a theoretical data spacing of 1.928  $cm^{-1}$  ranging from 650 to 4500  $cm^{-1}$  wavenumbers. Spectral interferences by atmospheric  $CO_2$  and  $H_2O$  were eliminated through background scans. Volatilization of samples was also done in the absence of metal capsule as the standard calibration tests for the quantification of samples. Weights of metal capsules were also measured before and after volatilization to investigate for capsule degradation.

### 3.4. Catalytic gas-solid reaction

Application of sample encapsulation for catalytic gas-solid reaction was investigated in gas-phase reduction of phenol over  $Ag/TiO_2$  catalyst. In the presence of supported metal catalyst, phenol will be reduced into benzene [33–35]. The reaction was carried out in TG crucible via

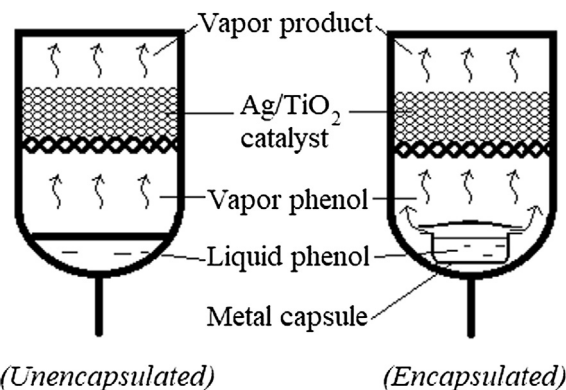


Fig. 4. Gas-phase reduction of phenol to benzene over  $Ag/TiO_2$  catalyst without and with sample encapsulation technique.

two different reactant setups as shown in Fig. 4: 1.) Unencapsulated liquid phenol which is subjected to conventional vaporization, 2.) Encapsulated liquid phenol which is subjected to delayed volatile release effect. Tin cylinder was used to encapsulate liquid phenol. Upon ramping up the temperature of reaction system, liquid phenol would vaporize and pass through  $Ag/TiO_2$  catalyst bed to be reduced into benzene. During the reduction, vapor products are continuously transferred to FTIR for evolved gas analysis. Both setups were done using the same amount of phenol (25 mg), catalyst (230 mg) and heating profile (25 °C–400 °C at 50 K/min) under a 100 mL/min of 5%  $H_2/N_2$  flow. A control experiment was also carried out in the absence of liquid phenol and no weight loss was observed, indicating the thermal stability of catalyst and reaction setup. Benzene yield was determined using the following equations:

$$\text{Benzene yield (mol\%)} = \frac{\text{Moles of benzene product}}{\text{Moles of initial phenol}} \times 100\% \quad (3)$$

## 4. Results and discussion

### 4.1. Post-vaporization conditions

Fig. 5 shows the conditions of metal capsules before and after the volatilization of liquid samples in TGA. Both tin cylinder and aluminum pan retained their structures after the release of vaporized volatile samples at higher temperatures. The seal rupture was formed through the entire detachment of crimped rims between lid and capsule which contributed to the release of vaporized volatile samples. As for tin pan, its shrinkage into a sphere may be attributed to melting and re-solidification of tin during volatilization. Weight of capsule after volatilization was equivalent with the weight of stock capsule with a maximum



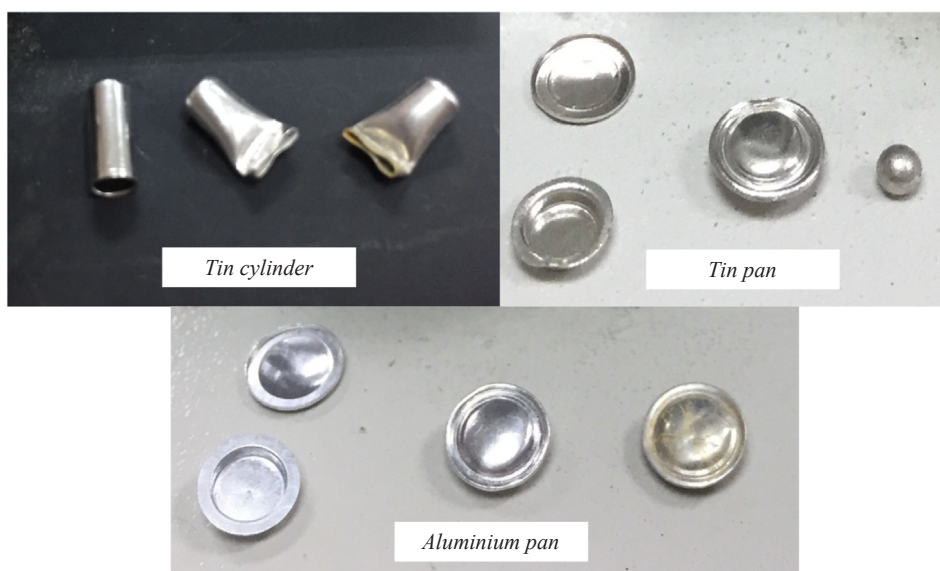


Fig. 5. Conditions of metal capsules: stock (left), before (middle) and after (right) experiment.

deviation of  $\pm 2\%$ . This indicates that metal capsules were thermally inert and stable throughout the volatilization. Likewise, FTIR spectra showed only the respective functional groups of phenol and guaiacol on experiments with different phenolic samples. Hence, the total weight loss in TGA curve would be entirely attributed to the weight of vaporized volatile sample.

#### 4.2. Delayed volatile release via sample encapsulation

Fig. 6 shows the TG and DTG curves of Al pan encapsulated guaiacol vaporization at heating rates of 30, 40 and 50 K/min. Based on DTG curve, two peaks were observed at 120 °C and 198 °C during guaiacol vaporization. The first peak accounts for evaporation of guaiacol which occurs below its boiling point (205 °C) while the second peak accounts for boiling of guaiacol. The maximum guaiacol vaporization rate ( $-3.79\%/s$ ) occurred at 198 °C which corresponded to the boiling state of guaiacol. Further release of guaiacol vapor until 217 °C also indicated the retention ability of capsule in delaying the release of boiled guaiacol. Nevertheless, guaiacol vaporization at lower temperatures was observed despite the physical confinement of guaiacol in metal capsule. This is because the hermetic seal of metal capsule is formed via mechanical crimping of the rims of capsule and lid without any sealants. Thus, the rupturing mechanism of the seal occurs through the progressive loosening of the mechanically crimped seal as it is continuously subjected to an increasing pressure or temperature. This seal would thus feature the steady delayed release of vapor over a range of

higher temperatures rather than outburst of vapors via an instantaneous capsule rupturing, i.e. explosion. If it is an instantaneous capsule rupturing, there would be a sharp and total decline in the weight change readings at a specific temperature which was not observed in this case. This feature is necessary to ensure the delayed volatile release is achieved without affecting the stability of catalyst bed and TGA system. The possibility of catalyst bed shaking due to gas release was also excluded as TG readings showed a smooth and steady decline in weight change. The TGA instrument has a high gravimetric sensitivity of  $0.025\mu g$  which is able to detect minute instability in catalyst bed and gas release. By increasing the heating rate from 30 K/min to 50 K/min, a greater portion of the vaporized sample was released at higher temperatures. For liquid sample physically confined in a hermetically sealed metal capsule, it will still undergo vaporization via evaporation before boiling point and boiling which is then being steadily released from the capsule via the progressive loosening of the hermetic seals over a range of elevated temperature. Thus, by increasing the heating rate, the initial volatile release of guaiacol via evaporation was reduced as guaiacol achieves its boiling state faster.

Fig. 7 shows the vaporization of Al pan encapsulated phenol and guaiacol which occurred via evaporation and boiling at different temperatures and extents. Phenol exhibited two vaporization peaks at 165.7 °C and 192.4 °C with the respective maximum release rates of  $-2.33\%/s$  and  $-0.87\%/s$  whereas vaporization peaks of guaiacol were at 120 °C and 198 °C with respective maximum release rates of  $-0.25\%/s$  and  $-3.79\%/s$ . The vaporization peak of phenol was

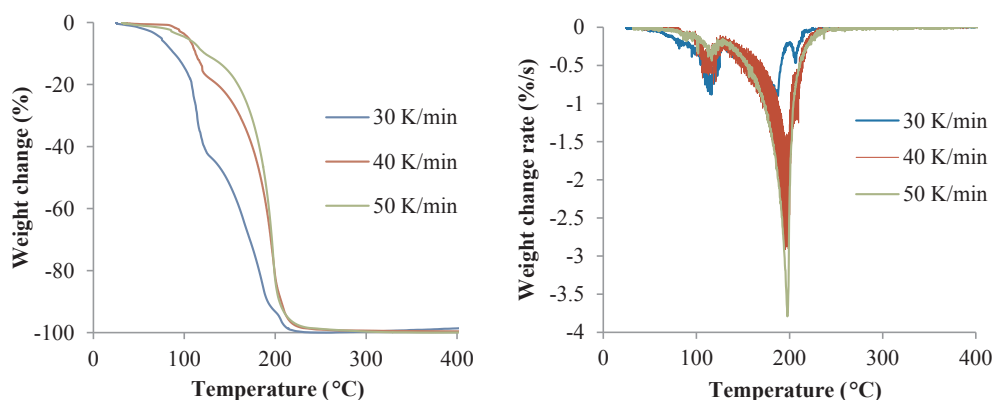


Fig. 6. TG (left) and DTG (right) curves of Al pan encapsulated guaiacol vaporization at different heating rates.

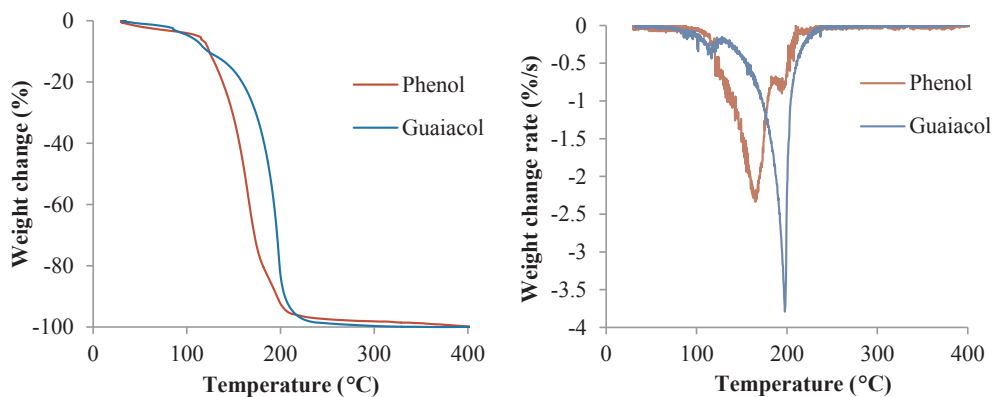


Fig. 7. TG (left) and DTG (right) curves of Al pan encapsulated phenol and guaiacol vaporization at 50 K/min.

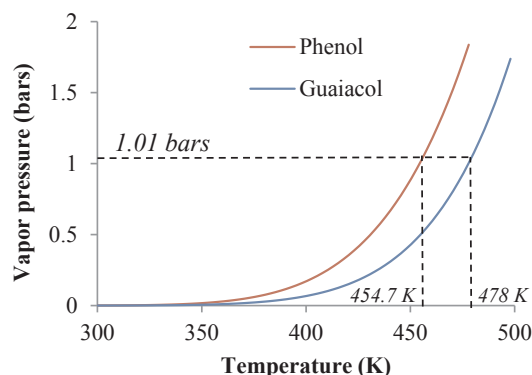


Fig. 8. Vapor pressure of phenol and guaiacol at different temperatures based on Antoine equation.

significant higher than guaiacol as phenol is more volatile than guaiacol. Besides that, vaporization of phenol also occurred at lower temperature due to its lower boiling point. The volatility and boiling point of a liquid sample are dependent on its saturation vapor pressure at a temperature. For instance, phenol has higher volatility and lower boiling point than guaiacol due to its higher saturation vapor pressure as computed from Antoine equation (Fig. 8) [36,37]. Hence, the accumulation of higher vapor pressure at lower temperature will expedite the rupturing of metal capsule as seen in the phenol vaporization case. The rupturing point of metal capsule was at the crimped edges which would throttle the release of vaporized samples up to temperatures of 209.8 °C and 217 °C which respectively exceeded the boiling points of phenol (181.7 °C) and guaiacol (205 °C).

As for the release of guaiacol vapor, it occurred at higher temperature range due to its higher boiling point and lower volatility.

However, its vapor release rate was observed to be higher than that of phenol. The release rate of vaporized sample is dependent on the pressure difference between the metal capsule interior and external surrounding. Likewise, a higher rate of pressure change would also increase the release rate of vaporized sample. By putting these into consideration, Clausius-Clapeyron relation (Eq. (1)) can be expressed in terms of the rate of temperature change of sample:

$$\frac{d \ln p}{dT} = \frac{d \ln p}{dt} \cdot \frac{dt}{dT} = \frac{1}{\beta} \frac{d \ln p}{dt} = \frac{\Delta_{\text{vap}} H^0}{RT^2} \quad (4)$$

$$\frac{d \ln p}{dt} = \beta \frac{\Delta_{\text{vap}} H^0}{RT^2} \quad (5)$$

where  $\beta = dT/dt$  is heating rate. The rate of sample temperature change was equated with heating rate with the assumption of negligible heat transfer limitation. Eq. (5) indicates that the rate of saturation vapor pressure change (natural logarithmic form) increases when heating rate or latent heat of vaporization increases. Since guaiacol (62.6 kJ/mol) has a higher latent heat of vaporization than phenol (58.8 kJ/mol) [38,39], the higher rate of saturation vapor pressure change of guaiacol would result in a higher release rate of guaiacol vapor as shown in DTG curve of Fig. 7. Likewise, by increasing the heating rate used for vaporization of the same sample, it would also cause the release rate of sample vapor to be higher as indicated in DTG curve of Fig. 6.

The vaporization trends of different metal capsules encapsulated phenol were shown in Fig. 9. Among the three tested capsules, tin cylinder pan was noted to delay the release of vaporized phenol to the greatest extent. Based on the TG curves, all encapsulated phenol samples were shown to have a delayed onset in the loss of vaporized phenol as compared with vaporization of non-encapsulated phenol in TG crucible. Tin cylinder and Al pan were observed to entirely delay the release of vaporized phenol by a temperature shift of 36 °C and 11 °C while such effect was not readily observed with the use of tin pan.

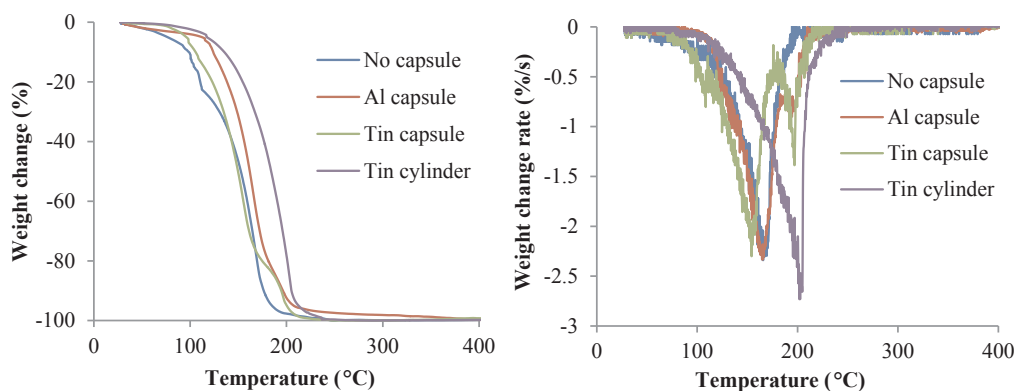


Fig. 9. TG (left) and DTG (right) curves of encapsulated phenol vaporization at 50 K/min.

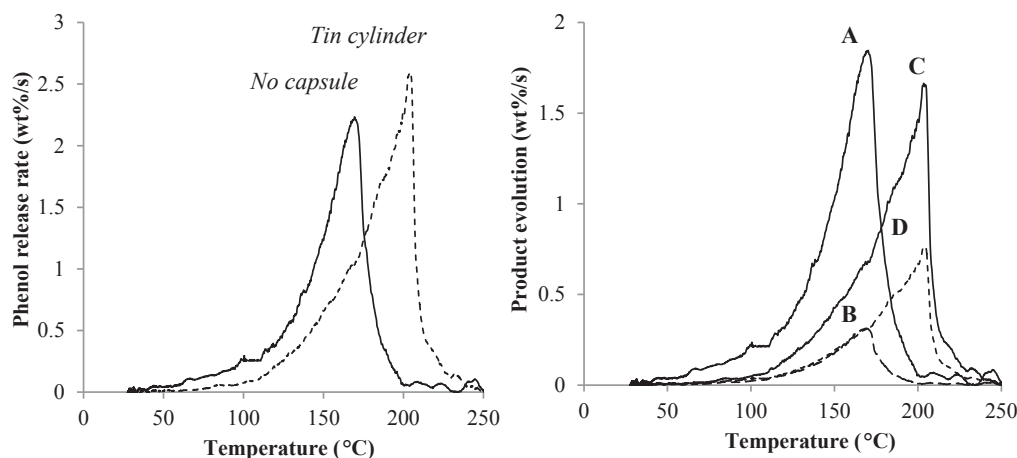


Fig. 10. Phenol release rates (left) and product evolution during phenol reduction (right): (A) unreacted phenol and (B) benzene without sample encapsulation; (C) unreacted phenol and (D) benzene with sample encapsulation.

When equal mass of phenol was allowed to be vaporized in TG crucible under the same conditions and without encapsulation feature, 95% of the initial phenol sample was observed to have been vaporized and escaped from the TG system prior to reaching its boiling point. The high evaporation rate of phenol was due to several reasons: 1.) high vapor pressure which would result in substantial amount of evaporated phenol if heating process was slow; 2.) constant flow of purge gas in TG system would continuously sweep vaporized phenol from the system, thus resulting in the non-equilibrium state of vapor-liquid phenol system and a positive concentration gradient from liquid component to vapor component of phenol. Therefore, by encapsulating the volatile liquid samples during TG analysis, the release of vaporized samples could be delayed to a higher temperature exceeding their boiling points.

Based on the DTG curves of encapsulated phenol samples, capsule material and geometry were also noted to significantly affect its efficiency in retaining the volatile samples. By comparing tin and Al capsules that are of identical geometries, Al capsule was able to retain the vaporized phenol for another 8.9 °C temperature higher than the retention temperature limit of tin capsule. The retention efficiency of metal capsule lies in its ability to withstand the accumulated vapor pressure before rupturing. Therefore, metal hardness is an important physical property which aids in this retention ability. For instance, Al capsule was able to withstand a slightly higher vapor pressure than tin capsule prior to their rupturing as the Mohs hardness values of aluminum and tin were 2–2.9 and 1.5–1.8 respectively [40].

By comparing tin pan and cylindrical capsules, the latter managed to retain the vaporized phenol for another 49 °C temperature higher than the retention temperature limit of the former. Likewise, DTG curve of phenol encapsulated by tin cylindrical capsule also showed minimal loss of volatile sample via evaporation as most of the vaporized phenol sample was released at temperature starting from its boiling point. The minimal loss of volatile sample via evaporation in tin cylindrical capsule was due to its geometry which resulted in the lowest surface area to volume of liquid sample ratio (Table 1). Thus, by minimizing the specific surface area of liquid sample, its evaporation can be reduced and the release of vaporized sample can be delayed to a higher temperature during TG analysis.

The effectiveness of sample encapsulation is verily dependent on capsule material and geometry. In this study, hermetically sealed aluminum and tin capsules were assessed on their sample encapsulation effectiveness. However, hermetically sealed pans are also made of other high purity materials such as Au, Ag, Cu, Pt, stainless steels, etc. By making use of the varying material hardness, the sample release temperature can be varied and applied differently based on the analysis preference. These features of sample encapsulation can thus be applied

to improve the existing analyses of solid-gas reactions via TGA. By altering the capsule configurations, different temperatures of sample release could also be obtained, which would enable solid-gas reactions to be carried out at different isotherms for a more comprehensive kinetic data acquisition. Hermetically sealed pans are generally able to withstand pressure of 2 atm before rupturing [41]. However, it was shown in this study that the rupturing onset of hermetic seal began at about 1.38 atm and progressed up to its rupture design pressure due to the progressive loosening of the hermetic seal over a range of elevated pressure. Contrariwise, high pressure metal capsules are stainless steel based and involve screw sealants as part of their sealing mechanism, thus being able to withstand higher pressure of up to 200 atm before rupturing [41]. Thus, the use of high pressure metal capsules may be potentially applied in TG analysis that requires a more significant delay in release of volatile samples. However, further studies on this matter have to be done in near future for its verification.

#### 4.3. Catalytic gas-solid reaction

The application of sample encapsulation in catalytic phenol reduction was done by encapsulating liquid phenol in tin cylinder. With the sample encapsulation technique, the temperature range for the release of vaporized phenol has increased by 49 °C as indicated in the phenol release rate graph in Fig. 10. Product evolution trend in Fig. 10 has also indicated higher benzene and lower unreacted phenol compositions in the vapor products of phenol reduction when sample encapsulation was applied. The delayed volatile phenomenon as induced by sample encapsulation has improved the efficiency of phenol reduction over Ag/TiO<sub>2</sub> catalyst. This is because the delayed release of phenol vapor enabled better activation of Ag/TiO<sub>2</sub> catalyst at higher temperature. In catalytic reactions, catalyst activation at sufficiently high temperatures is important to ensure the optimal catalytic activity of catalysts through the attainment of suitable oxidation states, active site dispersion, morphology and catalyst phase during catalyst activation [26–31]. At temperatures below 100 °C, negligible benzene yield was observed in the unencapsulated setup even though phenol vapor was passing through Ag/TiO<sub>2</sub> catalyst bed. Rather, the onset temperature of Ag/TiO<sub>2</sub> activation was at 100 °C and it was optimally activated at 150 °C onwards as shown in the significant increase in reduction activity from 150 °C to 200 °C. Besides that, the delayed release of vaporized phenol at higher temperatures also enabled the reduction of phenol at higher reaction temperatures. At higher reaction temperatures, phenol had higher kinetic energy to overcome the activation energy of reduction, causing a higher reduction rate of phenol into benzene [4,42]. Thus, without the use of sample encapsulation, unhindered volatilization effect of phenol at lower temperatures would adversely affect phenol

reduction rate as more phenol vapor passed through Ag/TiO<sub>2</sub> catalyst bed at lower temperatures. By considering the reduction of phenol across the heating profile, the benzene yield was increased from 19.2 mol% to 46.5 mol% when sample encapsulation was employed. Beyond the maxima of vaporization peaks, all product evolution rates decreased significantly due to the depletion of phenol reactants.

## 5. Conclusion

The technique of sample encapsulation in TG analysis, as described in this work, enabled a controlled delay in the release of vaporized volatile samples at higher temperatures which can be used in studies such as catalytic gas-solid reactions and reactions that are temperature sensitive and require catalyst activation at high temperature. The delayed volatile release effect was achieved through the progressive loosening of the hermetic seal of metal capsule over the range of elevated temperature. Sample release temperature could also be altered by varying the material and geometry of pan or capsule. The result of this work indicated that the sample release temperature could be increased by using pan or capsule which is of higher material hardness to withstand higher internal pressure or geometry that has lower surface area to volume of sample to minimize evaporation. The described sample encapsulation method widens the application range of TGA technique to cater for reactions involving high volatility chemicals. By encapsulating the volatile sample, pre-loss of volatile sample due to evaporation and purge flow environment can then be minimized which enable sufficient sample being available for analysis at the desired higher temperatures. Application of this method in catalytic phenol reduction has shown an increase in benzene yield from 19.2 mol% to 46.5 mol% when phenol is encapsulated by tin cylinder. Thus, these findings have formed the basis for more detailed studies on the sample encapsulation effectiveness of other hermetically sealed pans of various materials and geometries and high pressure metal capsules which would be the focus of future works.

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