ACTIVATION OF SILICA CATALYST MELAMINE PROCESS

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In recent process melamine can be synthesized from urea at a temperature of about 400°C and atmospheric pressure in the presence of silica gel. 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 which including 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. Due to poisoning of catalysts by 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 this catalyst is investigated by a washing system, a fluidized and fixed bed reactor. Results are illustrated as density vs time of regeneration and also size distribution of catalyst before and after regeneration. By using this method density of deactivated catalyst is reduced from 1.2 to 0.56 gr/cm^3.

Introduction. Melamine was discovered by J. Liebig in 1834. Some years later it was recognized to be the triamide of cyanuric acid, but only a hundred years later, 1935, it was discovered that the condensation products of melamine and formaldehyde could be cured to yield valuable resins. With this discovery melamine changed from a laboratory chemical to a technical product and its large scale production started.

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.

McKay discovered that melamine can be synthesize from urea at temperature ranging from 300-500°C with and without catalysts. In the presence of catalysts melamine can be obtained in good yield at atmospheric or slightly elevated pressure.

In recent process melamine can be synthesized from urea at a temperature of about 400°C and atmospheric pressure in the presence of catalyst [1-5]. 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[6-9]. 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.

Melamine Process. In this process, 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 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:

$$\text{Melamine} \longrightarrow \text{Melon} + \text{Melam} + \text{Melem} + \text{Ammonia}$$

$$\text{Melamine} \longrightarrow \text{Ammelide} + \text{Ammeline} + \ldots$$

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

Melamine leaves the reactor as a gas together with recycle and fresh gas. By-products 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 and filtration is sent to the reactor.

Catalyst Deactivation. If the reaction temperature is too high, a small part of the melamine is decomposed to melam and melem. These substances accumulate on the catalyst, thus decreasing its activity. A certain amount is volatile which contaminates the product. If the reaction temperature is too low the yield of melamine will be reduced.

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 the 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/cm3 (deactivated catalyst) and the surface area proportionally decreased, so the catalyst performance is reduced.

Regeneration method. In melamine process deposits such as salt, coke and side products poison the catalyst. A washing system (Fig. 1) with water as solvent is used for removing of salt and melamine from catalyst pores and a fluidized bed reactor (Fig. 2) is used for removing 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 the air, and a section for fluidization of catalyst.

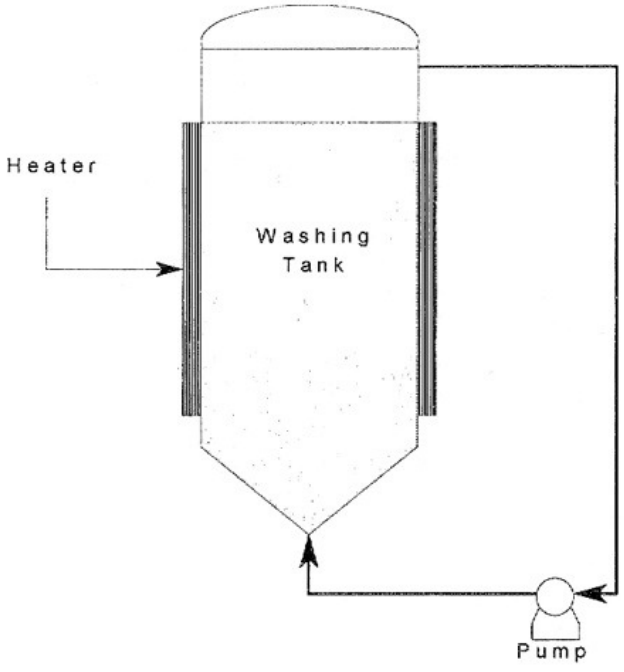

Fig. 1. Washing system for removing of salt and melamine from catalyst pores.

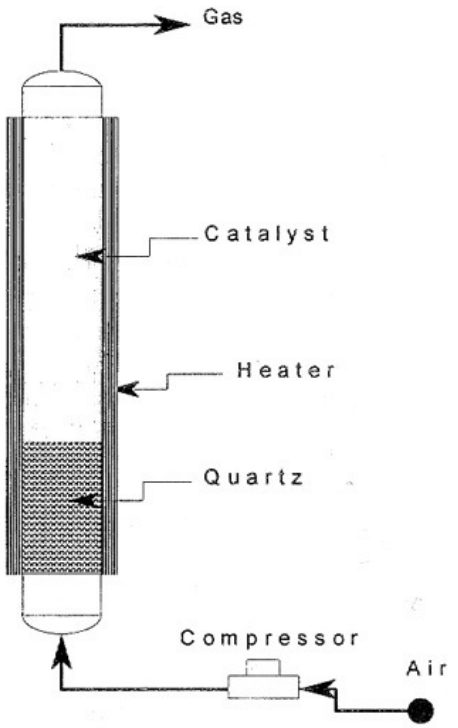

Fig. 2. Fluidized bed reactor for removing coke and side products from catalyst surface.

Results. 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.

Fig. 3 provides distribution of catalyst size before and after regeneration. Catalysts with small size are increased after regeneration in washing and fliudized bed system.

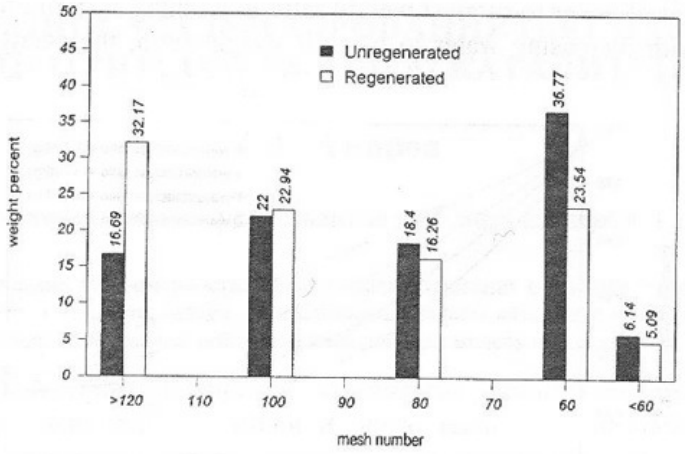

Fig. 3. Size distribution of catalyst before and after regeneration (weight percent).

Fig. 4 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 density of about 0.565 gr/cm3, but in fixed bed system (laboratory furnace) more than four steps are required to reach this density.

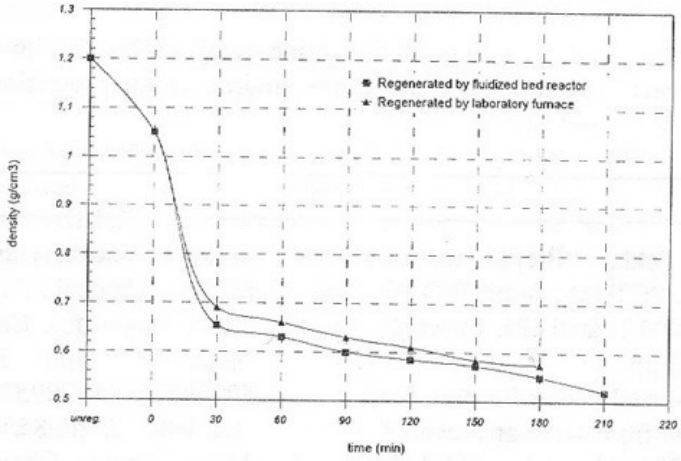

Fig. 4. Comparison of catalyst density regenerated by fluidized bed reactor and laboratory furnace.

Fig. 5 compares the density of regenerated catalyst in fluidized bed reactor and laboratory furnace vs time. It is shown that the performance of fluidized bed reactor is better than that of fixed bed systems.

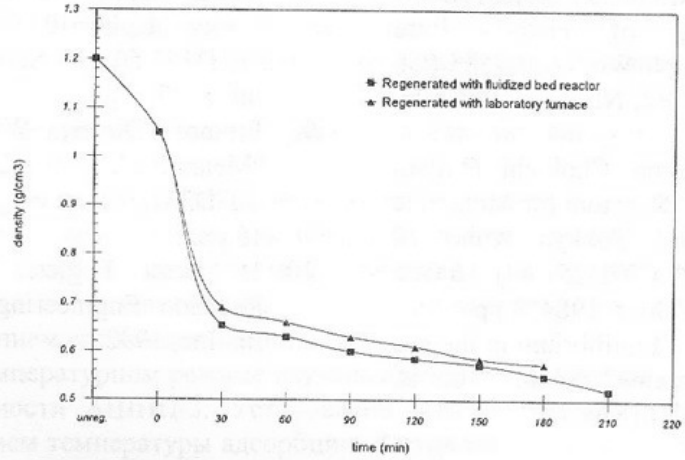

Fig. 5. Comparison of catalyst density regenerated by fluidized bed reactor and laboratory furnace.

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

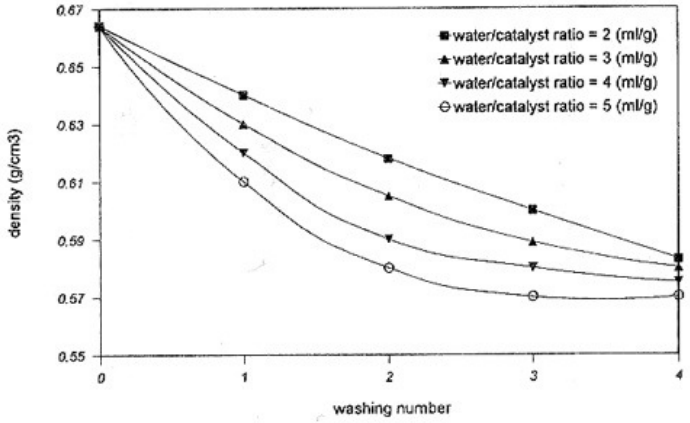

Fig. 6. Effect of water to catalyst weight ratio on catalyst density in washing system.

Conclusions. In this work density of deactivated catalyst of melamine process is reduced from 1.2 to 0.56 gr/cm3 by the use of a washing system and a fluidized bed reactor, so surface area of catalyst proportionally increased.

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

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