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Contribution to the Preparation of Melamine from Urea*

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Increased production of urea and lower costs of production focused the interest on the possibilities of melamine production using urea as a starting material instead of dicyandiamide usually employed. In this paper an aproach to this problem is described.

Kazarnovskij and Malkina[1] have shown that urea can give, when submitted to a multistep pyrolytic reaction high yields of melamine. Experiments were carried out in closed vessels under the pressure of gases evolved in the course of the reaction. According to their work yields of melamine reached a maximum at 400° after 15 min. Prolongation of heating decreased the yields very rapidly. The pressures corresponding to the various conditions used in their work were not measured and the highest experimental temperature was 400°.

A survey of the literature[2-4] revealed that the pressures recorded during the pyrolysis of urea in presence of ammonia reached hundreds of atmospheres. The highest experimental temperature studied was 425°[2,4]. It was further found that the pressures under the conditions employed by Kazarnovskij and Malkina were not reported. From the theoretical and practical point of view it was of interest to determine:

1 — Reaction conditions in a wider temperature range, specially covering temperatures higher than that already applied.
2 — Influence of the packing ratio on yield.
3 — Influence of the packing ratio on pressure.
4 — Pressures under the conditions performed.

In order to establish proper reaction conditions, a number of preliminary tests were carried out, under the conditions of maximum yields described in the literature. A series of experiments at constant packing ratio and temperature were performed and changes of yields caused by various reaction times were recorded. Bath temperatures from 360° to 560° and heating times from 5 to 90 minutes respectively, were surveyed. In addition, in some experiments pressure was also measured.

EXPERIMENTAL

Experiments were carried out in the preliminary test reaction vessel furnished by the American Instrument Co., Inc.** The capacity of the vessel was approxi-

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mately 103 ml., and Jena test tube liners 18×180 mm (closure 22×35 mm) were used. The desired temperatures were achieved by means of an electrically heated lead

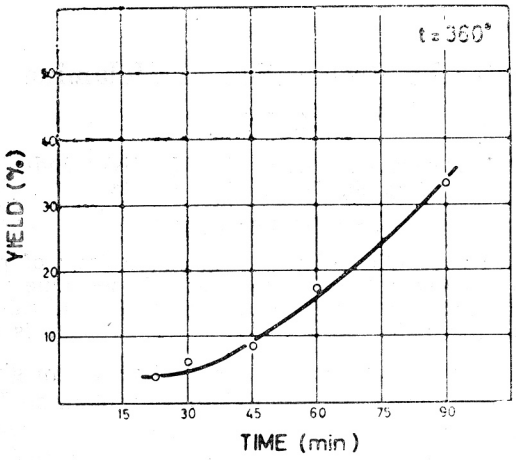

Fig. 1. Yield of melamine *vs.* heating time at 360° and constant packing ratio (0.2 g/ml). Pressure measured after 90 min was 150 p.s.i.

bath and recorded with a mercury termometer. Heating control was performed by means of a variable-voltage transformer. The Bourdon tube dial pressure gauge was used for pressure measurements.

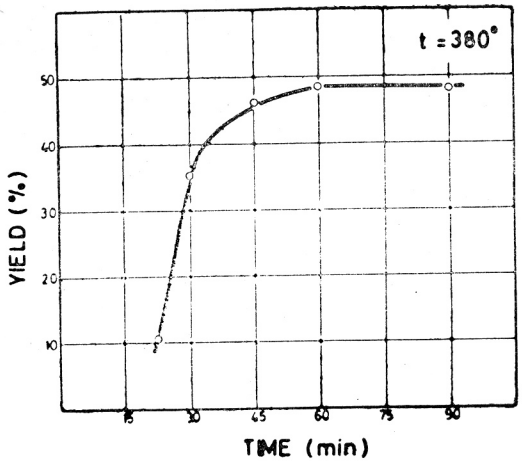

Fig. 2. Yield of melamine *vs.* heating time at 380° and constant packing ratio (0.2 g/ml). Pressure measured after 60 min was 160 p.s.i.

Initially three series of preliminary tests at a constant reaction time of 22.5 min.* were performed. In accordance with these tests packing ratio 0.2 g/ml

* The average of the times corresponding to maximum yields presented by Kazarnovskij and Malkina[1] and Giger[4].

was chosen as most convenient. Bulk density of urea crystals available (»Montecatini«) was approximately of the same order and it was necessary to melt urea when packing ratio 0.4 g/ml was desired. During the melting and moulding of urea deammonation took place and the percentage of biuret in moulded material increased. This was considered as a possible source of error and applied in a limited number of tests only.

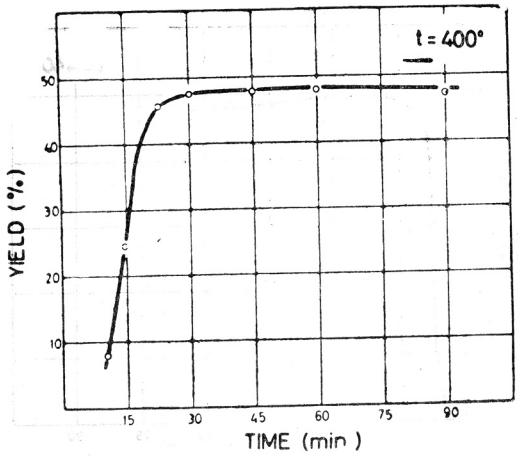

Fig. 3. Yield of melamine *vs.* heating time at 400° and constant packing ratio (0.2 g/ml). Pressures were measured after 10 min (160 p.s.i.), 15 min (170 p.s.i.) and 30 min (140 p.s.i.).

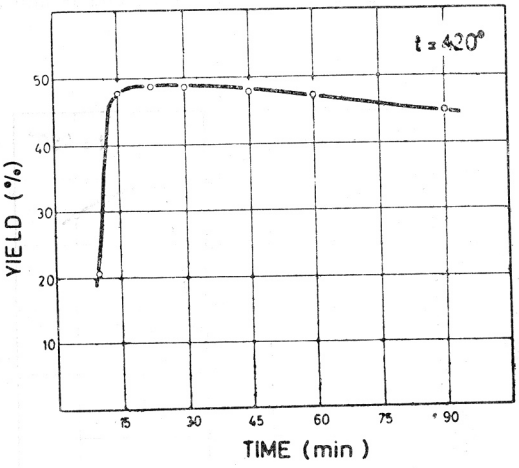

Fig. 4. Yield of melamine *vs.* heating time at 420° and constant packing ratio (0.2 g/ml). Pressures were measured after 5 min (200 p.s.i.) and 30 min (160 p.s.i.).

After the preliminary tests, experiments dealing with various reaction times at a constant temperature and packing ratio were performed. Reaction times were as follows: 5, 10, 15, 22.5, 30, 45, 60, and 90 min. Series of experiments under the conditions described were carried out at temperatures 360, 380, 400, 420, 440, 460, 480, 500, 520, 540, and 560°C. Pressures were measured in some experiments only. In the experiments where pressure was measured the samples of products were not representative due to sublimation of melamine. Therefore, additional experiments

were performed under the same conditions but without pressure measurement in order to obtain a proper sample of melamine present in the reaction product.

In all the experiments the products were analysed by means of the gravimetric determination of melamine as the practically insoluble salt of cyanuric acid[5]. The relative error of melamine determination was less than 1%.

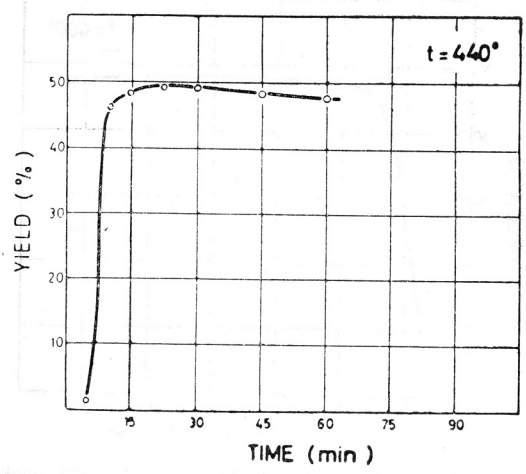

Fig. 5. Yield of melamine *vs.* heating time at 440° and constant packing radio (0.2 g/ml). Pressures were measured after 5 min (150 p.s.i.) and 15 min (130 p.s.i.).

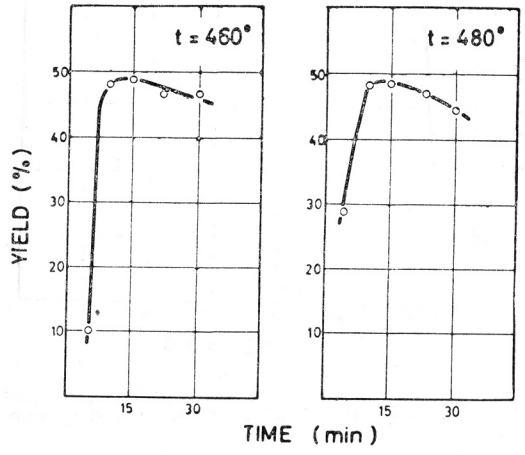

Fig. 6. Yield of melamine *vs.* heating time at 460° and 480° and constant packing ratio (0.2 g/ml). At 460° pressures were measured after 5 min (180 p.s.i.), 10 min (160 p.s.i.) and 15 min (150 p.s.i.); corresponding pressures at 480° were 190, 160, and 140 p.s.i.

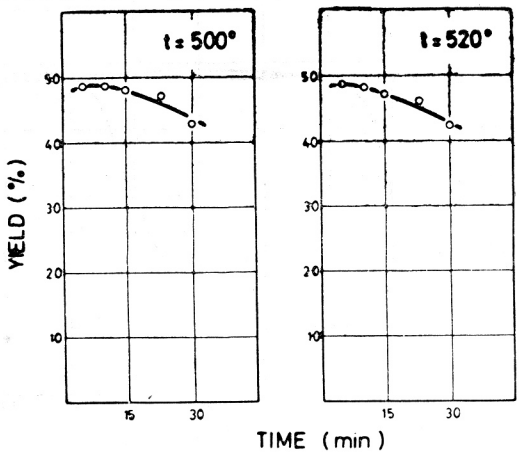

Fig. 7. Yield of melamine *vs.* heating time at 500° and 520° and constant packing ratio (0.2 g/ml). Pressures measured after 5 min were at 500° 140 p.s.i. and at 520° 130 p.s.i.

RESULTS

Table I presents the results of the preliminary tests carried out at constant reaction time 22.5 min.

TABLE I

Run No.	Packing ratio g/ml	Yield %			Pressure p.s.i.
		400°	420°	440°	
1	0.1	45.1	47.4	p.m.	170/440°
2	0.2	44.6	p.m.	48.3	130/420°
3	0.4	p.m.	47.2	48.0	160/400°

p. m. — pressure measurement

As shown in Table I pressure measurement was performed once at 440, 420, and 400°.

The results of the experiments are ploted in graphs presented in Figs. 1—8. The results obtained at various reaction times and highest temperatures are given in Table II.

TABLE II

Temperature °C	Time min	Pressure p.s.i.	Yield %
	5	150	46.9
540	10	—	46.3
560	5	140	46.7

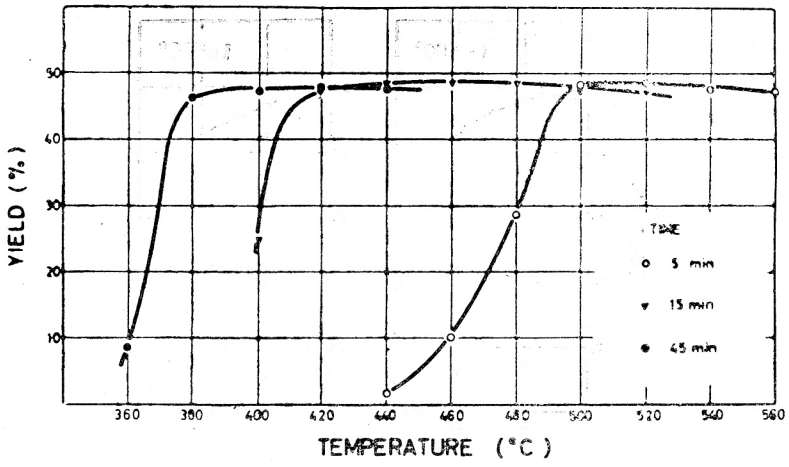

Fig. 8. Yield of melamine *vs.* temperature at various reaction times (5, 10, and 45 min) and constant packing ratio (0.2 g/ml).

DISCUSSION

The conclusions drawn from the preliminary tests can be summarized as follows:

1 — Pressures observed were of the order of 150 p.s.i. (aproximately 10 atm).
2 — There was no significant influence of packing ratio on resulting yields.
3 — There was no remarkable influence of packing ratio on the recorded pressures.

The most interesting result of the preliminary tests was the existence of relatively low pressures during the reaction under the conditions examined. The same fact was also proved in the numerous experiments performed over a wide range of temperatures. There was also a good evidence that the yields obtained were of the order of those previously reported, with the exception of the results presented by Kazarnovskij and Malkina[1]. These authors prepared melamine from urea with the maximum yield of 63%. Our experiments, performed under conditions very similar to those applied by Kazarnovskij and Malkina, gave significantly different results and appeared to correspond better with the data supplied by other authors[2–4,6].

Besides this, it should be mentioned that there were some discrepancies in the presentation of data due to the existence of two alternative formulas for the stoichiometric calculation:

$$3\,H_2NCONH_2 \longrightarrow (H_2NCN)_3 + 3\,H_2O \qquad (I)$$

$$6\,H_2NCONH_2 \longrightarrow (H_2NCN)_3 + 3\,CO_2 + 6\,NH_3 \qquad (II)$$

Neither formula I nor II is acceptable without objection because it was established that gaseous products consisted of water, ammonia and carbon dioxide[6]. Moreover, the solid product was always a mixture containing variable amounts of melamine. These formulas were used in spite of their inexact character for the purpose of simplicity in the presentation of data.

Yields presented in this paper are in accordance with formula I. It is obvious that the calculated yields would have the double numerical value by using formula II.

It is interesting to point out the observed fact that with the increased packing ratio the corresponding pressures were approximately of the same value. If we consider the final stages of melamine formation during the pyrolysis of urea as an amination of cyanuric acid and related hydroxyamino--*s*-triazines, the process can be assumed as an equilibrium process of replacement of hydroxyl groups by amino groups. The gaseous mixture contains increasing amounts of water as the process proceeds and less ammonia, while the nitrogen content of solid products increases with the increased temperature. It seems there is no reason for a pressure increase, since ammonia entering into the solid products evolves an equivalent quantity of water. This consideration is in accordance with the observed pressures of 10 atm which vary within the narrow limits of ± 2 atm aproximately.

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REFERENCES

1. S. N. Kazarnovskij and N. I. Malkina, *Zhur. Priklad. Khim.* **31** (1958) 452.
2. H. Kinoshita, *Rev. Phys. Chem. Japan* 23 (1953) 1; *cf. C. A.* **49** (1955) 340e.
3. H. Kinoshita, *Rev. Phys. Chem. Japan* 24 (1954) 19; *cf. C. A.* **49** (1955) 14007i.
4. P. Giger, *Thesis, ETH-Zürich* 1958.
5. S. N. Kazarnovskij and O. I. Lebedev, *Ref. Zhur. Khim.* **1957**, 19739.
6. E. Lienhard, *Thesis, ETH-Zürich* 1954.

IZVOD

Prilog poznavanju priprave melamina iz uree

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Opisani su uslovi priprave melamina iz uree u zatvorenom sistemu bez dodatka amonijaka. Kod toga preliminarni eksperimenti pokazuju da su nastali pritisci bili reda veličine 150 p.s.i., a ispitani omjeri punjenja nisu značajno utjecali na izmjerene pritiske. Nije zapažen utjecaj omjera punjenja na postignute prinose.

Tokom eksperimenata provedenih u temperaturnom intervalu 360—560° uz konstantan omjer punjenja (0,2 g/ml), i promjenom vremena zagrijavanja (5 — 90 min.), izmjereni pritisci bili su u skladu s vrijednostima zapaženim u preliminarnim pokusima. Odatle se može zaključiti da ni temperature unutar ispitanog područja nemaju značajnog utjecaja na rezultirajuće pritiske. Postignuti su maksimalni prinosi od oko 48%.

Zanimljivo je da proces pirolize uree prate relativno niski pritisci, za razliku od dosada objavljenih podataka. Ovo se može obrazložiti kao posljedica ravnotežnih reakcija aminiranja hidroksiamino-*s*-triazina, pri kojima se hidroksilne grupe zamjenjuju amino skupinama. Amininranje slijedi iz djelovanja amonijaka nastalog dekompozicijom uree pri čemu se oslobađa ekvivalentna količina vode.

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