Designing a Process for the Reusability of Hygroscopic or Air Sensitive Materials

Submitted as a part of the requirement for the partial fulfillment of the course work of CSIR-Harnessing Appropriate Rural Interventions and Technologies (CSIR-HARIT) for the award of Degree of Ph.D.

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Declaration – I Azeem Khan, hereby certify that the work presented in this Report entitled "Designing a Process for the Reusability of Hygroscopic or Air Sensitive Materials" in partial fulfillment of the course requirement for the award of the Degree of Ph.D., being submitted to CSIR-HARIT Unit, CSIR-Indian Institute of Petroleum, Dehradun, is an authentic record of project research work carried out by me at CSIR-IIP Dehradun Uttarakhand during the period of Ph.D. course work and under the supervision of Dr. Anil Kumar Sinha.

Date 08/10/2020

Signature of the Student

Table of Content.

1. Background

CSIR-HARIT (CSIR-800), is a program to leverage its strong scientific and technological knowledge base for the benefit of most common people of the country lying at the bottom of the economic pyramid. It is assigned to every Ph.D. scholar to do innovative work that can help either to society or to industry. I have targeted to do research for “Designing a Process for the Reusability of Hygroscopic or Air Sensitive Materials” as this work can be beneficial for the industry and also it could be beneficial for the environment and improve the working conditions of the personals handling these materials.

2. Objective

Our objective is to make a process for the production of some specific chemicals & petrochemicals, which are produced from the hygroscopic and air-sensitive materials, in such a way that it can be synthesis at lesser cost and with the least impact on the environment by making necessary changes/optimizing the process and the process equipment’s (reactor). The limitation of this process is that it could be only used for reaction processes which results in high selectivity towards reaction products and are irreversible. And the main motive of this innovation is to make full use of hygroscopic or air sensitive materials by keeping this material away from the air and moisture.

3. Introduction

We all know that nowadays the chemical industry and refineries are going through a very tough competition with their fellow refineries or chemical industries. Innovation in terms of work/working conditions etc. can make a huge difference in terms of economy, environment, and manpower. Innovation can be in any form, it could be in process, reaction or it could be in reactor type.

According to Jeffrey Baumgartner, Innovation is, “The implementation of creative ideas in order to generate value, usually through increased revenues, reduced costs or both” [1].

My research topic is “catalytic route for the synthesis of high energy density fuels”. Nowadays fuels for fighter jets and missiles require the use of higher volumetric energy content. Exo-THDCPD (exo-tetrahydrodicyclopentadiene) can be easily obtained from endo-THDCPD through the isomerization reaction. Both the endo and exo-isomer have almost similar properties, but only exo-THDCPD can only be used as a high energy density fuel due to suitable flashpoint (55 °C), low freezing point (-79 °C), and a higher energy density (39.6 MJ/L) [2]. Besides this, exo-THDCPD has many applications in paints, dyes, surfactants, washing of semiconductors, etc. Due to higher energy density exo-THDCPD provides maximum propulsion to the aircraft, making it traveling to more distance with a small amount of fuel therefore a small fuel tank requires while compared with other fuel sources such as aviation jet fuel therefore it can leave some space for the electronic parts or material in the aircraft. The main drawback of endo-THDCPD as fuel is the high freezing point (80°C), as at higher altitudes the fuel tends to be frozen out. Hence the endo-THDCPD cannot be used in JP-10 fuel, so it needs to be isomerized into exo-isomer by isomerization step. Endo-THDCPD can be synthesized from the dicyclopentadiene (DCPD) via catalytic hydrogenation route [3–5]. DCPD is obtained as a side-product after the pyrolysis of naphtha [6,7]. DCPD is the side product of naphtha pyrolysis so it is suitable for use as a fuel. There is a US patent on exo-THDCPD production and they used $AlCl_3$ for the isomerization step. The aluminium trichloride to endo-THDCPD ratio was 0.6. They performed this reaction in a round bottom flask [8]. Still, $AlCl_3$, generally used in the production of exo-THDCPD [3]. We have taken this topic for the production of exo-THDCPD but it can be applied to any other reaction processes which result in high selectivity towards reaction products and are irreversible

4. Assumption

We were assuming that "If we are using material which is very sensitive to air or moisture and the reaction has resulted in high selectivity towards reaction product and is an irreversible process. Then we can use a reactor from which we can take out the product to that extent that a thin layer of the product remains on the catalyst or reagent (Aluminium trichloride). Now by doing this we can reuse this material more time as compared to other typical processes where complete drainage of the product takes place. This process can be used only for reaction, those are irreversible and highly selective towards products otherwise the product which is left on the catalyst surface could be revert back to the reactant and this process can be failed.

4.1 Reaction vessel (Design according to our assumption)

The reactor setup was modified with the idea to reuse the catalyst/reagent. We have to design/ modify the setup based on our batch size for the experiment. Two and three-liter 3-neck glass round bottom flasks were modified into a 2 Liter (L) volume flask (prepared with the help of the glass blowing section). The 3-L flask was used to jacket the 2 L flask. This jacket is made on this flask to circulate water in the jacket to control the reaction temperature with the help of a chiller. These three necks can be used for measuring the temperature, charging the feed, and middle neck for stirring. A drainage tube with a valve is fixed to drain the product. This tube is fixed at a position where we can design an experiment such that we can drain greater than 90% of the product and a very thin layer remains on the catalyst surface so that this hygroscopic or air-sensitive material remains under the liquid and the reusability of this material can be increased. We need to keep a note of the position of the tube while planning our experiments (Figure 2).

5. Experimental:

Experiments are designed in two ways to compare the effect of our design process with the typical laboratory process. The typical laboratory process where complete product drain before reuse, is labeled as Process 1, and the new design as explained above is labeled as Process 2 (Our approach).

5.1 Typical Process (Process 1)

In this process, we use the typical process and simple jacketed flask for the reaction which is completely covered by the Teflon sheet. The temperature in this reactor controlled by the water circulation and tubes were connected to the chiller (for controlling the temperature), vessel diagram shown in figure 1. A mechanical stirrer used for the stirring and the reaction is performed at room temperature, 500 RPM, for 60 minutes. Endo-THDCPD feed (566 g) mixed with solvent dichloromethane (DCM) charged in the reaction flask and the ratio of DCM/feed was 0.75. $AlCl_3$ charged after charging the feed, the ratio of $AlCl_3$ to feed was 0.6. Then according to the above mention reaction condition, the reaction started for 60 minutes, after 60 minutes stirring stopped and 5 minutes given for sedimentation, after sedimentation, the product completely drained from the flask and fresh feed mixture with solvent charged immediately and again reaction started to reuse the $AlCl_3$. This process was repeated several times. The reaction scheme is shown in scheme 1.

Scheme 1. Isomerization of endo-THDCPD to exo-THDCPD.

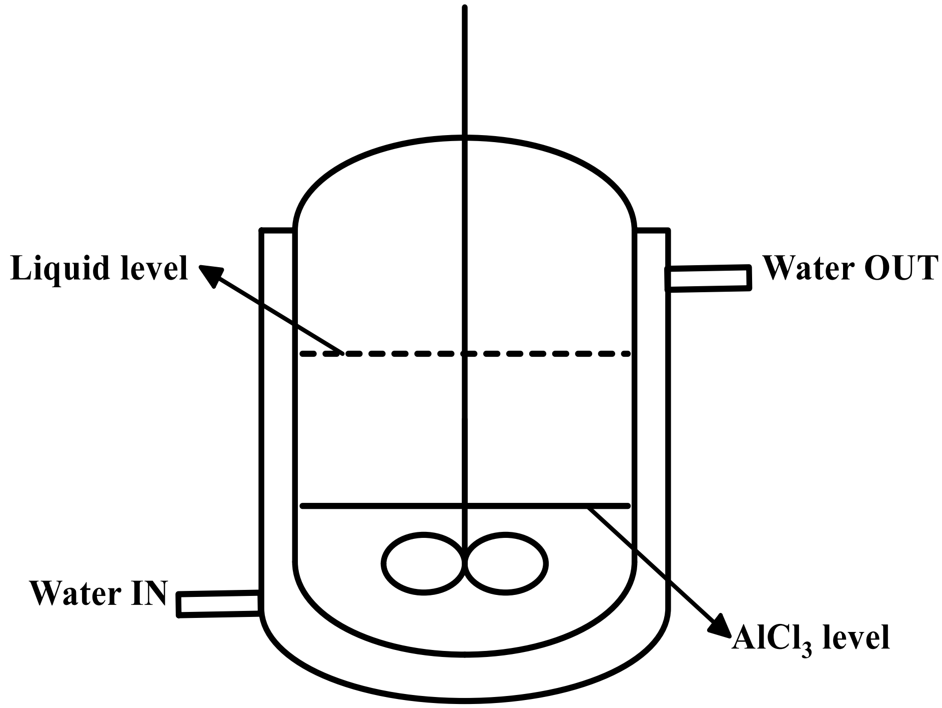

Figure 1. The reaction vessel of Process 1 without drainage tube

5.2 Our Approach (Process 2)

The product drainage tube is fitted at such height that we can design our batch size so that the catalyst layer remains below that tube level or we can fit the drainage tube according to the batch size but in both the cases we have to make sure that the catalyst layer should be below that drainage tube (Figure 2 & 3). In this reactor also, feed (same amount as in process 1) with DCM and $AlCl_3$ charged similarly as in Process 1. After charging all these material stirring started and this condition hold for 60 minutes. Completion of the reaction time, stirring of the reaction stopped and again similar to Process 1, time given for sedimentation of the $AlCl_3$. The product drained through the drainage tube, this step is different from Process 1. In this process after draining the product, some amount of product remains on the $AlCl_3$ surface, which is shown in figure 3 (diagram after drainage of product). Similar to process 1, fresh feed with solvent charged immediately in the flask and the reaction started to reuse the $AlCl_3$. This reusability process also repeated several times.

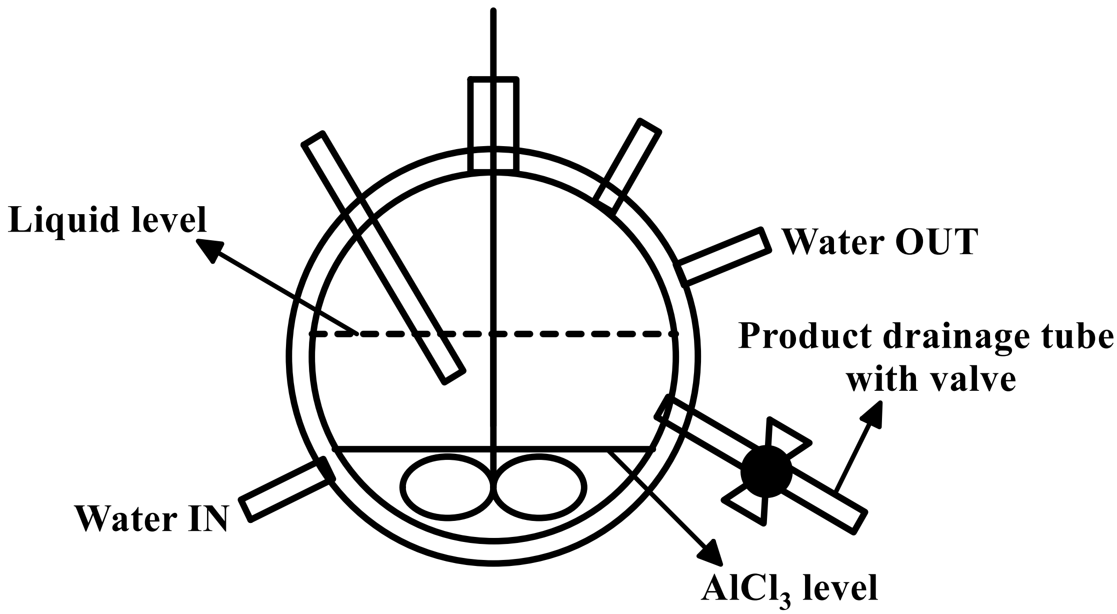

Figure 2. Diagram of the reaction flask of Process 2.

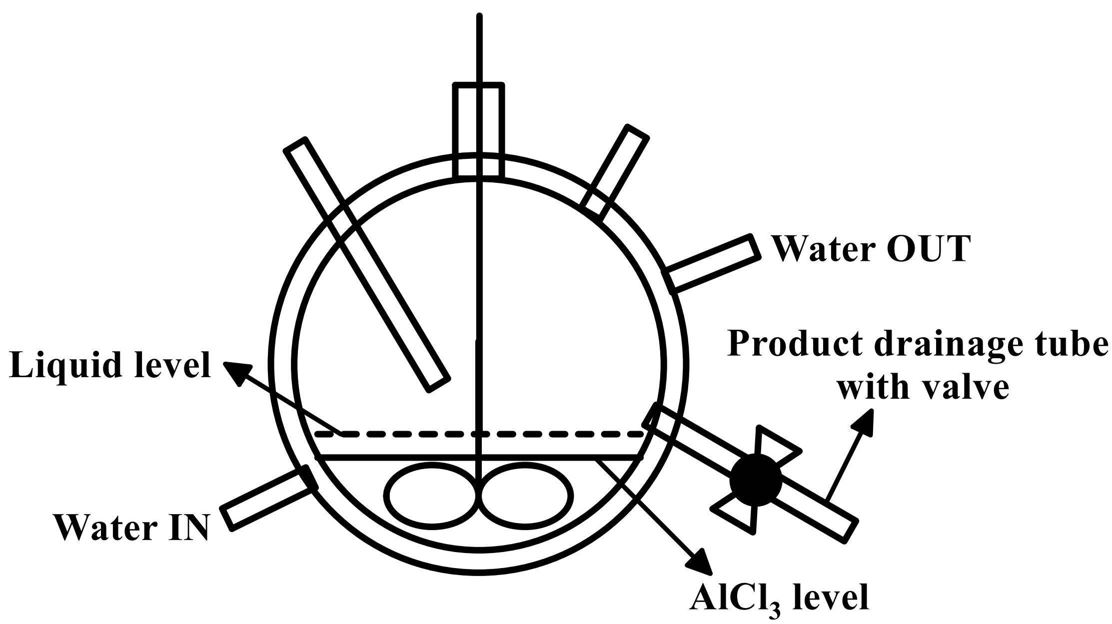

Figure 3. Reaction flask of Process 2 after draining the product.

6. Results and discussion

In this process, exo-THDCPD (Tetrahydrodicyclopentadiene) is the product and it is a thermodynamically more stable compound as compared to the endo-THDCPD [2]. It is a different process from the typical process, as in typical processes, after the completion of reaction time, the complete product is drained from the reactor. So there are more chances of this material to be in contact with air or moisture directly, but to avoid this problem, inert atmosphere of gases like nitrogen used to protect air and moisture sensitive material. We did this reaction without using inert gas like Nitrogen.

After completion of the reaction, the product was taken out, and analysis of the product was done by using GCXGC (Agilent) with two columns (the first one is nonpolar and second is polar).

Results obtained from both the processes (i.e. Process 1 & Process 2), plotted and shown in figure 4.

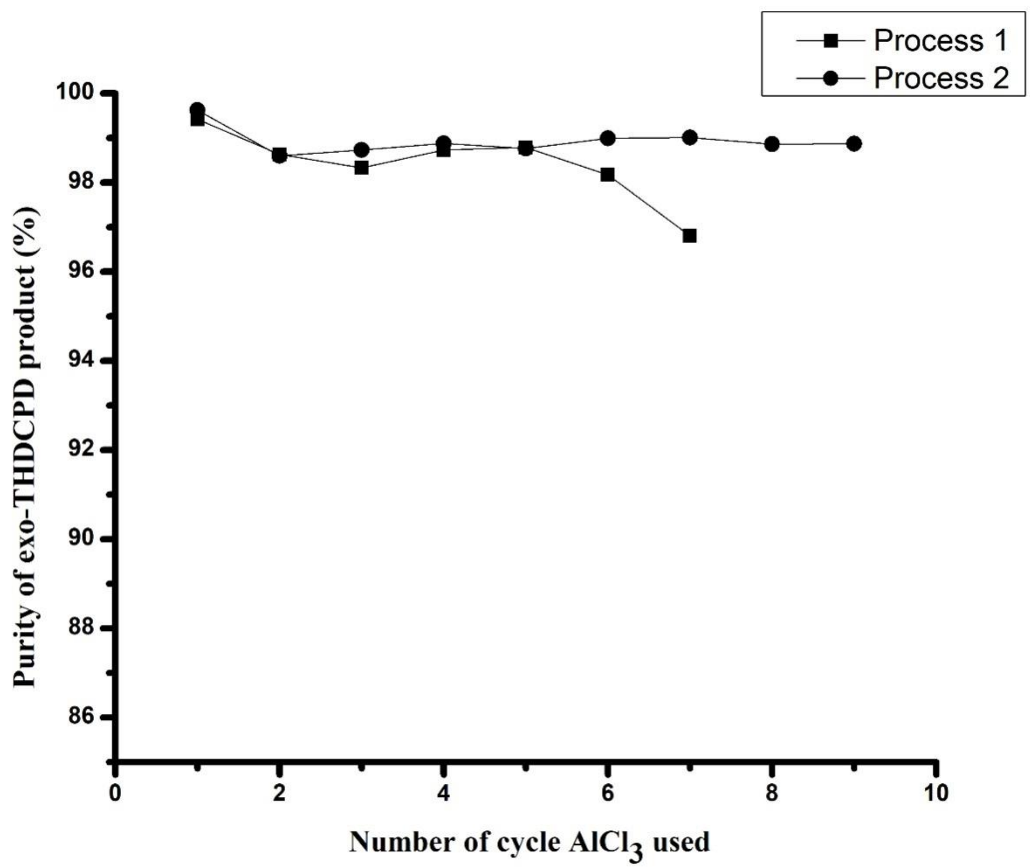

Figure 4. Results of the products of both Process 1 and Process 2.

From these results, it is observed that at the beginning i.e. from fresh $AlCl_3$ to 5^{th} cycle, results are almost similar in both the processes, but after the 5^{th} cycle, there is a decrease in the purity of the desired product (exo-THDCPD) in Process 1. But in Process 2, the purity remains almost the same till the 9^{th} cycle of reusability experiments. In Process 2, in all the batches we obtain almost JP-10 purity (98.5% exo-THDCPD). The reason for better reusability results could be that reaction media which is leftover $AlCl_3$ layer to protect it from the air and moisture present in the air as it is a moisture and air-sensitive compound. The modification in the process and the reaction setup resulted in protecting the hygroscopic and air-sensitive material. The material's reusability was established and successful utilization of up to 9 reaction cycle was demonstrated. The reuse of the material will also lead to a lesser environmental footprint, which was earlier caused in the typical process due to the inability of catalyst/material recycle. The reusability also leads to economical savings in terms of the product throughput/amount of the catalyst material used.

7. Conclusion

It can be concluded from this work that the new modified process and setup is better than the typical process. If we use any hygroscopic, air-sensitive material, with the modified setup and process, we can reuse it for many reaction cycles as compared, and also reduce the environmental footprint when compared to the typical process. The process equipment needs to be designed considering the batch size and can be utilized for reaction processes which result in high selectivity towards reaction products and are irreversible. By protecting the layer of catalyst/hygroscopic material using the reaction media from air and moisture, it can be reused more times than the typical process.

8.Acknowledgments

Glass blowing section of CSIR-IIP.

HRFA/BFD Team

9. References

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