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S. Darweech
Chemical Department, 12 Ramsis St. Cairo (Ministry of Ind.

A. Ramadan
University of Helwan.

A. Nasser
Department of Chemistry, Faculty of Science, Al-Azhar University

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CATALYTIC CONDENSATION REACTION BETWEEN BIS-PHENOL A OR ITS DERIVATIVES WITH UNCONJUGATED FREE FATTY ACIDS

S.Darweech*, A. Ramadan** and A. M. Nasser***

* Chemical Department, 12 Ramsis St. Cairo (Ministry of Ind.)
** University of Helwan.
*** Department of Chemistry, Faculty of Science, Al-Azhar Univ.

تأثير الحفازات على تفاعلات ثنائية الفينول أو مشتقاتها مع الاحماض الدهنية غير المشبعة

الغرض من هذا البحث زيادة سرعة التفاعل بين المشتقات ثنائية الفينول مع الاحماض العضوية غير المشبعة التي تعتبر المرحلة الاولى لاستخدام المنتج كعامل للبيوبات العائمة. تمت دراسة أكاسيد الاقلاء الارضية للمجموعة الثانية في الجدول الدورى كحفازات لهذا التفاعل من حيث تأثير درجة الحرارة ونسبة الحفز وقدرت سرعة التفاعل بقياس القيمة الحمضية للخليط على فترات زمنية وقد تم تقدير معدل التفاعل والطاقة الفعالة للحفازات وقد وجد أن أكسيد الكالسيوم أفضل هذه الحفازات حيث أنه أنقص زمن التفاعل الى ٣٫٣٠ ساعة حيث أنه بدون حفز لا ينتهي التفاعل الا بعد حوالى ٢٤ ساعة .

SUMMARY

The esterification reaction between Bis (4-hydroxy phenyl) propane and unconjugated fatty acids has been catalysed by the presence of one of the oxides of group II elements, viz: MgO, CaO, SrO and BaO. The reaction was followed by determining the acidity of samples withdrawn periodically from the reaction mixture. The working conditions of applying the alkaline earth metal oxides as catalysts, have been discussed. The optimum conditions for completion of the reaction at the minimum time are given.

Previous work on the effect of CaO on the esterification process draw the attention to investigate the rest of G II elements.

INTERDUCRION

Various catalysts were employed for the preparation of bisphenol A esters. These cotalysts include Mg-MgO[1],alkali metal hydroxides[2-5], organic amines[6]and H_3BO_3-H_2SO_4[7]. Many of these compounds were incrporated in the preparation of water-soluble vehicles for paints[8]. The aim of the present investigation is mainly concerned with studying the feasibility of applying the oxides of group II elements (MgO, CaO, SrO and BaO) to activate the esterification process of bisphenol A- [Bis (3,5-dihydroxyphenyl) propane] or its derivatives with linseed oil fatty acids.

EXPERIMENTAL:

All chemicals and reagents were of the highest purity available. These were oleic acid, linseed oil fatty acids, potassium hydroxide, ethyl alcohol, benzene and phenol phthalein indicator.

Method of preparations[8]:

Fusion method:

A mixture of bisphenol A (0.1 mole; 22.8g), linseed oil fatty acids (0.2 mole; 56g) and the catalyst was heated at 383 K, 413 K and 443 K under continuous stirring and inert gas blanket. During heating aliquate samples were withrawn periodically for acid value determinations. The catalysts investigated were MgO, CaO, SrO and BaO, at 0.02, 0.04 and 0.06 mole concentration .

The reaction was terminated when an acid value below 20 mg KOH was reached.

Calculation of the apparent energy of activation (E_a) was carried out using the conventional method[9], by applying the Arrhenius equation :

$$\log \frac{K_2}{K_1} = - \frac{E_a}{2.303\ R} \frac{(T_2-T_1)}{T_2\ T_1}$$

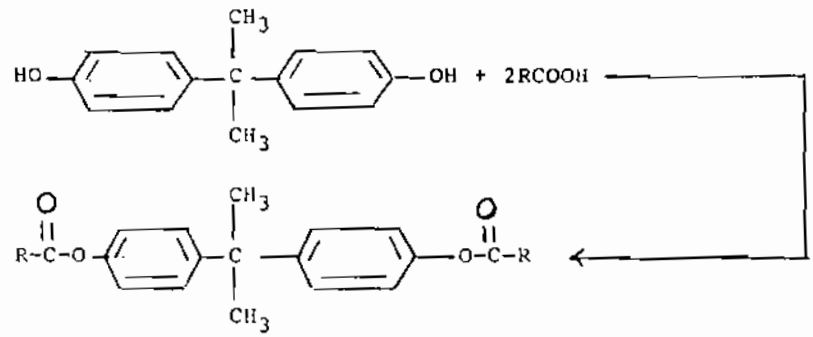
where:K_1,K_2 the activation constants at temperaturesT_1,T_2 and R=1.985 calories. Integration gives:

$$\log K = - \frac{E_a}{2.303\ R} \cdot \frac{1}{T}$$

where, K is the velocity constant, T is the absolute reaction temperature. Plotting log K against 1/T give a straight line.

RESULTS AND DISCUSSION :

The esterification of bisphenol A and fatty acidsis represented by the equation:



The effect of adding an alkaline earth metal oxide on the esterification reaction between linseed oil fatty acids and bisphenol A has been studied. The esterification reaction is of importance in the filed of surface coating technology, in particular for water soluble paints.

Trials were first performed using pure oleic acid and CaO as a catalyst at 443 K.[8]

Table (1): Effect of CaO on the esterification process of bisphenol A with oleic acid at 443 K .

Mole CaO	0.02	0.04	0.06
Time(hrs.)		Acid value	
0.5	138	75	52
1.5	118	60	35
2.5	89	55	32
3.5	84	55	25
4.5	82	50	23

Table (1) shows the effect of CaO on the esterification process of bisphenol A with oleic acid.

Table (2) shows the effect of the alkaline earth metal oxide on the esterification yield of bisphenol A or its derivatives with linseed oil fatty acids. The procedure used to achieve the extent of esterification was the acid value determination method at different temperature and different concentration of the alkali metal oxide.[11]

The table is self explanatory and indicates that CaO is the most effective of the group in temoving water from the rection medium at a minimum time. This sequel is quite clear inspite that it agrees with the law of periodicity of the group. This may help in assessing that the reaction is not affected by the properties of the metal oxide added. In other words, the catalyzing effect of the metal oxide depends ptimarily on either the ptoperties of the bisphenol A or those of the fatty acids. The comparison between the acid values in Table 1 and Table 2 at the same CaO concentration and at the same temperature indicates that CaO does not play any role with the acid but most probably its effect is connected with the bisphenol A. Moreover if the effect of the metal oxide is related to the fatty acid, there would be a saponification reaction occurring simultaneously with the esterification reaction. Such phenomenon does not observed except in case of MgO. The results of magnesium oxide(Table 2) reveal

Table (2) : Effect of the alkaline earth metal oxide (AEMO)on the esterification yield of bisphenol A and linseed oil fatty acids

Temperature (K)		383					413				443			
AEMO (Mole)	Time (hrs)	Acid Value												
		Without catalyst	MgO	CaO	SrO	BaO	MgO	CaO	SrO	BaO	MgO	CaO	SrO	BaO
0.02	0.5	-	112	197	-	202	156	198	-	128	141	138	-	161
	1.5	-	120	196	-	151	124	173	-	145	166	118	-	166
	2.5	-	168	198	-	100	143	145	-	147	140	89	-	157
	3.5	-	182	-	-	130	158	145	-	146	144	84	-	149
	4.5	-	-	-	-	-	-	135	-	138	-	82	-	135
0.04	0.5	-	162	190	-	133	140	173	-	117	170	74	203	132
	1.5	-	129	140	-	130	122	69	-	142	170	60	182	118
	2.6	-	150	135	-	130	142	103	-	145	160	54	170	105
	3.5	-	168	120	-	132	15	86	-	150	138	54	-	92
	4.5	-	171	115	-	130	-	89	-	-	129	49	-	83
0.06	0.5	190	122	176	-	125	11	122	193	102	159	52	191	122
	1.5	179	139	89	-	118	120	74	187	96	153	35	170	104
	2.5	163	140	84	-	105	140	50	186	91	145	32	163	101
	3.5	150	-	53	-	105	140	40	183	89	-	23	157	105
	4.5	-	-	73	-	87	-	46	-	100	-	23	-	-

that the mixture is more acidic i.e, a release of hydrogen ions takes place. This may be due to a substitution reaction between hydrolysable hydrogen of the bisphenol A and magnesium oxide. The ionic character of MgO [10] dictates the correctness of this interpretation. Moreover the comparison between the acid values in the presence and absence of MgO indicates insignificant improvement of the reaction .

Order of the reaction :

Figures 1,2,3 and 4 shows the sequence of conversion of the acid value as function of time taking into consideration that the standard acid value is 220. Figure 5 shows that the order of the reaction according to the graphical method[9] is zero order, a straight line is depicted, from which the rate constant of the reaction K can be obtained .

At normal condition, i.e, without addition of any of the AEMO the reaction may not be completed after 24 hrs where the acid value is nearly about 150 mg KOH On the other side, the addition of CaO reduces the acid value to 23 mg KOH after 3.5 hrs.

The activation enegry (E_a) calculated from Arrhenius equation for metal oxide at 0.06 mole are shown in Table (3)

Table (3): The activation engery(E_a) for metal oxide at 0.06 mole

Metal oxide	Temperature (K)	Time (hrs)	E_a (joul/mole)
MgO	383-413	1	2.3
SrO	383-413	2	3.2
BaO	383-413	2	0.8

In case of CaO, the activation enerygy E_a was calculated from figure (6) and found to be 4.5 joul/mole.

CONCLUSIONS :

Raising the reaction temperature leads to decrease in the converasion percentage in the case of MgO and increase in case of CaO, SrO and BaO. Increasing the catalyst concentration leads to an increase of the rate of converastion in all employed oxides and also inceasing the reaction time leads to increase in the conversion percentages.

CaO is an excellent catalyst for the reaction at 0.06 mole concentration and 443 K. However the activity of the other oxides employed can be arranged in the order BaO>MgO>SrO.

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FIGURE CAPTIONS:

Figure 1: The conversion percentage of esterificantion of fatty acids and bisphenol A in the presence of 0.06 mole at 443 K;(1) MgO , (2) CaO (3)SrO and (4) without catalyst and BaO at 443 K .

Figure 2: The coversion percentage in presence of(1) 0.02(2),0.04 and(3) 0.06 mole CaO at 383 K.

Figure 3: The conversion percentage in presence of(1) 0.02(2), 0.04 and (3) 0.06 mole CaO at 413 K.

Figure 4: The conversion percentage in presence of(1) 0.02,(2) 0.04 and (3) 0.06 mole. CaO at 443 K.

Figure 6 : Log Rate versus 1/T at different concentrations of CaO (0.02,0.04 and 0.06 mole) at 383, 413 and 443 K.

Figure 5 : Measurements of the order of the reaction of alkaline earth X versus t at 0.04 mole catalyst at 443 K .

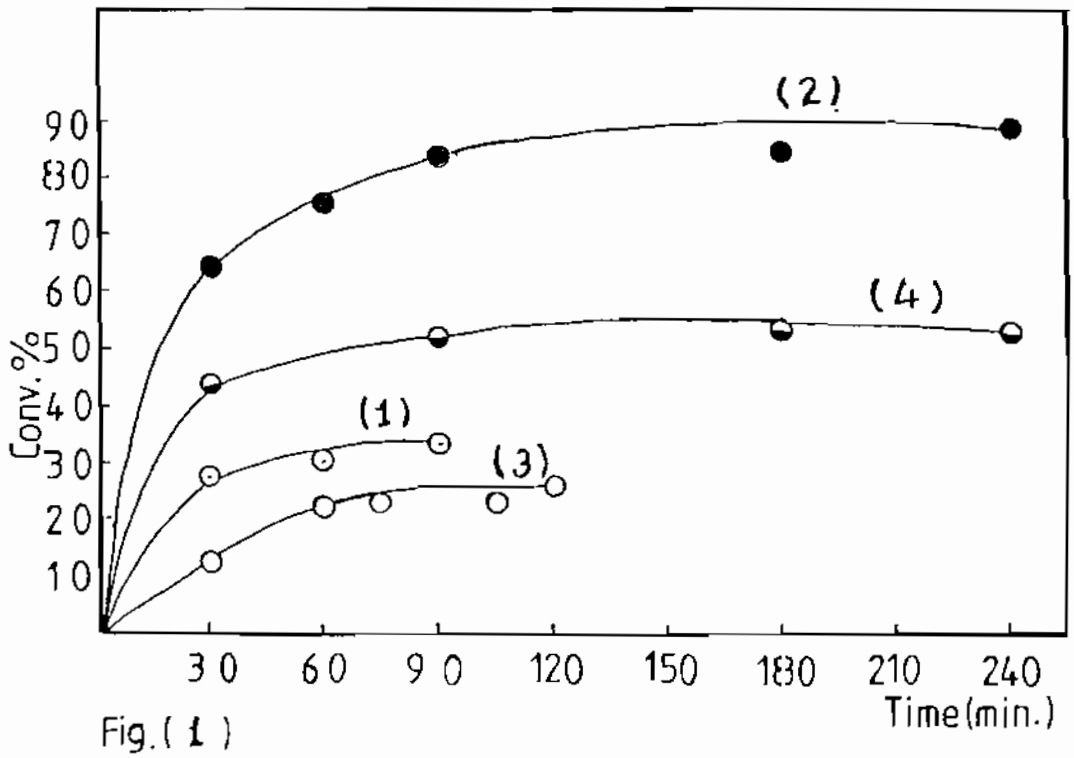
(2)
(4)
(1)
(3)
Conv.%
90
80
70
60
50
40
30
20
10
30
60
90
120
150
180
210
240
Time(min.)

Fig.(1)

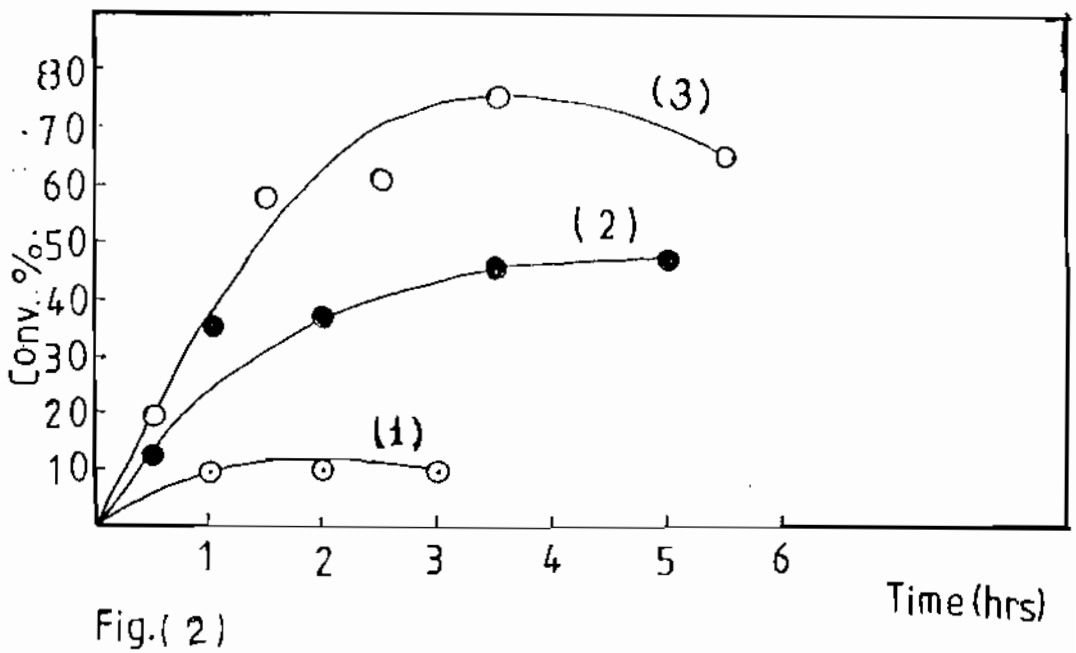
(3)
(2)
(1)
Conv.%
80
70
60
50
40
30
20
10
1
2
3
4
5
6
Time(hrs)

Fig.(2)

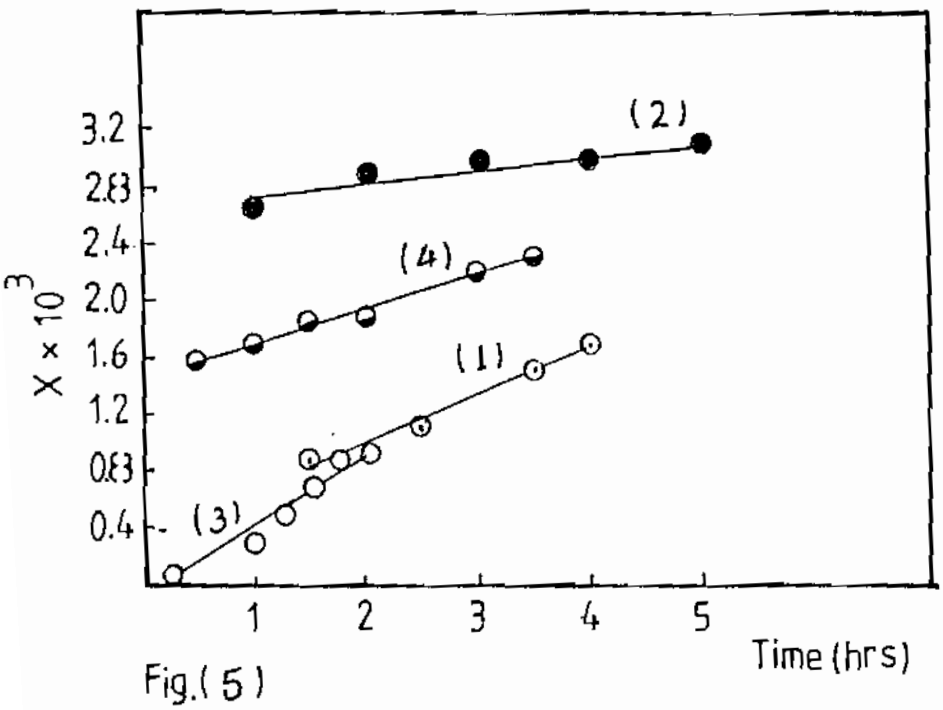
X × 10^3
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
(2)
(4)
(1)
(3)
1
2
3
4
5
Time (hrs)

Fig.(5)

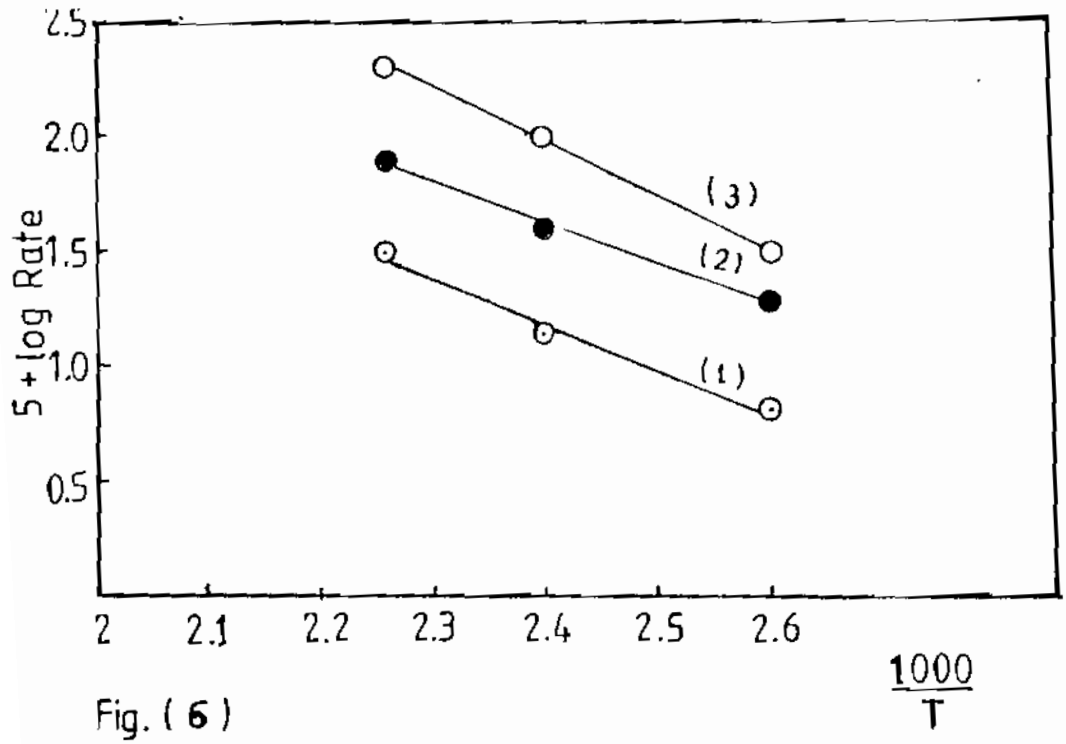
5 + log Rate
2.5
2.0
1.5
1.0
0.5
(3)
(2)
(1)
2
2.1
2.2
2.3
2.4
2.5
2.6
1000/T

Fig. (6)

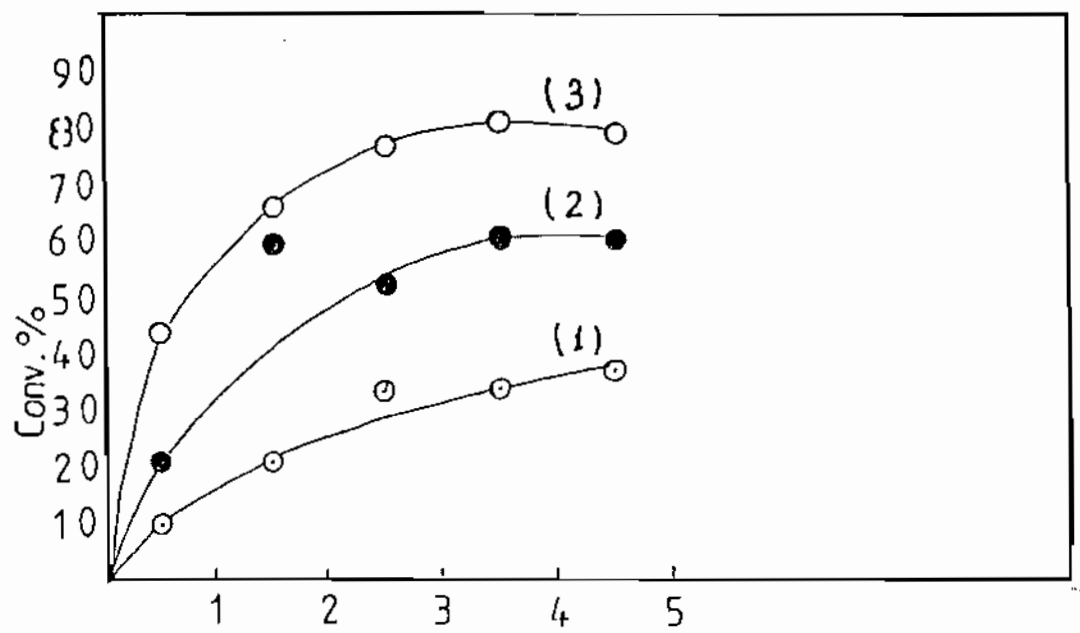
90
80
70
60
50
40
30
20
10
Conv.%
(3)
(2)
(1)
1
2
3
4
5
Time (hrs)

Fig.(3)

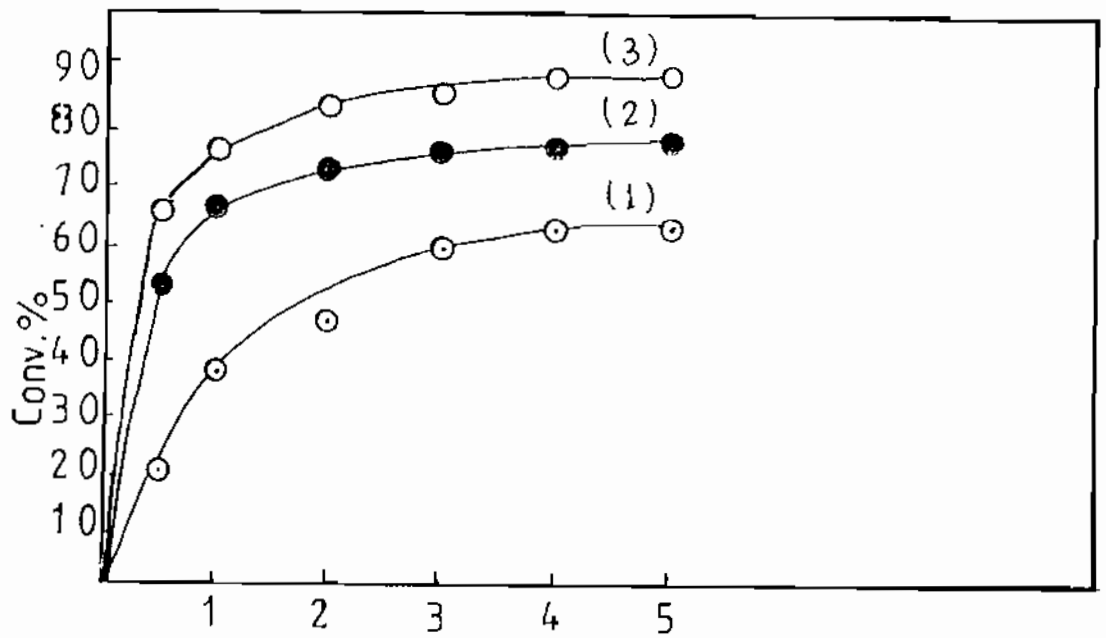
90
80
70
60
50
40
30
20
10
Conv.%
(3)
(2)
(1)
1
2
3
4
5
Time (hrs)

Fig.(4)