

STUDY THE KINETIC OF NEW PHOTO-STABILIZER (4-STEAROYLRESORCINOL) PRODUCTION USING BATCH REACTOR

Dr. M.M. Alfaize, Dr. S.A. Niema, G.J. Alhamar

Chemical Engineering Department, College of Engineering, Basrah University,
Basrah, Iraq

Abstract

4-Stearoylresorcinol was prepared by acylation of resorcinol with stearoyl chloride in the presence of zinc chloride as catalyst in a batch reactor. The temperature range of reaction was (50–80)°C. The rate of acylation increased with temperature up to (70 °C). The conversion of reactants appeared to follow second order kinetic model. The reaction rate constant was (0.0031 l/mol.min) and was higher at higher temperatures. Activation energy was (16.8258 kJ/mol). The optimal catalyst concentration was (2.9936 mol/l). Also, a quantitative relationship was derived to represent the weight of the product as a function to the reaction variables. The quantitative relationship gave mean deviation equal to (5%). The product concentration was measured by UV spectroscopy.

Keywords: - kinetic, Friedel–Craft reaction, photo–stabilizer, batch reactor.

الدراسة الحركية لتفاعل انتاج مثبت ضوئي جديد (4-ستيرويل ريسورسينول) باستعمال مفاعل الدفعات

أ.م.د. مصطفى محمد رضا الفائز، أ.م.د. صلاح عبد الوهاب نعمة، غدير جاسم محمد الحمر
قسم الهندسة الكيميائية، كلية الهندسة، جامعة البصرة

الخلاصة

حُضِر المَثَبِث الضوئي 4-ستيرويل ريسورسينول من تفاعل الريسورسينول مع كلوريد الستيرويل بوجود كلوريد الخارصين كعامل مساعد في مفاعل الدفعات. حيث تم دراسة تأثير ظروف التفاعل على معدل سرعة التفاعل عند درجات حرارية مختلفة وقد كان مدى درجة الحرارة المدروسة (50-80)°م. لوحظ أن معدل سرعة التفاعل يزداد بارتفاع درجة الحرارة وقد كانت أعلى قيمة له عند (70°م). أظهر التحليل الحركي للنتائج العملية أن التفاعل من المرتبة الثانية وأن ثابت سرعة التفاعل مساوي إلى (0,0031 لتر.مول.دقيقة). وأن طاقة التنشيط تساوي (16,8258 كيلوجول/مول) كما وجد أن التركيز الأمثل للعامل المساعد يساوي (2,9936 مول/لتر). كما تم اشتقاق علاقة كمية تمثل وزن المادة الناتجة كدالة لظروف التفاعل. ولقد كانت نسبة الخطأ للمعادلة المشتقة تساوي (5%). لقد استخدم جهاز تحليل الأشعة فوق البنفسجية لتتبع سير التفاعل وذلك بقياس تركيز المادة الناتجة ضمن مجال ظروف التشغيل المدروسة.
كلمات البحث :- الحركية، تفاعل فريدل كرافت، مثبت ضوئي، مفاعل الدفعات.

Introduction

Synthetic and natural polymers vary in their sensitivity to environmental influences. Ultraviolet radiation in sunlight plays a critical role in selecting plastics for

outdoor applications because it has sufficient energy to break chemical bonds [1]. The absorbed UV light cause the plastic material to become brittle, discolored, cracked and loss the mechanical properties [2]. This

problem was solved by incorporating or coating the plastics with a special chemical compounds called photo-stabilizers. Photo-stabilizers work by absorbing incident UV radiation and then re-emitting the absorbed energy as harmless heat not as radiation [3]. In recent decades, plastics have undergone a spectacular rate of growth. Whereas, initially they were mostly regarded as substitutes for other materials, Today, they are used in all branches of industry and everyday life and represent useful modern technical materials with versatile and to some extent irreplaceable applications.

Plastics are based on polymers, polymers are raw materials for plastics and they become plastics only after physical compounding and/or chemical hardening [1]. The term plastics refer to the final products that include not only the homogeneous polymeric starting material but also many additives such as stabilizers, fillers, plasticizers and pigments [4].

The weathering behavior of a plastic is one of the most important limiting factors in assessing and selecting a plastic for outdoor applications. The selection of a material by simple mechanical properties is ineffective if the material loss strength or discolors in service. Weathering involved the following factors solar radiation, temperature, humidity and pollutants [5].

Ultraviolet Light (UV) in solar radiation is a very high energy type of light that will easily damage plastics [6]. UV energy absorbed by plastics can excite photons which then create free radicals [7]. As further radicals are formed, the degradation of the polymer proceeds indefinitely in a chain reaction [8]. The

presence of catalyst residues and other impurities will act as free radical receptors and degradation occurs [7].

There are many ways of avoiding UV degradation in plastics such as the using of UV Stabilizers; they are colorless or nearly colorless organic substances [9]. They work by interrupting the photo degradation cycle to slow down or prevent the cycle from completing [5].

The production of any compound such as photo-stabilizer need a reactor in which the reaction occurs. Batch reactors are usually used for testing and studying new processes that have not been fully developed [10]. Batch reactors are very used in studies of reaction kinetics and thermal effects modeling because of reaction system that may be quite complex and not entirely known [11].

Yang H.M. and Wu H.E. investigated the kinetic of synthesizing dibenzyl phthalate via solid-liquid phase-transfer catalysis under anhydrous conditions in a stirred batch reactor. The effect of reaction conditions were all studied. The results showed that the reaction rate increases with increasing agitation speed, polarity of organic solvent, and temperature even without adding water and the reaction can be described by the pseudo-second-order kinetics. The reaction rate was extremely slow without using catalyst even at a higher temperature [12].

Pakdehi S.G. studied the kinetic of production methyl formcel from the reaction of trioxan and methanol. The reaction kinetics was studied in the presence of sodium hydroxide as catalyst in a temperature range of (25-50°C). The results showed that

the reaction followed second order kinetics at first stages of reaction and a third order kinetics at the rest stages. Also the activation energy was calculated which was equal to (18.3 kJ/mol) [13].

Izci A. and Hosgun H.L. studied the kinetics of synthesis isobutyl propionate from the reaction of propionic acid with isobutanol in the presence of (Amberlyst-15) as a catalyst using a stirred batch reactor at temperature range of (318 – 348) °K. The effects of reaction conditions were investigated. A pseudohomogeneous model was developed from the experimental data. The results showed that the reaction was depended on temperature, the mixing speed has a little effect on the reaction, the activation energy and the equilibrium constant was found equal to (52.03 kJ.mol⁻¹ and 5.19) respectively [14].

Motivation of study this acylation reaction is that without additives, plastics would not work but with them they can be made safer, cleaner, tougher and more colourful. Additives such as photo-stabilizers reduce the production costs and make products last longer, they help to save money and conserve the world's precious raw material reserves [15].

In the present research the reaction kinetic was studied to determine the order of the reaction, rate law constant and the apparent activation energy. Also, a quantitative relationship was studied to represent the weight of the product as a function to the reaction variables.

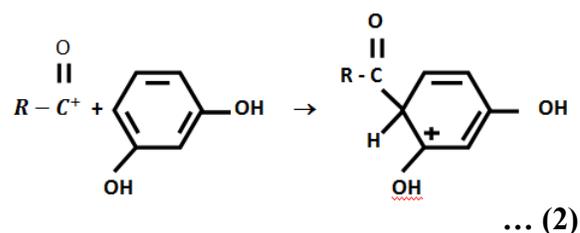
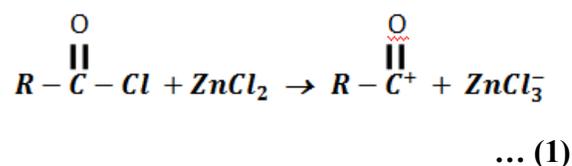
Background Information

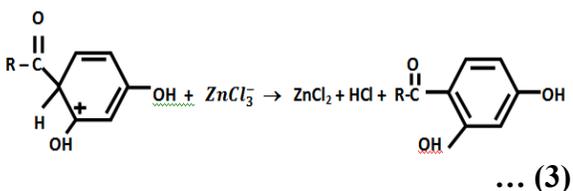
A Friedel-Craft acylation reaction is carried out by reacting resorcinol with

stearoyl chloride in order to substitute an acyl group onto the aromatic ring of resorcinol. The aromatic compounds are stable unsaturated ring systems that typically favor reactions that maintain the aromatic ring intact. In the electrophilic reaction of aromatic compounds, a hydrogen atom is substituted by an electrophile [16].

The mechanism of the reaction contains two steps: the substitution of the electrophile forms a carbon cation, then the elimination of one proton reestablish the aromatic character of the product. Friedel-Craft reaction is an example of a substitution of aromatic compounds in which a new carbon-carbon bond is formed by the substitution of an acyl group [16].

In the present reaction, zinc chloride (a Lewis acid) reacts with stearoyl chloride to form a charged electrophile (the acylium ion). Then the acylium ion reacts with the aromatic ring of resorcinol in a two steps substitution with the formation of 4-stearoylresorcinol.





Experimental Procedure

❖ Materials:-

The chemicals used in this work are as follow:-

- 1- Phosphoryl Chloride (POCl_3); it was supplied from Fluka Company.
- 2- Stearic Acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$); Stearic acid with purity (99%) was supplied from Fluka Company.
- 3- Resorcinol ($\text{C}_6\text{H}_6\text{O}_2$); Resorcinol with purity (98%) was supplied from Fluka Company.
- 4- Zinc Chloride (ZnCl_2); Zinc Chloride with purity (97%) was supplied from Thomas Baker Company.

❖ Procedure:-

Acylation reaction was performed in a (100 ml) three necked round bottom flask equipped with a reflux condenser, a thermometer and a nitrogen flow meter. The reactor was immersed in a constant temperature water bath. The water bath controlled within (± 0.5 °C). Agitation was provided with a mechanical stirrer which set at a constant speed throughout the experiment. Initially, the reactor was charged with (5.68 gram) stearic acid and (10 ml) phosphoryl chloride. The mixture was stirred with heating for (30 min) then (2.42 gram) resorcinol and (4.08 gram) of freshly fused zinc chloride were added to the reaction vessel with continuous mixing. After two hours the reaction was stopped, cooled, then (250 ml) of distilled water was added to the mixture, the product was filtered,

recrystallized from ethanol and dried in a vacuum oven at (75 °C) for (24 hrs) which gave pale yellow precipitate[17].

At various times, a sample was withdrawn quickly from the reactor with (1 ml) pipet. (0.1 ml) of the reaction medium is added to (50 ml) volumetric flask filled with distilled water to the marker. Then (10 ml) of chloroform is added that make the product (4-stearoylresorcinol) which precipitate after adding water dissolved in chloroform. From the lower layer (chloroform and dissolved product) withdrawn (0.1 ml) and dilute again in (10 ml) chloroform volumetric flask.

Analysis

The samples were analyzed by using UV spectroscopy (PD-303UV) at a wavelength (316 nm). Chloroform was used as the blank solvent.

Fig. (1) Shows the laboratory reaction system.



Reaction Kinetic

The reaction kinetic for the production of the photo-stabilizer is studied

❖ Test the Reaction Order:-

This usually achieved by measuring the concentration as a function of time then

using the differential or integral method to determine the reaction order and reaction rate constant (k) [18].

❖ Initial Rate Method:-

The initial rate method is a simple way to obtain reaction order. It consists of doing a series of experiments in which the initial concentration of reactants varied. The initial rates found by differentiating the data and extrapolating to zero time. Then the initial rates are compared, from which the reaction order can be deduced [19].

$$\frac{(\text{Rate})_1}{(\text{Rate})_2} = \frac{[A]_1^\alpha}{[A]_2^\alpha} * \frac{[B]_1^\beta}{[B]_2^\beta} * \frac{[C]_1^\gamma}{[C]_2^\gamma} \quad \dots (4)$$

❖ Integral Methods:-

These methods used to determine the order of a reaction by graphical plotting of the data for a particular experiment. The experimental data are plotted in several different ways by assuming a zero order reaction, first order reaction and a second order reaction and so forth. The order of the reaction is determined by which graph gives the best fit to the experimental data [19].

For zero order reaction

$$C_A = C_{A^\circ} - k t \quad \dots (5)$$

For first order reaction

$$\ln C_A = \ln C_{A^\circ} - k t \quad \dots (6)$$

For second order reaction (one reactant)

$$\frac{1}{C_A} = \frac{1}{C_{A^\circ}} + k t \quad \dots (7)$$

For second order reaction (two reactants)

$$k t = \frac{1}{C_{A^\circ} * (\theta_B - 1)} * \ln \left[\frac{(\theta_B - x)}{\theta_B * (1 - x)} \right] \quad \dots (8)$$

Figs. (9) to (11) show the non-linear relationship between the concentration data against different times for different temperatures. So in order to find the order of the reaction, the initial rate method will be used as follow:-

- At temperature = 70 °C, stearoyl chloride concentration = 1.8968 mol/l and resorcinol concentration = 2.1978 mol/l

Since

$$r_A = - \frac{dC_A}{dt} = - \frac{\Delta C_A}{\Delta t} \quad \dots (9)$$

Then

Time	Conversion	concentration
0	0	1.8968
20	0.1925	1.5316

$$r_{A^\circ} = 0.0183 \text{ mol.l}^{-1}.\text{min}^{-1}$$

$$r_{A^\circ} \cong 0.02 \text{ mol.l}^{-1}.\text{min}^{-1}$$

- At temperature = 70 °C, stearoyl chloride concentration = 3.7937 mol/l and resorcinol concentration = 2.1978 mol/l

Time	Conversion	concentration
0	0	3.7937
20	0.2008	3.0319

$$r_{A_1} = 0.038 \text{ mol.l}^{-1}.\text{min}^{-1}$$

$$r_{A_1} \cong 0.04 \text{ mol.l}^{-1}.\text{min}^{-1}$$

- At temperature = 70 °C, stearoyl chloride concentration = 1.8968 mol/l and resorcinol concentration = 4.3956 mol/l

Time	Conversion	concentration
0	0	1.8968
20	0.3673	1.0200

$$r_{A_1} = 0.0348 \text{ mol.l}^{-1}.\text{min}^{-1}$$

$$r_{A1} \cong 0.04 \text{ mol.l}^{-1}.\text{min}^{-1}$$

The order of the reaction with respect to each component found by equation (1):-

$$\frac{(\text{Rate})_1}{(\text{Rate})_0} = \frac{[A]_1^\alpha}{[A]_0^\alpha} * \frac{[B]_1^\beta}{[B]_0^\beta}$$

For the first case

$$\frac{0.04}{0.02} = \left[\frac{3.79372}{1.89686} \right]^\alpha * \left[\frac{2.198}{2.198} \right]^\beta \rightarrow \alpha = 1$$

For the second case

$$\frac{0.04}{0.02} = \left[\frac{1.89686}{1.89686} \right]^\alpha * \left[\frac{4.396}{2.198} \right]^\beta \rightarrow \beta = 1$$

Then the reaction rate equation has the form

$$(-r_A) = k C_A C_B$$

Since

$$\ln k = \ln A - \frac{E}{R} * \frac{1}{T}$$

Table (1) Rate constant logarithm vs. temperatures inverse

T (K)	1/T	K	Lnk
333	0.003003	0.0031	-5.77635
338	0.002959	0.0039	-5.54678
343	0.002915	0.0063	-5.06721
348	0.002874	0.0043	-5.44914
353	0.002833	0.0045	-5.40368

Then from fig. (12)

$$\ln k = 0.4541 - 2023.8 * \frac{1}{T}$$

$$\therefore \ln A = 0.4541 \rightarrow A = 1.5747$$

$$\text{and } -\frac{E}{R} = -2023.8 \rightarrow$$

$$E = 16825.8732 \frac{\text{J}}{\text{mol}}$$

$$\therefore E = 16.8258 \frac{\text{KJ}}{\text{mol}}$$

This is the activation energy of the reaction.

Correlation

Box-Benken design method is a type of statistical experiment especially applicable to optimization analysis [20]. By using this method, the effect of reaction variables such as reaction time (X_1), reaction temperature (X_2), stearoyl chloride concentration (X_3) and resorcinol concentration (X_4) that maximize the yield (Y) of the chemical reaction are investigated and analyzed. The technique is used to find a suitable relationship between the four variables and the observed response (Y).

The number of experiments (N) needed is estimated according to the following equation [21]:

$$N = n_j + n_\alpha + n_0 = 2^z + 2 * z + n_0 \\ = 16 + 8 + 1 = 25$$

In order to design the experiments, the operating range of the variable is first specified from laboratory experiments, thus
 c_1 = Reaction time (60 - 140) min.
 c_2 = Temperature of reaction (60 - 80) °C.
 c_3 = Stearoyl chloride concentration (1.8968 – 5.6906) mol/L.
 c_4 = Resorcinol concentration (2.1978 – 6.5935) mol/L.

The relationship between the coded variable (X) and the corresponding real variable as following [21]

$$X_{\text{coded}} = \frac{(c_{\text{actual}} - c_{\text{center}})}{(c_{\text{center}} - c_{\text{minimum}})}$$

$$X_1 = \frac{(c_1 - 100)}{40}$$

$$\begin{aligned}
 X_2 &= \frac{(c_2 - 70)}{10} \\
 X_3 &= \frac{(c_3 - 3.7937)}{1.8968} \\
 X_4 &= \frac{(c_4 - 4.3956)}{2.1978} \quad \dots (10)
 \end{aligned}$$

Usually, a low order polynomial in some region of the independent variables is employed. If the response is well- modeled by a linear function of the independent variables, then the approximating function is the first order model;

$$Y = B_0 + B_1 X_1 + B_2 X_2 + \dots + B_k X_k + \text{Error} \quad \dots(11)$$

$$Y = B_0 + B_1 X_1 + B_2 X_2 + B_3 X_3 + B_4 X_4 + B_{12} X_1 X_2 + B_{13} X_1 X_3 + B_{14} X_1 X_4 + B_{23} X_2 X_3 + B_{24} X_2 X_4 + B_{34} X_3 X_4 + B_{11} X_1^2 + B_{22} X_2^2 + B_{33} X_3^2 + B_{44} X_4^2 \quad \dots (13)$$

The regression coefficients are determined as follow [21]:-

$$B_i = \frac{\sum_1^{18} X_{iu} Y_u}{\sum_1^{25} X_{iu}^2} = \frac{\sum_1^{18} X_{iu} Y_u}{20}$$

$$B_{ij} = \frac{\sum_1^{16} X_{iu} X_{ju} Y_u}{\sum_1^{25} (X_{iu} X_{ju})^2} = \frac{\sum_1^{16} X_{iu} X_{ju} Y_u}{16}$$

$$B_{ii} = \frac{\sum_1^{25} X_{iu}^2 Y_u}{\sum_1^{25} (X_{iu})^2} = \frac{\sum_1^{25} X_{iu}^2 Y_u}{8}$$

$$B_0 = \frac{\sum_1^{25} Y_u}{\sum_1^{25} N} = \frac{\sum_1^{25} Y_u}{25}$$

$$\begin{aligned}
 Y_b &= 10.5677 + 1.8603X_1 + 0.8643X_2 + 4.1825X_3 + 0.1034X_4 + 0.0867X_1 X_2 + \\
 &1.0427X_1 X_3 - 0.8304X_1 X_4 - 0.0017X_2 X_3 + 0.1502X_2 X_4 - 0.2568X_3 X_4 - \\
 &0.5167X_1^2 - 0.5798X_2^2 - 0.7619X_3^2 - 0.9263X_4^2 \quad \dots (15)
 \end{aligned}$$

For (N=25), a check of lack of fit of the regression model is done by calculating the variance as follow [21]:-

If there is a curvature in the system, the polynomial of higher degree, such as the second order model must be used [22];

$$Y = B_0 + \sum_{i=1}^k B_i X_i + \sum_{i=1}^k B_{ii} X_i^2 + \sum_{i < j}^k \sum_j B_{ij} X_i X_j \quad \dots (12)$$

A second order polynomial mathematical model is employed to the independent variables. The general form of second order polynomial for four variables is representing by equation (13).

$$\begin{aligned}
 B_0 &= B_0 - 0.8 B_{11} - 0.8 B_{22} - 0.8 B_{33} - 0.8 B_{44} \\
 (X_{iu})^2 &= X_{iu}^2 - \frac{\sum_1^{25} X_{iu}^2}{N} \quad \dots (14)
 \end{aligned}$$

After the regression coefficients were determined, the second order model equation has the form represent by equation(15).

$$S_{AD}^2 = \frac{\sum_1^{25} n (Y_u - Y_b)^2}{N - \frac{(k+2)(k+1)}{2}} = \frac{25 \cdot 27.97197}{25 - 15} = 69.929 \quad \dots (16)$$

Reproducibility variance of the experiment is determined from four additional points in the experimental center as following:-

$$Y_0 = \frac{\sum_1^4 Y_0}{4}$$

$$S_{y_0}^2 = \frac{\sum_1^4 (Y_{0i} - Y_0)^2}{n_0 - 1}$$

$$S_{y_0}^2 = S_{y_0}^2 * N \quad \dots (17)$$

$$\therefore S_{y_0}^2 = 65.9975$$

$$F_R = \frac{69.9299}{65.9975} = 1.0595 \quad \dots (18)$$

A tabular value $F_T = 1.83$ is obtained for $f_{AD} = 10$ and $f_E = 25(25-1) = 600$ and $1-\alpha = 95\%$, from figure of **F-distribution**.

The regression model is adequate with 95% confidence because $F_R < F_T$ (Fisher's value < tabular value). By using the following equations, estimate the statistical significance of regression coefficient

$$S_{B^0}^2 = \frac{S_{y_0}^2}{25} = \frac{2.6399}{25} = 0.1055 \rightarrow$$

$$Y_b = 10.5677 + 1.8603X_1 + 0.8643X_2 + 4.1825X_3 + 1.0427X_1X_3 - 0.8304X_1X_4 \quad \dots (20)$$

Results and Discussions

The influence of changing the reaction conditions on the production of 4-stearoylresorcinol is discussed as follows:-

Effect of Reaction Time

Fig. (2) shows the effect of reaction time on the production of 4-stearoylresorcinol at different stearoyl chloride concentrations. Fig. (3) shows the

$$\Delta B_0 = \mp 2 * \sqrt{0.1055} = \mp 0.6496$$

$$S_{B_i}^2 = \frac{S_{y_0}^2}{20} = \frac{2.6399}{20} = 0.1319 \rightarrow$$

$$\Delta B_i = \mp 2 * \sqrt{0.1319} = \mp 0.7263$$

$$S_{B_{ij}}^2 = \frac{S_{y_0}^2}{16} = \frac{2.6399}{16} = 0.1649 \rightarrow$$

$$\Delta B_{ij} = \mp 2 * \sqrt{0.1649} = \mp 0.8121$$

$$S_{B_{ii}}^2 = \frac{S_{y_0}^2}{8} = \frac{2.6399}{8} = 0.3299 \rightarrow$$

$$\Delta B_{ii} = \mp 2 * \sqrt{0.3299} = \mp 1.1487 \quad \dots (19)$$

A check of statistical significance of regression coefficients indicates that regression coefficients $B_4, B_{12}, B_{23}, B_{24}, B_{34}, B_{11}, B_{22}, B_{33}$ and B_{44} are statistically insignificant. The final form of the second order regression model with 95% confidence may be given by equation (20) [21]:

effect of reaction time on the production of 4-stearoylresorcinol at different resorcinol concentrations.

In these figures, it is clear that the reaction time has a major effect on the production of 4-stearoylresorcinol and the product seemed to be increased with increasing the time of the reaction up to (2hrs). After that period of time, increasing the time of reaction has a little effect on the production. And that because the concentration of the reactants decrease to

small values that make the rate of the reaction decreased which lead to decreasing the production.

Effect of concentrations

The effect of stearoyl chloride and resorcinol concentrations on the production of 4-stearoylresorcinol is shown in figures (4) and (5).

It is clear that the production of 4-stearoylresorcinol increases with increasing the concentration of reactants because the number of collisions in unit time between the reactants will increase, that will increase the rate of the reaction which lead to increasing the production of 4-stearoylresorcinol [23]. The figures showed that, the stearoyl chloride concentration (limiting reactant) has a noticeable effect on the production of 4-stearoylresorcinol other than resorcinol concentration (excess reactant) which has little effect on the production almost not noticeable.

Effect of Catalyst Concentration

Fig. (6) shows the effect of adding $ZnCl_2$ as catalyst on the production of 4-stearoylresorcinol. The figure show that the production of 4-stearoylresorcinol increases by adding $ZnCl_2$ as catalyst, that because $ZnCl_2$ accelerates the reaction by providing alternate paths to products, each step of it has activation energy less than that for the reaction without $ZnCl_2$. In another words, the catalyst lowers the activation energy required for the reaction [24].

Fig. (6) shows also the effect of changing $ZnCl_2$ concentration on the production of 4-stearoylresorcinol. The figure shows that doubling the catalyst

concentration has a little effect on the reaction almost not noticeable. As shown in reaction mechanism, zinc chloride reacts with stearoyl chloride to form the acylium ion. Then the acylium ion reacts with resorcinol. From the mechanism it's clear that stearoyl chloride concentration controlled the reaction, in another word all stearoyl chloride will react with the 2.9936 mol/L so doubling the zinc chloride concentration will do nothing since stearoyl chloride concentration did not change.

Effect of Mixing Speed (rpm)

Fig. (7) shows the effect of mixing speed on the production of 4-stearoylresorcinol. The figure shows that the production increases with increasing the mixing speed. Since the rate of the reaction depends on the number of collisions (contacts) per unit time then increase the mixing speed will increase the collisions per unit time which lead to increasing the rate of the reaction (increasing the product).

Effect of Nitrogen Gas Flow

The effect of nitrogen gas flow rate on the production of 4-stearoylresorcinol is shown in fig. (8). It is clear that the continuous addition of (0.5 l/hr) of nitrogen gas to the reaction vessel increases the production of the photo-stabilizer. Since the water inhibited the reaction due to the strong adsorption of water on active sites of the catalyst ($ZnCl_2$) and since the heating medium is a water bath then using nitrogen gas is to rid the moisture that could enter the reaction vessel from the surrounding. Then minimize the moisture increasing the production of 4-stearoylresorcinol.

The same figure shows the effect of changing nitrogen flow rate on the production of 4-stearoylresorcinol. It's clear that doubling nitrogen gas flow rate has no effect on the production of 4-stearoylresorcinol, that because nitrogen gas do not takes part in the reaction it just rid the moisture from the reaction vessel.

Effect of Temperature

The influence of reaction temperature on the production of the photo-stabilizer at different time is shown in fig. (9). It can be seen that the product increases with increasing the temperature. Since increasing temperature increase the rate constant (eq. (22)) and since the rate constant related to the reaction rate by eq. (21) then increasing temperature increases the reaction rate.

Since

$$r_A = k C_A C_B \quad \dots (21)$$

And

$$k = A \text{Exp.} \left(-\frac{E}{RT} \right) \quad \dots (22)$$

From these two equations it's clear that increasing temperature increases the reaction rate and then increasing the production of the photo-stabilizer.

Since the two reactions are endothermic reactions which mean that the reactions need to absorb heat to happen then at (50 °C) the heat absorbs by the first reaction was not enough to start the reaction. Because the first reaction did not take place at (50 °C) that why the minimum temperature used in this work was (60 °C).

Conclusions

- 1- A quantitative relationship between the product (4-stearoylresorcinol) and the main effective variables is well represented by a second-order polynomial model.
- 2- The production reaction of photo-stabilizer was found to follow a second order kinetics model.
- 3- The reaction kinetics described by a homogeneous phase reaction model.
- 4- The activation energy for the reaction is equal to 16.8258 (KJ/mol).
- 5- The reaction was very slow without using catalyst.
- 6- The mixing speed and Nitrogen gas flow rate have a noticeable effect on the production.
- 7- The reaction was more safety to run at 70°C.

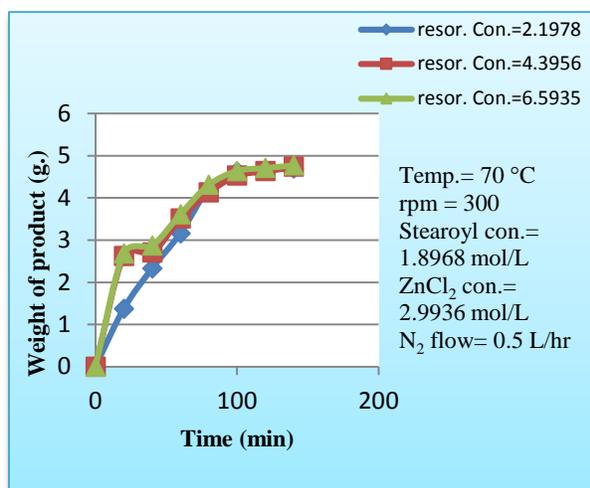


Fig. (2) Weight of product vs. reaction time at different stearoyl chloride concentrations.

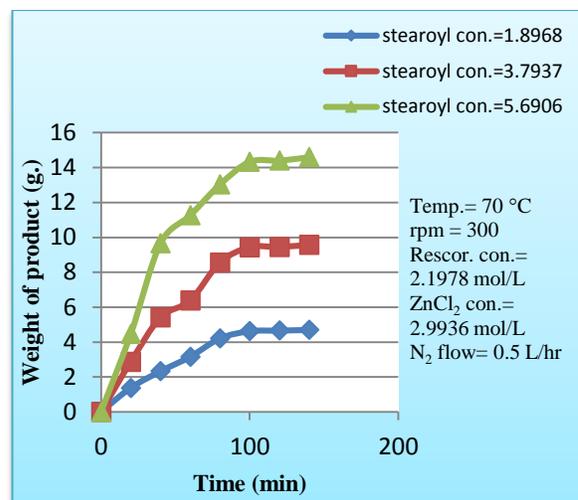


Fig. (4) Weight of product vs. stearic acid concentration at different catalyst concentrations

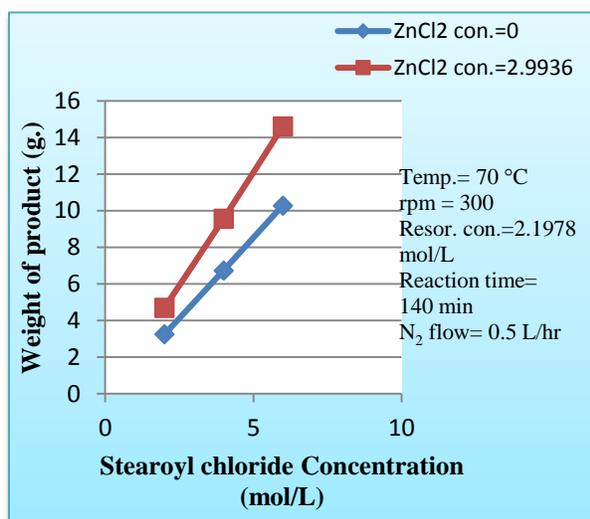


Fig. (3) Weight of product vs. reaction time at different resorcinol concentrations

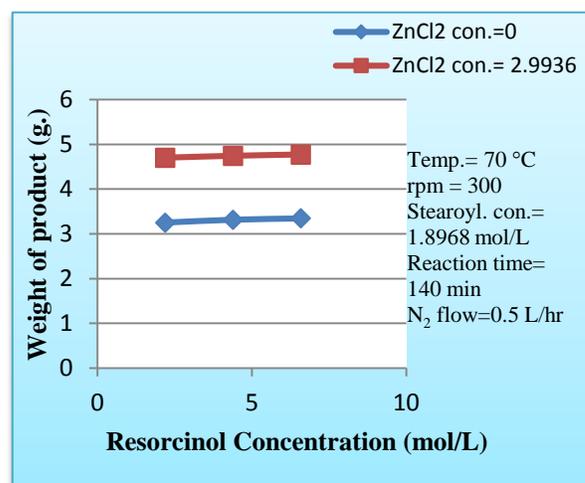


Fig. (5) Weight of product vs. resorcinol concentration at different catalyst concentrations

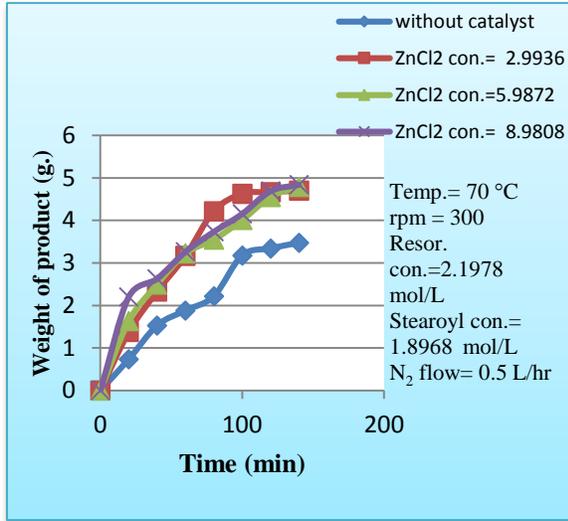


Fig. (6) Weight of product vs. time at different catalyst concentrations

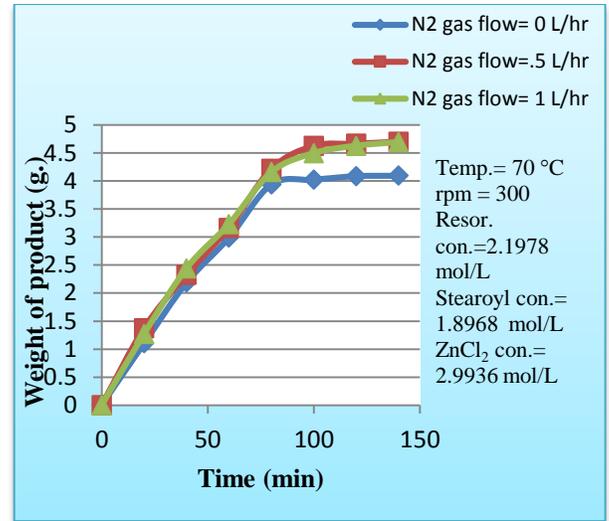


Fig. (8) Weight of product vs. time at different nitrogen gas flow rate

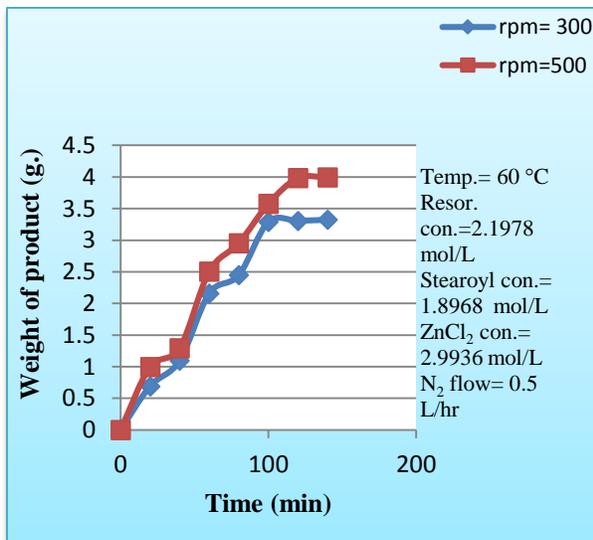


Fig. (7) Weight of product vs. time at different mixing speed

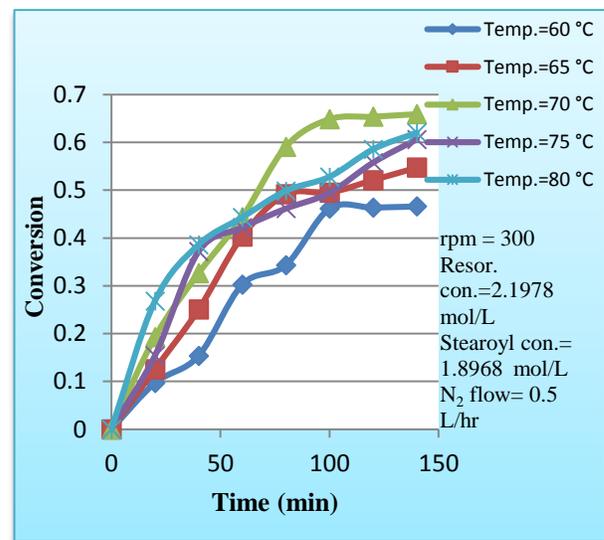


Fig. (9) Conversion vs. time at different temperatures

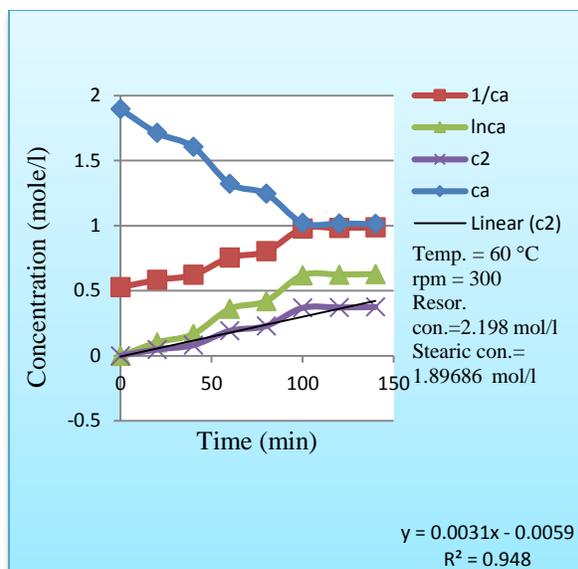


Fig. (10) Concentration vs. time at 60°C

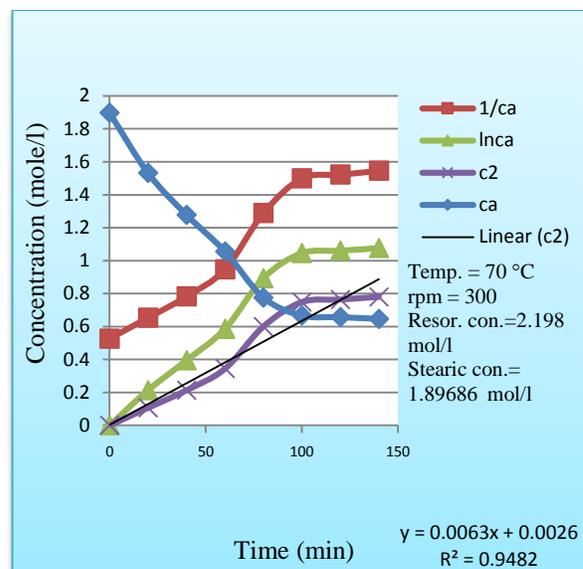


Fig. (12) Concentration vs. time at 70°C

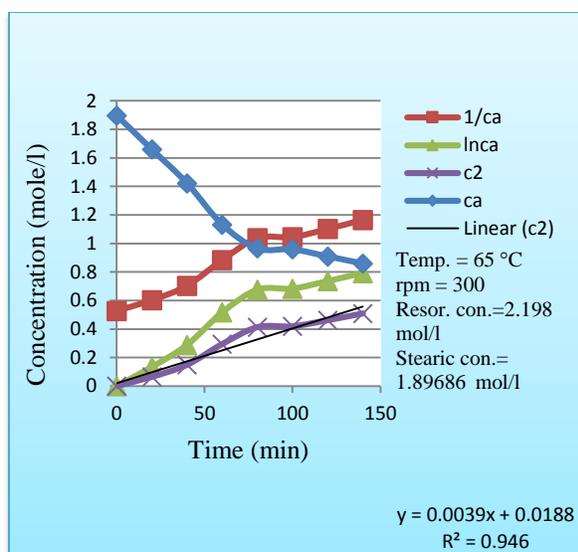


Fig. (11) Concentration vs. time at 65°C

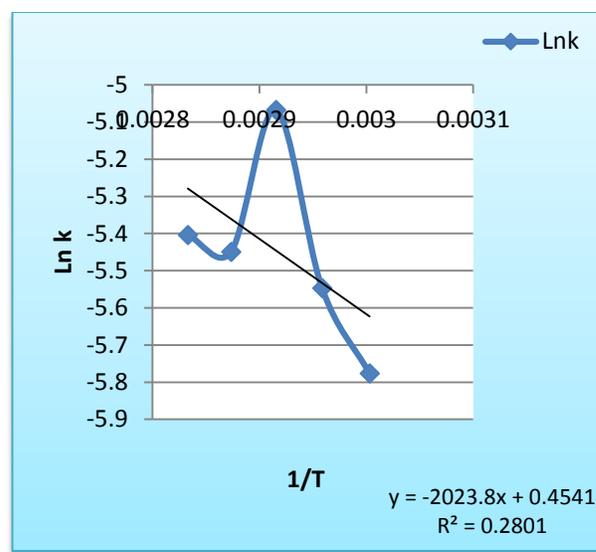


Fig. (13) Rate constant logarithm vs. temperatures

Nomenclature:-

Symbol	Description	Unit
A	Frequency factor	-
[A]	Concentration of component A	mol/l
[B]	Concentration of component A	mol/l
B_i, B_{ii}, B_{ij}	Regression coefficient parameters	-
C_A	Concentration of limiting component	mol/l
C_A⁰	Initial concentration of limiting component	mol/l
C_B	Concentration of co-reactant	mol/l
C_B⁰	Initial concentration of co-reactant	mol/l
ln ca	First order kinetic test	-
1/ca	Second order kinetic test	-
c₂	Second order kinetic with two components	-
E_a	Activation energy	J/mol
Error	Random experimental error	-
f_{AD}	Degree of freedom of total variance	-
f_E	Degree of freedom of variance of experiment in center points	-
F_T	Tabular value	-
F_R	Fisher's value	-
k	Reaction rate constant	l/mol.min
N	Total number of experiments	-
n_j	No. of core points experiments	-
n_α	No. of starlike points experiments	-
n_o	No. of null points experiments	-
r_A	Reaction rate	mol/l.min

rpm	Rotation per minute	cycle/min
S_{AD}	Total variance of experiments	-
S_{B0}, S_{Bi}, S_{Bii}, S_{Bij}	Variance of regression coefficients	-
S_{y0}	Total variance of experiments in center points	-
S_{y0}	Average variance	-
T	temperature	K
t	Reaction time	min.
X	Coded variable	-
x	conversion	-
Y_b	Calculated value	gm.

Greek Symbols:-

Symbol	Description	Unit
θ	constant	-

Subscripts:-

Symbol	Description	Unit
A	Limiting reactant	-
B	Co-reactant	-
0	Null points	-
1	First state	-
2	Second state	-

Superscripts:-

Symbol	Description	Unit
α	Reaction order with respect to component A	-
β	Reaction order with respect to component B	-
o	Initial state	-

References

- [1] Ullmann's "Encyclopedia of Industrial Chemistry", Electronic release Wiley-VCH-Weinheim. Germany, Sixth Edition, (2002).
- [2] Team Innovation, "Carbon Black and Plastics".
- [3] Zeus Industrial Products, "Weathering of Plastics", technical whitepaper, (2006)
- [4] National Silicates, "Leading Through Technology---Glossary".
- [5] Zeus Industrial Products, "Weathering of Plastics", technical whitepaper, (2006).
- [6] CleoSci, "About UV light and its dangers", website, (2004).
- [7] Zeus Industrial Products, "UV Properties of Plastics: Transmission and Resistance", technical whitepaper, (2006).
- [8] BASF Chemical Company, "Get a grip on light with Uvinul".
- [9] Othmer K., "Encyclopedia of Chemical Technology", Volum23, Wiley, Third Edition, (1983).
- [10] NationMaster, "Batch Reactor", Encyclopedia.
- [11] Grau M.D., Bonsfills A., Puigjaner Y.L. and Nougues J.M., "Kinetic and Thermal Studies in an Experimental Batch Reactor", Proceedings 7th Mediterranean Congress of Chemical Engineering, pp.155, Barcelona, (1996).
- [12] Yang H.M. and Wu H.E., "Kinetic Study for Synthesizing Dibenzyl Phthalate via Solid-Liquid Phase-Transfer Catalysis", Ind. Eng. Chem. Res., Vol.37, No.12, P.4536-4542, (1998).
- [13] Pakdehi S.G., "A kinetic study on the catalytic preparation of formaldehyde", Encyclopedia of Chemical Engineering, (2007).
- [14] Izci A. and Hosgun H.L., "Kinetics of Synthesis of Isobutyl Propionate over Amberlyst-15", Turk. J. Chem., Vol. 31, P.493 – 499, (2007).
- [15] British Plastics Federation, "Plastics Additives", (2008).
- [16] Hunt I., "Reaction of Arenes. Electrophilic Aromatic Substitution", Department of Chemistry, University of Calgary.
- [17] Niema S.A., "Synthesis, Characterization and Evaluation of Some New Triazole Derivatives as UV Stabilizer for Polyethylene", Ph.D. Thesis, Basrah University, (2003).
- [18] Fogler H.S., "Elements of Chemical Reaction Engineering", Prentice-Hall, (1986).
- [19] Ebbing D.D., Gammon S.D., Ragsdale R.O., "Essentials of General Chemistry", Houghton Mifflin, (2003).
- [20] Al-Badran F.A., "Chlorinted polyethylene Wax from Industrial Waste: Production, Characterization, Modeling and Kinetic Study" M.Sc. Thesis, Basrah University, (2003).
- [21] Montgomery D.C., "Design and analysis of experiments", Wiley and Sons, Fourth Edition, (1997).
- [22] Lazic Z.R., "Design of Experiments in Chemical Engineering", Wiley-VCH, (2004).
- [23] Rattan S., "Engineering Chemistry", Kataria & Sons, Second Edition, (2003).
- [24] Smith J.M., "Chemical Engineering Kinetics", McGraw-Hill, Second Edition, (1970).