REGENERATION OF MELAMINE CATALYSTS ENVIRONMENTAL PROTECTION

M. A. Kaynejad, M. Haghighi
Sahand University of Technology, Tabriz, Islamic Republic of Iran

A.T.Khudiev
Institute of Petrochemical Processes, Academy of Science of Azerbaijan, Baku, Azerbaijan

ABSTRACT

At recent process melamine can be synthesized from urea at a temperature about 400°C and atmospheric pressure in the presence of silica gel as catalyst. The reaction is endothermic (153 kcal/mol) and accrued in a fluidized bed reactor. In this process a number of problems poison silica gel catalyst. Due to poisoning of catalysts with formation of coke and side products, the density of silica gel increased from 0.5 (new catalyst) to 1.2 gr/cm^3 (deactivated catalyst) and the surface area proportionally decreased. In this research regeneration of these catalysts are investigated. Density of deactivated catalysts is reduced from 1.2 to 0.56 gr/cm^3 by the use of a washing system and a fluidized bed reactor.

INTRODUCTION

Melamine is a more important raw material in molding, resins, adhesives, varnishes, leather, paper and other industries. Melamine formally was produced almost exclusively from calcium cyanamide via dicianamide using a complex multistage process. At recent process melamine can be synthesized from urea at a temperature about 400°C and atmospheric pressure in the presence of catalyst [1, 2, 3, 4, 5]. The reaction is endothermic (153 kcal/mol) and accrued in a fluidized bed reactor. Catalysts such as γ-alumina, silica gel, etc. with a large surface area are used in this process[6, 7, 8, 9]. In this work melamine process with silica gel(surface area = 400 m^2/gr, density = 0.5 gr/cm^3, size(mesh) = 40 to 120) as catalyst is examined and deactivation of this catalyst and regeneration of them is investigated.

PROCESS DESCRIPTION

Figure 1 shows process flow sheet of melamine production. Solid urea is fed into the fluidized bed reactor and silica gel is used as catalyst. Fluidization is maintained by recycle gas (ammonia) which has been preheated to about 360°C. to maintain a reaction temperature of 390 to 400°C for the endothermic reaction, heating coils are provided inside the fluidized catalyst bed to supply additional heat. For this heat transfer a molten salt circulation is used.

The injected urea is converted to melamine, carbon dioxide and ammonia according to the following reaction:

$$6(NH_2)_2CO \xrightarrow{400^\circ C} C_3N_3(NH_2)_3 + 6NH_3 + 3CO_2$$

and many side reactions such as production of melem, ammelide etc. are occurred in the catalyst bed:

Melamine ⟶ Melon + Melam + Melem + Ammonia

Melamine ⟶ Ammelide + Ammeline + ...

$$3H_2O + 3(NH_2)_2CO \longrightarrow 3CO_2 + 6NH_3$$

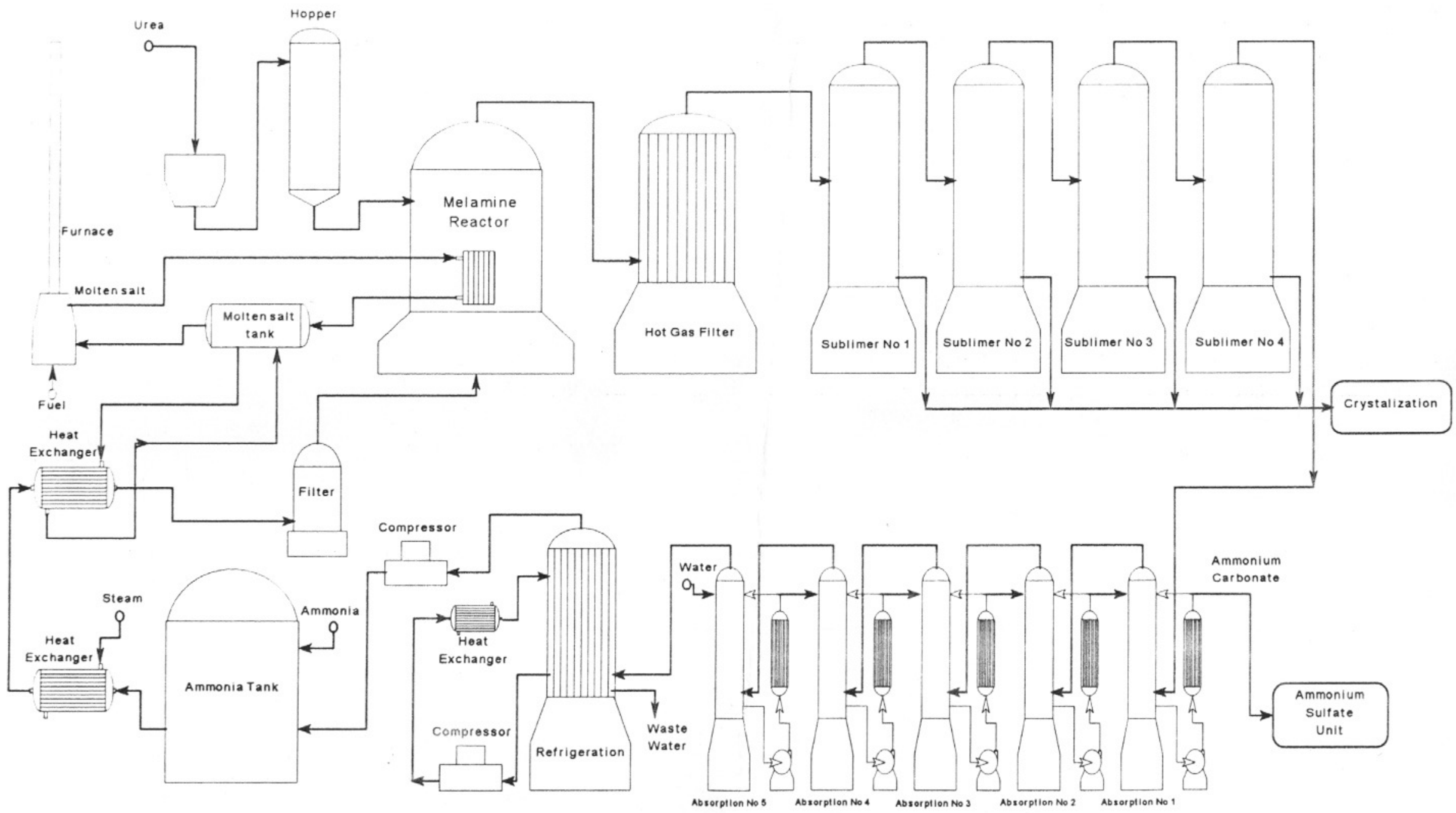

Fig. 1. Flow sheet of melamine process.

Melamine leaves the reactor as a gas together with recycle and fresh gas. Byproducts formed by side reactions, such as melem, are removed by a gas filter along with catalyst fines. After hot filtration, the reaction gases are sent to sublimers. Melamine is crystallized in these sublimers and sent to the purification unit. Residual gas (ammonia) after absorption of its carbon monoxide and excess ammonia, drying, heating, filtration is sent to the reactor.

CATALYST DEACTIVATION

In this process a number of problems such as diffusion of oil from reciprocate compressors to recycle gas(ammonia), incomplete recovery of water from recycle gas(which cause side reactions), diffusion of steam from heat exchanger, diffusion of molten salt from heat exchanger and reactor coils, presence of moisture in urea feed etc. poison silica gel catalyst. Due to above problems and poisoning of catalysts with formation of coke and side products, the density of silica gel increased from 0.5 (new catalyst) to 1.2 gr/cm^3 (deactivated catalyst) and the surface area proportionally decreased, so the catalyst performance is reduced.

REGENERATION METHOD

In this process deposits such as salt, coke and side products poison the catalyst. A washing system (Figure 2) with water as solvent is used for removing of salt and melamine from catalyst pours and a fluidized bed reactor (Figure 3) is used for removing of coke and side products from catalyst surface by burning of them(550-570°C)[10]. This system comprises a compressor, tubular quartz reactor, electrical heater, inert bed (quarts) for preheating of air, and a section for fluidization of catalyst.

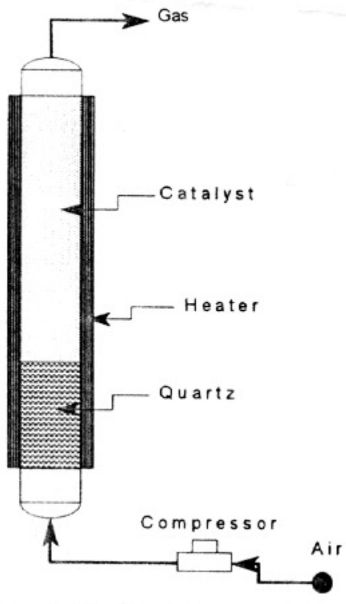

Fig. 3. Fluidized bed reactor.

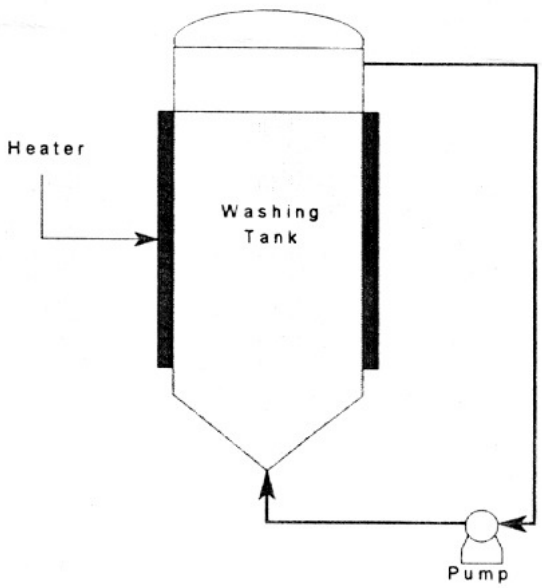

Fig. 2. Washing Tank.

CONCLUSIONS

In this work density of deactivated catalysts is reduced from 1.2 to 0.56 gr/cm^3 by the use of a washing system and a fluidized bed reactor, so surface area of catalyst proportionally increased. Deactivated catalyst is washed with solvent in various proportions of solvent to catalyst weight, temperatures and times of washing, then it is regenerated in a fluidized bed reactor at various temperatures and times. Surface area of catalyst proportionally increased which as density decreased. The size reduction of catalyst is also examined.

Figure 4 provides distribution of catalyst size before and after regeneration. Catalysts with small size are increased after regeneration in washing and fliudized bed system.

Figure 5 compares density of regenerated catalyst with fluidized bed reactor and laboratory furnace vs. number of washing. It is shown that in fluidized system one stage of washing is required for obtaining of density about 0.565 gr/cm^3, but in fixed bed system (laboratory furnace) more than four step is required to reach this density.

Figure 6 shows effect of water to catalyst weight ratio in washing system on catalyst density vs. washing number. It is shown that with increasing of water to catalyst weight ratio, the catalyst density is proportionally.

Finally, regeneration and recycling of melamine catalysts reduce variable cost (catalyst charge), increase reactor performance and cause environmental protection by reducing of useless side products and reuse of deactivated catalysts.

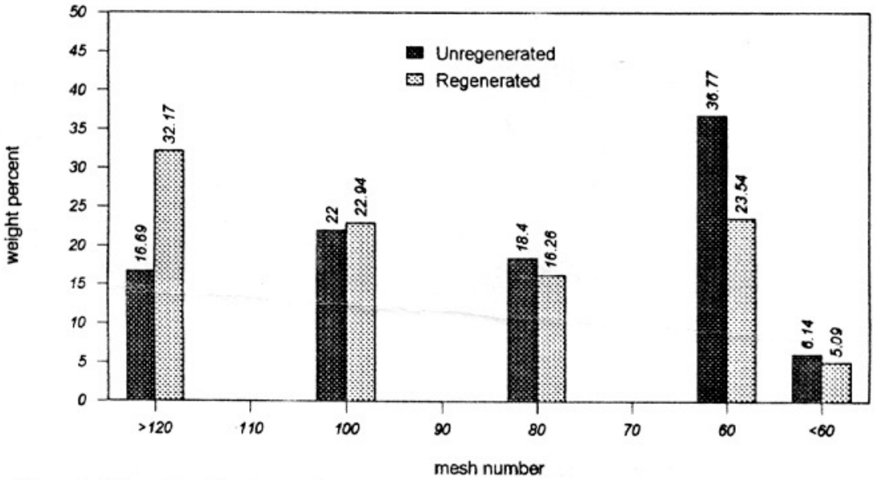

Fig. 4. Size distribution of catalyst before and after regeneration(weight percent).

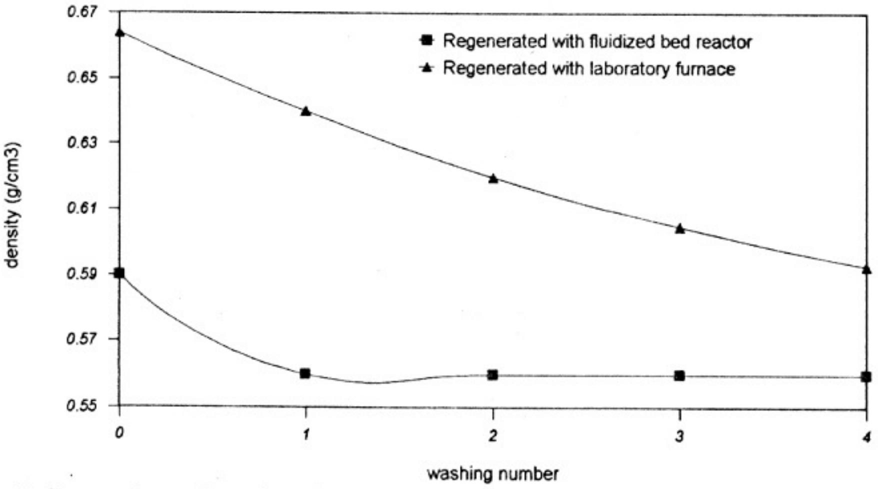

Fig. 5. Comparison of catalyst density regenerated by fluidized bed reactor and laboratory furnace.

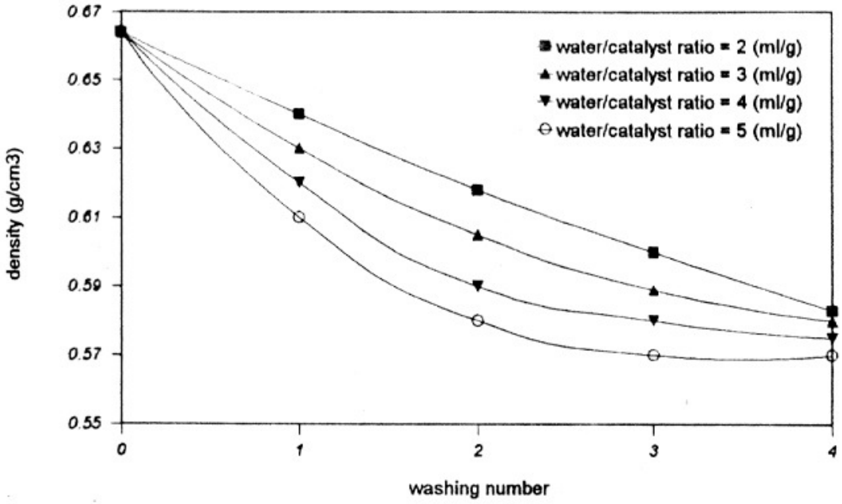

Fig. 6. Effect of water to catalyst weight ratio on catalyst density in washing system.

REFERENCES

[1] Turunen Ilkka, Oinas Pekka, "Preparation of Highly Pure Melamine", PCT Int., Appl. WO 95 01345 (Cl. C07D251/60), 12 Jan 1995, FI Appl. 93/3033, 01 Jul. 1993, 22 pp.

[2] Lee Jing M. "Fluidized-bed Reactor Process for Manufacturing Melamine from Urea at Elevated Temperature", U.S. US 5384404 (Cl. 544-201, C07D251/60), 24 Jan 1995, Appl. 147848, 05 Nov. 1993, 6 pp.

[3] Van de Moesdijk, Cornelis Gerardus, Janssen Hendrik Jan, Schroijen Josephus Cordless(DSM N. V.), "Manufacturing of Highly Pure Melamine", PCT Int. Appl. Wo 92, 09585 (Cl. C07D251/60), 11 Jun. 1992, NL Appl. 90/2606, 29 Nov. 1990, 18 pp.

[4] Sonoda Kisuke, Sumitomo Chokichi (Mitsui Toatsu Chemicals Inc.), "Reactors for Melamine Production", Jpn. Kokai Tokkyo Koho JP 6020771 [85204771] (Cl. C07D251/60), 16 Oct. 1985, Appl. 84/59628, 29 Mar. 1984, 3 pp.

[5] Altshuler L. N. (USSR), "Equilibrium in the gas phase synthesis of melamine", Khim. Prom-st. (Moscow), 1987, (6), 350-1 (Russ).

[6] Sonoda Kisuke, Hasuike Yasumasa, Fukahara Misao (Mitsui Toatsu Chemicals Inc.), "Recycling of Catalysts in Preparation of Melamine", Jpn. Kokai Tokkyo Koho JP 60209575 [85209579] (Cl. C07D251/60), 22 Oct. 1985, Appl. 84/65955, 04 Apr. 1984, 3 pp.

[7] Mitsui Toatsu Chemicals Inc., "Fluidized-bed Catalysts", Jpn. Kokai Tokkyo Koho JP 81147626 (Cl. B01J8/24), 16 Nov. 1981, Appl. 80/49605, 17 Apr. 1980, 5 pp.

[8] Mitsui Toatsu Chemicals Inc., "Melamine", Jpn. Tokkyo Koho JP 58 40951 [83 40951] (Cl. C07D251/60), 08 Sep 1983, Appl. 77/85655, 19 Jul. 1977, 3 pp.

[9] Fromm Dieter, Widmann Alfred, et al., "Melamine", Ger. Offen. DE 3302833 (Cl. C07D251/56), 02 Aug. 1984, Appl. 28 Jan 1983, 16 pp.

[10] H. Scott Fogler, "Elements of Chemical Reaction Engineering", 2nd Ed, Prentice-Hall Int. Inc, 1992.