

# Kinetics and Thermodynamic Study of the Acetylation of *Cucumeropsis mannii* Seed Shell

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**Abstract:** The use of lignocellulosic materials for oil sorption from aqueous medium has directed attention to acetylation as a means of increasing the hydrophobicity of these materials. In this paper, acetylation of *Cucumeropsis mannii* seed shell, a readily available agricultural waste, was studied. Effects of different acetylation conditions on the extent of acetylation of the seed shell was investigated. The kinetics of the acetylation process was studied using pseudo first order, pseudo second order, and intraparticle diffusion models. The thermodynamics of the acetylation process was also studied. FTIR analysis provided evidence of successful acetylation of the seed shell. The extent of acetylation increased with increase in acetylation duration, temperature and catalyst concentration. Pseudo second order kinetics best described the acetylation process, with minimum extent of acetylation and rate constant values of 0.317 and  $-0.0148 \text{ min}^{-1}$ , respectively. Thermodynamic studies revealed that the acetylation process was endothermic in nature. The critical extent of acetylation, heat capacity at constant pressure, and change in entropy values were 1.002, 0.162  $\text{kJ.mol}^{-1}.\text{K}^{-1}$ , and 0.020  $\text{kJ.mol}^{-1}.\text{K}^{-1}$ , respectively. The acetylation process was spontaneous at temperatures of 328 K – 348 K, but non-spontaneous at lower temperatures (308 K and 318 K). The critical temperature of acetylation was 419 K, which shows that acetylation of CMSS can easily take place at mild conditions.

**Keywords:** Acetylation, *Cucumeropsis mannii* Seed Shell, Kinetics, Thermodynamics

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## 1. Introduction

Lignocellulosic materials are substances made up of lignin, cellulose and hemicellulose. Agricultural wastes belong to this class of materials, and due to their low cost, renewability and biodegradability, they are usually employed for numerous purposes which include paper manufacture, biofuel production, cement preparation, and as sorbents for removal of organic and inorganic pollutants from aqueous medium. Most of these agricultural wastes are hydrophilic in nature due to the abundance of hydroxyl groups in their cell wall [1]. This hydrophilic nature affects their oil sorption performance in aqueous medium. In order to address this, hydrophobic modifications are usually performed on these materials. One of the most popular modification methods is acetylation, which converts the hydrophilic properties of these lignocellulosic

materials to hydrophobic ones by raising their acetyl contents and lowering their hydroxyl contents [2]. Previous studies have been carried out on the acetylation of various agricultural materials such as corn cob [3], *Delonix regia* pods [4], sugarcane bagasse and groundnut husk [5], *Pinus taeda* wood [6], oil palm empty fruit bunch fiber [2, 1], wheat straw [7], coconut coir [8], pride of Barbados and cocoa pods [1], *Ensete ventricosum* plant fibre [9], and *Borassus aethiopum* coir [10].

*Cucumeropsis mannii*, commonly called white-seed melon, is a species of melon native to tropical West-Africa [11]. It is a tendril climber or crawling annual crop with a fibrous and shallow root system that is used primarily as a subsidiary crop inter-planted with early maize and yam in the savanna belts of Nigeria [12]. It is often grown for its seeds which are high in protein and oil content [13]. The seed shell is not edible and is usually discarded, thereby constituting environmental pollution. This study investigates the suitable conditions for the

acetylation of these seed shells. Also, the kinetics and thermodynamics of the acetylation process were assessed.

## 2. Materials and Methods

### 2.1. Materials

All the chemicals used in this work were of analytical grade and were used without further purification. *Cucumeropsis mannii* seeds were purchased from Eke market in Awka, Anambra State, Nigeria. The seeds were de-shelled, and the shells were washed, dried, ground, and then sieved. The particles that were retained by size 36 British standard sieves were used for the acetylation reactions.

### 2.2. Characterization of *Cucumeropsis mannii* Seed Shell

The lignin, cellulose and hemicellulose contents of *Cucumeropsis mannii* seed shell (CMSS) were determined according to TAPPI T13m-54 and TAPPI T19m-54 as described by Guimarães *et al.* [14]. Infrared spectra of the CMSS were obtained using an FTIR spectrophotometer (Nicolet iS5) in the range of 4000 – 400 cm<sup>-1</sup>.

### 2.3. Soxhlet Extraction

Soxhlet extraction was first carried out on the CMSS to reduce the influence of fiber extracts on the acetylation process. For this, 10 g of the sieved CMSS was contacted with a 4:1 (v/v) mixture of n-hexane and acetone for 5 hours. The treated CMSS was subsequently dried in a laboratory oven for 16 hours.

### 2.4. Acetylation Reaction

Acetylation of the CMSS was done under mild conditions in the presence of iodine as a catalyst using the method of [2], which involves a reaction with acetic anhydride in a solvent-free system. The reaction conditions were 1:20 (g dried CMSS/mL acetic anhydride), 30°C, 1 hour and 1% catalyst, respectively. The acetylated CMSS (ACMSS) was thoroughly washed with ethanol and acetone to remove unreacted acetic anhydride and the acetic acid byproducts, and subsequently dried in an oven at 60°C.

Infrared spectrophotometry was used to study the effect of different acetylation conditions on the extent of acetylation of the samples. The extent of acetylation ( $\Theta$ ) of the samples was quantitatively determined by calculating the ratio between the intensity of the acetyl C=O stretching and the intensity of C-O stretching vibration of the cellulose backbone as shown in equation 1 [10].

$$\Theta = \frac{I_{1740}}{I_{1020}} \quad (1)$$

The effect of catalyst concentration on the extent of acetylation of the MCSS was determined by varying the concentration of the iodine catalyst from 0.5% to 2.5% at 0.5% interval. For the effect of acetylation duration, the reaction time was varied from 30 minutes to 150 minutes at 30 minutes

interval. The data from this analysis were used for the kinetic study of the acetylation process. For the effect of acetylation temperature, the reaction temperature was varied from 35°C to 75°C at interval of 10°C. The data from this analysis were used to study the thermodynamics of the acetylation process.

### 2.5. Kinetic Studies

The pseudo first order, pseudo second order and intraparticle diffusion kinetic models were employed to identify the mechanism and potential rate-controlling step of the acetylation process.

#### 2.5.1. The Pseudo First Order Model

The pseudo first order equation for acetylation process is expressed in equation 2 [15].

$$\ln \Theta_t = \ln \Theta_0 - k_1 t \quad (2)$$

$\Theta_t$  is the extent of acetylation at time  $t$ ,  $\Theta_0$  is the minimum extent of acetylation, and  $k_1$  is the pseudo first order constant. A plot of  $\ln \Theta_t$  versus  $t$  gives a straight line graph yielding  $k_1$  and  $\Theta_0$  from its slope and intercept, respectively.

#### 2.5.2. The Pseudo Second Order Model

The pseudo second order equation for acetylation process is as shown in equation 3 [4].

$$\frac{1}{\Theta_t} = k_2 t + \frac{1}{\Theta_0} \quad (3)$$

$\Theta_t$  is the extent of acetylation at time  $t$ ,  $\Theta_0$  is the minimum extent of acetylation, and is the pseudo-second order constant. A plot of  $\frac{1}{\Theta_t}$  versus  $t$  gives a linear relationship with the slope and as the intercept.

#### 2.5.3. Intra-Particle Diffusion Model

The intra-particle diffusion equation for acetylation is as expressed in equation 4 [16].

$$\Theta_t = K_{id} t^{0.5} + C \quad (4)$$

$\Theta_t$  is the extent of acetylation at time  $t$ ,  $K_{id}$  is the rate constant of intra-particle diffusion (mg/(g·min<sup>0.5</sup>)),  $C$  is the square root of the time, and  $C$  is the intercept.

### 2.6. Thermodynamic Studies

The thermodynamics of the acetylation process is studied using equation 5 [15].

$$\ln \Theta_T = - \frac{\Delta H}{RT} + \frac{\Delta H}{RT_0} + \ln \Theta_c \quad (5)$$

A plot of  $\ln \Theta_T$  versus  $T^{-1}$  yields a straight line graph whose slope is  $-\frac{\Delta H}{R}$  from which the change in enthalpy ( $\Delta H$ ) can be obtained. The intercept on the y-axis is from which  $T_0$  can be calculated while the intercept on the x-axis is  $\ln \Theta_c$ , from which  $\Theta_c$  can be calculated.  $T_0$  is the critical temperature, that is, the temperature above which the acetylation process is not favourable, while  $\Theta_c$  is the critical degree of acetylation, which is the degree of acetylation above which the

mechanism of acetylation is diffusion mechanism [16].

The heat capacity ( $C_p$ ) of the acetylated samples at constant pressure is calculated using equation 6 [17].

$$\Delta H = C_p \int_{T_1}^{T_2} dT = C_p (T_2 - T_1) \quad (6)$$

$C_p$  represents the quantity of heat needed to raise the temperature of acetylation by one degree.  $T_2$  and  $T_1$  are the final and initial temperatures, respectively.

The change in entropy of acetylation ( $\Delta S$ ) is obtained using equation 7 [18].

$$\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_2}{P_1} \quad (7)$$

$\Delta S$  is the change in entropy,  $T_2$  and  $T_1$  are the final and initial operating temperatures, and  $P_2$  and  $P_1$  are the final and initial operating pressures, respectively. Acetylation process is usually carried out at the same pressure, hence the second term on the right-hand side of the equation becomes zero, and the equation becomes.

$$\Delta S = C_p \ln \frac{T_2}{T_1} \quad (8)$$

Change in Gibb's free energy for the acetylation process can be determined at different operating temperatures using equation 9 [19].

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

The value of  $\Delta G$  indicates the extent of spontaneity of an acetylation process as follows:  $\Delta G < 0$  indicates a spontaneous and feasible process that does not require any external energy source,  $\Delta G = 0$  implies an equilibrium process where no net change is noticed, and  $\Delta G > 0$  depicts that the process is not spontaneous. A higher negative value reflects a more energetically favorable process. A positive value of  $\Delta H$  indicates an endothermic reaction process while a negative value indicates an exothermic reaction. A negative value of  $\Delta S$  suggests a degree of orderliness during the acetylation process while a positive value suggests a degree of disorderliness [15].

### 3. Results and Discussions

#### 3.1. Characterization of *Cucumeropsis Mannii* Seed Shell

The lignin, cellulose and hemicellulose contents of CMSS

were 31.426%, 50.498% and 9.103%, respectively. The high cellulose content reflects the hydrophilic nature of CMSS, since cellulose contains large amounts of hydroxyl molecules which are hydrophilic [20]. The amount of lignin in the MCSS shows that it also has some degree of hydrophobicity, since lignin is responsible for the level of hydrophobicity of lignocellulosic materials [21].

#### 3.2. Infrared Spectroscopy

The FTIR spectra of the raw and acetylated CMSS are shown in Figures 1a and b, respectively. The obtained spectra indicate that CMSS is a lignocellulosic material, as the observed peaks are those corresponding to lignin, cellulose and hemicellulose. The hydroxyl (O-H) stretching characteristic of cellulose, hemicellulose, and lignin were indicated by the broad band with midpoint at  $3300 \text{ cm}^{-1}$  [22]. The C-H asymmetric stretching of methyl ( $-\text{CH}_3$ ) and methylene ( $-\text{CH}_2$ ) groups were observed at  $2900 \text{ cm}^{-1}$  [23]. Cyanide ion stretching was indicated by the shift at  $2030 - 2038 \text{ cm}^{-1}$  [24]. Carbonyl (C=O) stretching was observed in the region of  $1637 - 1722 \text{ cm}^{-1}$  [14]. C=C stretching and C-H bending of acetyl group showed peaks in the region of  $1507 - 1517 \text{ cm}^{-1}$  and  $1316 - 1429 \text{ cm}^{-1}$ , respectively [25]. The C-O stretching appeared as a sharp and intense peak at  $1028 - 1263 \text{ cm}^{-1}$  [26].

A comparison of the spectrum of acetylated CMSS (ACMSS) with that of the raw CMSS (RCMSS) showed a shift, mainly downward shift, in the wavenumber of the absorption bands. The observed shifts in absorption band were:  $3377$  to  $3324 \text{ cm}^{-1}$  for O-H stretching;  $2900$  to  $2901 \text{ cm}^{-1}$  for C-H stretching;  $2038$  to  $2030$  for  $\text{C}\equiv\text{N}$  stretching;  $1722$ - $1637$  to  $1712$ - $1653 \text{ cm}^{-1}$  for C=O stretching;  $1508$  to  $1507 \text{ cm}^{-1}$  for C= stretching;  $1422$ - $1371$  to  $1421$ - $1370 \text{ cm}^{-1}$  for C-H bending; and  $1263$ - $1032$  to  $1262$ - $1028 \text{ cm}^{-1}$  for C-O stretching. In addition, the FTIR spectra of the ACMSS showed a decrease in the intensity of the O-H stretching absorption band, and a broadening of the C=O stretching band, reflecting the acetylation of the CMSS. Similar observations were reported by Nwadiogbu et al. [15] and Nnaji et al. [16] for the acetylation of corncob and *Dacryodes edulis* leaf, respectively. The absence of absorption peaks at  $1700 \text{ cm}^{-1}$  (carboxylic group) and in the range of  $1760 - 1840 \text{ cm}^{-1}$  in the spectra of ACMSS indicates that successful removal of unreacted acetic anhydride and acetic acid byproduct in the purification step [7].

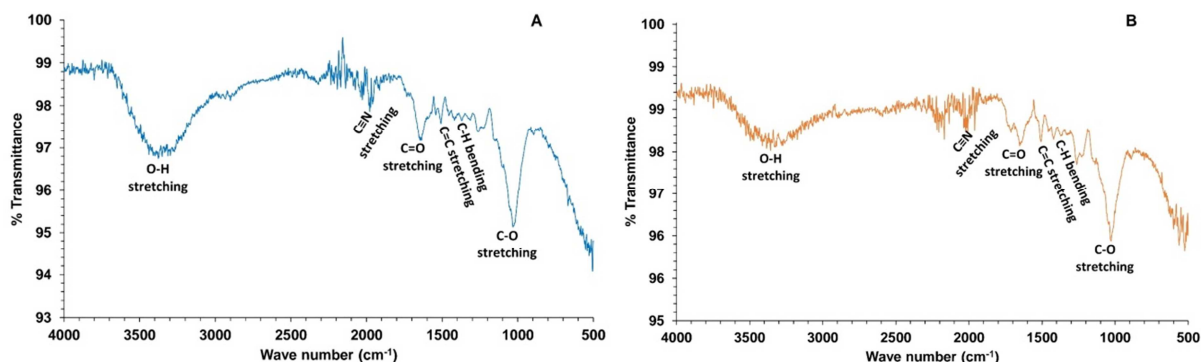


Figure 1. FTIR spectra of (a) raw and (b) acetylated *Cucumeropsis mannii* seed shell.

### 3.3. Effects of Acetylation Conditions

The effects of acetylation duration, temperature and catalyst concentration on the extent of acetylation of CMSS are shown in Figures 2a, b, and c, respectively.

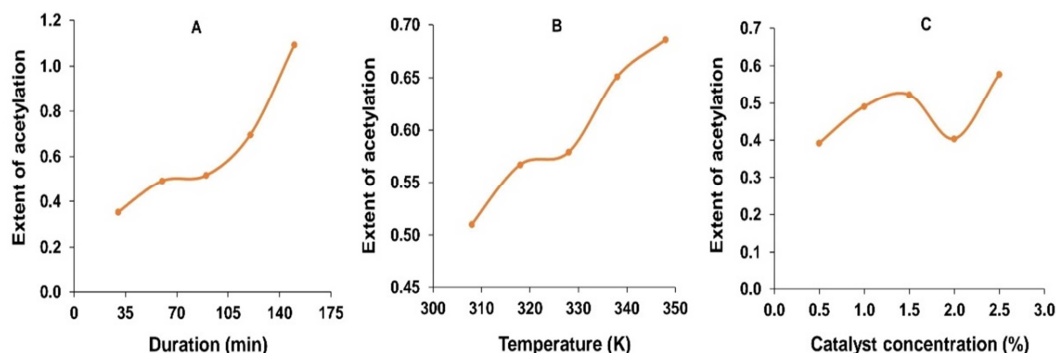


Figure 2. Effects of (a) acetylation duration (b) temperature, and (c) catalyst concentration on the extent of acetylation of *Cucumeropsis mannii* seed shell.

As acetylation time increased from 30 minutes to 150 minutes, the extent of acetylation also increased. This is likely because longer acetylation times resulted in more acetic anhydride diffusing into and being absorbed by the cell wall of the lignocellulosic materials, thereby increasing the extent of acetylation [2].

Just like with increase in acetylation duration, increase in acetylation temperature from 308 K to 348 K also led to increase in the extent of acetylation of CMSS. This may be due to the fact that higher acetylation temperatures induce the hydrogen bonding network in the hydroxyl groups of the CMSS to enlarge and rupture, producing reactive chemical sites for the acylating agent to bind to [8].

The extent of acetylation increased with increase in catalyst concentration from 0.5% to 1.0% and then decreased at catalyst concentration of 2.0%, which was followed by an increase at catalyst concentration of 2.5%. The increase in extent of acetylation as catalyst concentration increased suggests that the iodine catalyst increased the rate of acetylation. Although the exact function of iodine was unclear, it is likely that it provided  $I^-$ , which in turn activated the carbonyl group of acetic anhydride to create a highly reactive acylating agent. This acylating agent then reacted with hydroxyl group of the CMSS, which upon elimination of  $I_2$ , produced acetylated CMSS [27]. However, as the iodine concentration increased, a significant amount of undecomposed iodine was adsorbed on the active sites of the

CMSS, leading to a reduction in the contact area between acetic anhydride and hydroxyl. This effectively inhibited the acetylation reaction and led to a low extent of acetylation [7].

The trend of extent of acetylation with increase in catalyst concentration may also be attributed to a combination of acetylation and de-acetylation mechanisms as reported by [28]. During the increase in extent of acetylation at varied catalyst concentrations, acetylation mechanism may have outweighed de-acetylation while during decrease in extent of acetylation, de-acetylation mechanism may have outweighed acetylation mechanism. Thus, it appears that the problem of de-acetylation may be overcome for CMSS by increasing the amount of catalyst beyond 2%, which is suggested by the sharp increase in extent of acetylation at 2.5% catalyst. Similar behavior was observed by [28] for the acetylation of cotton using 4-dimethylaminopyridine as catalyst. The extent of acetylation was found to increase with increase in amount of catalyst up to 5%, which was followed by decrease in the extent of acetylation, with subsequent increase beyond 8% catalyst.

### 3.4. Kinetic Studies

The pseudo-first order, pseudo-second order and intraparticle diffusion plots for the acetylation of CMSS are shown in Figures 3a, b, and c, respectively. The obtained kinetic parameters are shown in Table 1.

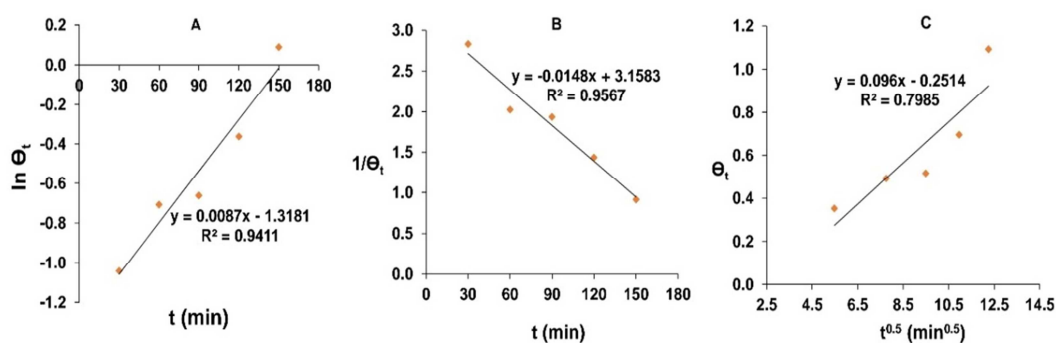


Figure 3. (a) Pseudo first order (b) pseudo second order, and (c) intraparticle diffusion plots for the acetylation of *Cucumeropsis mannii* seed shell.

**Table 1.** Kinetic parameters for the acetylation of *Cucumeropsis mannii* seed shell.

Parameter	Value
$\Theta_{o,exp}$	0.353
Pseudo first order kinetics	
$R^2$	0.9411
$k_1$ ( $\text{min}^{-1}$ )	-0.0087
$\Theta_{o,theo}$	0.2676
Pseudo second order kinetics	
$R^2$	0.9567
$k_2$ ( $\text{min}^{-1}$ )	-0.0148
$\Theta_{o,theo}$	0.3166
Intra-particle diffusion model	
$R^2$	0.7985
$K_{id}$ ( $\text{mg.g}^{-1}.\text{min}^{-0.5}$ )	0.0960
C	-0.2514

The linear regression coefficient ( $R^2$ ) values for the pseudo first order, pseudo second order, and intra-particle diffusion models are high, with values of 0.9411, 0.9567 and 0.7985, suggesting that acetylation of CMSS involved surface (physical) reaction, chemical reaction as well as intra-particle diffusion. A comparison of the kinetic models in terms of the  $R^2$  values shows that pseudo second order kinetics gave the best fit, with  $R^2$  value of 0.9567. This shows that pseudo second order kinetic model is the most suitable for describing the acetylation process, and thus suggests that the acetylation of CMSS was largely by chemical reaction [4]. The minimum extent of acetylation ( $\Theta_o$ ) calculated by this model was found to be 0.317 and the rate constant was  $-0.0148 \text{ min}^{-1}$ . Suitability of the pseudo second order kinetic model in describing acetylation of lignocellulosic materials has been reported by Arinze-Nwosu et al. for acetylation of *Borassus aethopum* coir [10].

### 3.5. Thermodynamic Study

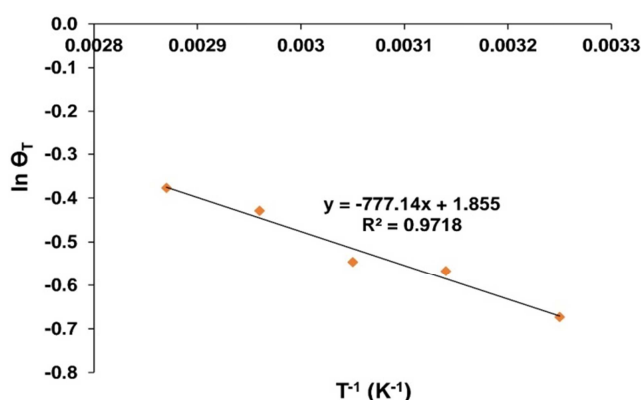
The thermodynamic plot and parameters for acetylation of CMSS are shown in Figure 4 and Table 2, respectively.

**Table 2.** Thermodynamic parameters for the acetylation of *Cucumeropsis mannii* seed shell.

Parameter	Value
$\Delta H$ ( $\text{kJ.mol}^{-1}$ )	6.461
$C_p$ ( $\text{kJ.mol}^{-1} \text{ K}^{-1}$ )	0.162
$T_o$ (K)	419
$\Theta_c$	1.002
$\Delta S$ ( $\text{kJ.mol}^{-1} \text{ K}^{-1}$ )	0.020
$\Delta G$ ( $\text{kJ.mol}^{-1}$ )	
308K	0.301
318K	0.101
328K	-0.099
338K	-0.299
348K	-0.499

The enthalpy change ( $\Delta H$ ) for acetylation of CMSS was  $6.461 \text{ kJ.mol}^{-1}$ . The positive value shows that the acetylation process was endothermic in nature. This also explains the

increase in the extent of acetylation of CMSS with increase in temperature observed in section 3.3.2. The critical temperature of acetylation ( $T_o$ ) was 419 K, which shows that acetylation of CMSS can easily take place at mild conditions. The critical extent of acetylation ( $\Theta_o$ ), heat capacity at constant pressure ( $C_p$ ), and change in entropy ( $\Delta S$ ) were 1.002, 0.162  $\text{kJ.mol}^{-1}.\text{K}^{-1}$ , and 0.020  $\text{kJ.mol}^{-1}.\text{K}^{-1}$ , respectively. The positive entropy value shows that there was increased disorderliness during the acetylation of CMSS. The Gibb's free energy ( $\Delta G$ ) was also positive, with values of 0.101 and 0.301  $\text{kJ.mol}^{-1}$  at 308 K and 318 K, respectively. But as the temperature was increased further, the  $\Delta G$  values became negative, with values of -0.099, 0.299, and -0.499  $\text{kJ.mol}^{-1}$  at 328 K, 338 K, and 348 K, respectively. This suggests that though acetylation took place at lower temperatures of 308 K and 318 K, the process was not spontaneous. But at higher temperatures (328 K – 348 K) it became spontaneous, showing that acetylation of CMSS took place by absorption of heat from the environment. Similar behavior was reported by Onwuka et al. for the acetylation of oil palm empty fruit bunch which gave  $\Delta G$  values of 943.3, -934.70, -2812.70 and -4690.70  $\text{J.mol}^{-1}$  at 303 K, 323 K, 343 K, and at 363 K, respectively [1].

**Figure 4.** Thermodynamic plot for the acetylation of *Cucumeropsis mannii* seed shell.

## 4. Conclusion

Acetylation of *Cucumeropsis mannii* seed shell was successful. The extent of acetylation increased with increase in acetylation duration, temperature and catalyst concentration. The acetylation process was endothermic in nature and was best described by the pseudo second order kinetics. The critical extent of acetylation, heat capacity at constant pressure, and change in entropy values were 1.002, 0.162  $\text{kJ.mol}^{-1}.\text{K}^{-1}$ , and 0.020  $\text{kJ.mol}^{-1}.\text{K}^{-1}$ , respectively. Spontaneous acetylation occurred at temperatures of 328 K – 348 K, but at lower temperatures (308 K and 318 K), the reaction was non-spontaneous. The critical temperature of acetylation was 419 K, which shows that acetylation of CMSS can easily take place at mild conditions, and so is an energy efficient process.



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