

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The adsorption of metallic mercury in substituted condensate of n-heptane in a batch system was studied. The experiments were carried out for Zeolites NaX, NaY, L, Omega, Beta and CMG 273. Little adsorption was observed for Zeolites X and Y while no adsorption was found in case of Zeolites Omega, Beta and L which indicates cage structure are better than straight channel structures. For adsorbate, the size of mercury atom (3\AA) plays important role. The pore openings of Zeolites (7.4\AA) were too big to have interaction with small mercury atoms. However, small adsorption on Zeolites NaX and NaY may be due to the cage structure which can provide some storage of mercury in cages. Polarity also plays important role in making non-polar mercury molecules incompatible to polar adsorbents. Kinetic study shows first order rate kinetics for mercury removal on Zeolites X and Y but no limitation of diffusion was observed. For CMG273 more than 95% removal was achieved due to presence of active element (CuS on alumina) which trapped mercury, however, limit of pore diffusion was also seen.

Langmuir model was found suitable and used to correlate mercury concentration between solid and liquid phases for Zeolites X, Y, Omega, Beta, L and CMG273. The increased removal with increased temperatures confirms chemisorption for CMG273 while increased removal with decreased temperatures indicated physical adsorption for Zeolites.

In continuous system, CMG273 was tested for breakthrough curve and a 20 hrs breakthrough time was achieved for 0.5g of catalyst. External mass transfer resistance was found less effective as compare to internal mass transfer resistance and surface reaction.

5.2 Observations

5.2.1 Instability of Mercury

Unlike batch operation, a very different kind of behavior of metallic mercury has been seen in continuous operation. Breakthrough curve could not be derived at first attempt but several tests were performed before coming to final Figure 4.12. Some data are collected during the experiment and listed in APPENDIX F.

In the adsorption phase, a drop in mercury concentration in feed drum against prepared stock concentration was seen. In Test 3, feed-drum concentration was decreased at the end of feed (heavy naphtha). There may be two possibilities of mercury loss, either due to adsorption of mercury on stainless steel wall of feed drum or due to evaporation during opening of feed-drum for changing feed. However, chances of evaporation dominates, as, unsaturated mercury solution are very unstable (because in Test 4 saturated n-heptane solution is very stable and no loss was observed). While in Test 1, only one feedstock was used so, there was no opening of feed-drum and, hence, chances of evaporation were minimized. However, increased concentration of mercury indicates settling of micro particles of mercury at the bottom of feed drum. This is also confirmed after looking at the reactor bottom concentration which increased abruptly. Even at concentrations, 5276 ppb mercury in heavy naphtha (Test 3) and 4000 ppb Hg^0 in n-heptane (Test 1) which are out of solubility limit of solvents. Secondly, tests were started with much lower concentrations but high concentration at reactor bottom indicates strongly accumulation of heavy mercury molecules (SG 13.6 against 0.67 for n-heptane and for 0.76 for heavy naphtha) in the form of suspended particles. The important conclusion came out from this discussion that metallic mercury may not form homogeneous solution.

In desorption tests, apart from use of pure n-heptane/heavy naphtha, some mercury contamination in feed drum indicate release of adsorbed metal mercury (from adsorption phase) from walls. Test 4 was performed under stirring condition in feed drum while no stirring was used in Test 1, 2 and 3. The very high

level of mercury contamination in desorption step of Test 4 indicates faster release of mercury from walls due to stirring.

5.2.2 Analytical

As an analytical part, sampling technique using micro pipette with ultrasonic mixing for measuring mercury concentration was tested against conventional measurement using micro syringes with manual mixing (Figure 5.1). Results suggests use of micro pipette and ultrasonic mixing of samples ,however, more data points are needed before coming to any strong conclusion.

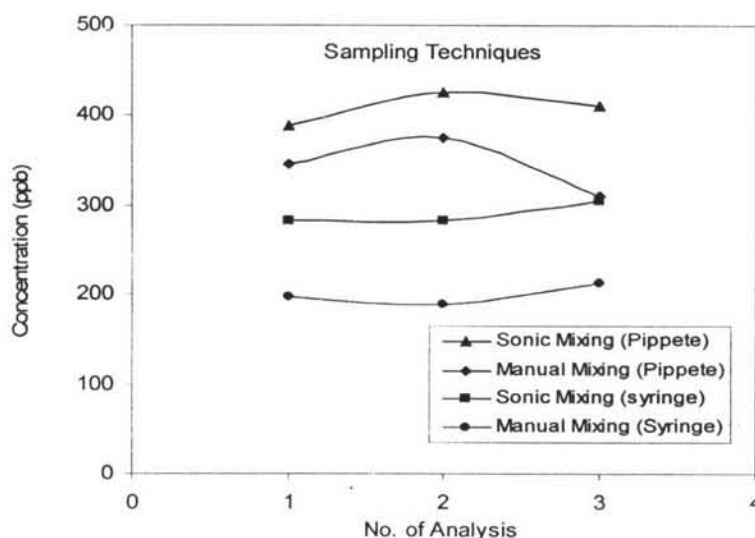


Figure 5.1 Different sampling techniques using (1) pipette with ultra sonic mixing, (2) pipette with manual mixing, (3) syringe with ultra sonic mixing and (4) syringe with manual mixing.

In order to reduce the cost of very expensive reagent (additive B) in NIC SP-3D for mercury analysis, regeneration was done and regenerated reagent was calibrated against fresh reagent (Figure 5.2). The mercury concentration obtained from regenerated reagent thus could convert equivalent to fresh reagent through calibration curve. A total of 100,000 Baht was saved through this procedure.

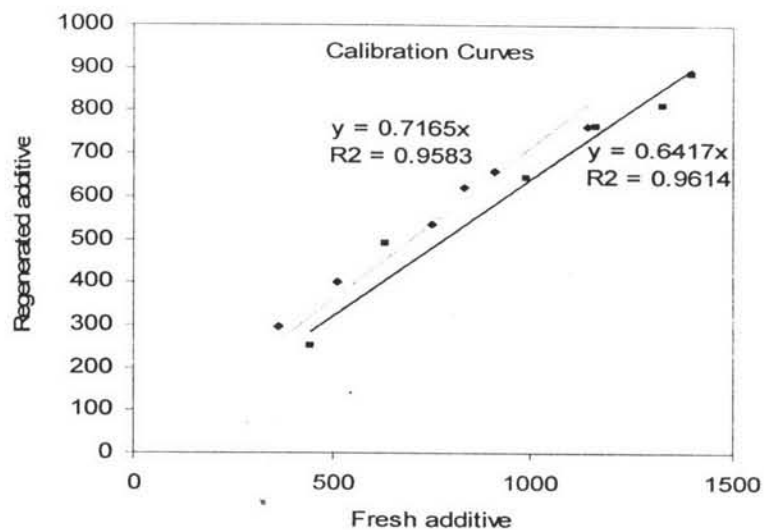


Figure 5.2 Performance of regenerated additive B against fresh additive B.

5.3 Recommendations

Upon the completion of this study, a little adsorption of metallic mercury on Zeolites X and Y was found. The improvement in removal efficiency can be expected in further study towards the smaller pore size Zeolites such as 3A^o and 4A^o while higher Si/Al ratio zeolites should also be tested in order to understand effect of pore size and polarity on adsorption. Understanding the interaction of adsorbate-adsorbent by impregnation of metals such as S and Ag can also help in achieving higher removal efficiency.

A mathematical model can be constructed as a future study and can be validated based on the information available in this thesis. As a part of analytical determination of mercury concentrations, several sampling procedure should be tested using micro-pipette and micro syringe with/without manual and ultrasonic way of mixing.