# Synthesis of Tri-chloroacetyl Chloride using Green and Sustainable Manufacturing Process

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## Abstract

Chemical Reuse, Reprocess and Recycling is an emerging theme in Green Chemistry which has the potential to contribute to a low carbon protecting environment, resource efficient and sustainable economy; however, it is still at an early stage of development. The present work reports a cost-effective method for synthesis of Tri-chloroacetyl chloride which is commercially important Chemical Intermediate and is a Key raw material for synthesis of various commercial Agro and Pharma products. The reported method involves various steps like, Purification of Mother Liquor (ML) of MCA, Synthesis of Chloroacetyl Chloride and Synthesis of Tri-chloroacetyl chloride. In synthesis of Tri-chloroacetyl chloride various steps are involved. The basic raw materials used are, Mother Liquor (ML) of MCA, Liquid Chlorine and Sulfurmonochloride (SMC) and phase transfer catalysts. Various catalysts are used, but we Pyridine catalyst gives higher yield. The overall yield obtained is up to 95% which is comparable with Tri-chloroacetyl chloride manufactured by using other methods. The processes developed for Chloroacetyl chloride synthesis from Mother Liquor (ML) of MCA is comprehensively evaluated to reveal the future opportunities of Tri-Chloroacetyl chloride broad-scale production and utilization.

## Keywords

Green Chemistry, Sustainability, Synthesis, Chloroacetyl chloride, Trichloroacetyl chloride

  

## Introduction

Trichloroacetyl chloride is a colorless to light yellow color liquid with a strong chlorine odor. It Chemical formula is CCl3COCl and molar mass 181.8. It's boiling plant is 118$^{o}$C & is soluble in alcohol. It is denser than water and having specific gravity in the range of 1.602 – 1.612 at 30$^{o}$C. It is having multiple applications. It is very important chemicals and used as intermediates chemicals for synthesis of various pharmaceuticals & Agro-chemicals used plant protection compounds[1]. In the production of pesticides like Chlorpyrifos, Tri-chloroacetyl chloride is extensively used as an important intermediate. It can also be utilized in the production of trifluoroacetic acid as key starting material[2]. Additionally, Trichloroacetyl chloride can be used for the manufacture of the esters and the anhydrides of trichloroacetic acid[3-4].

Tri-acetyl chloride was initially manufactured on industrial scale by partial chlorination of acetyl chloride in liquid phase in presence of homogenous catalysis. This required the discontinuous operation of reactor leading to higher turnaround time (TRT) in plants. Moreover, the product could be obtained only after distillation from dissolved catalyst[5]. Since, more steps are involved in manufacturing, the production efficiency decreases with respect to power and chemical consumption. These disadvantages tremendously affect carbon footprint and sustainability.

The later procedures implemented for synthesis included chlorination of acetyl chloride or acetaldehyde with the aid of heterogeneous catalyst like active charcoal[1]. Other synthesis routes explored were like, i) Reaction of Tri-chloroacetic acid and Thionyl chloride, or DMF in the presence of activated carbon, ii) Thermal decomposition reaction of tri-chloroacetic acid in the presence of a catalyst like KCl, CsCl, $K_2CO_3$ and quaternary ammonium salts[6]. However, all of them suffered from disadvantages like low yield, operational constraints & lot of reaction waste.

To counter the disadvantages, industries switched to Chloroacetyl chloride (CAC), for synthesis of Tri-chloroacetyl chloride using acetic acid as main raw material[7-9]. Currently, the increasing price of acetic acid has inflated the production cost of chloroacetyl chloride and thus affecting the cost of Tri-chloroacetyl chloride.

The objective of the present invention is to provide a cost effective and greener manufacturing process for Tri-Chloroacetyl Chloride. Chloroacetyl chloride used in synthesis is produced from Mother Liquor (ML) of MCA, liquid chloride and sulfurmonochloride. Mother Liquor (ML) of MCA can be used completely or in combination with Acetic Acid. The new process recycles and reuses the chemicals, helps in better management of chemical inventories and thus, eliminating the negative impact on environment as well as the disposal costs of industries. Thus, our reported method of synthesis will contribute to a low carbon, resource efficient and sustainable economy. Tri-Chloroacetyl chloride-derived chemicals have already mature market and it is confirmed that this improved process is a promising pathway to expand the market and gain more environmental and energy benefits.

## Results and Discussion

The following steps are involved in the manufacturing process:

**Step – 1: Purification of Mother Liquor (ML) of MCA:** The step includes heating of Mother Liquor at temperature of 100~120°C for 1 to 3 hours and then distillation to collect pure Mother liquor having moisture content less than 2%.

**Step – 2: Synthesis of Chloroacetyl Chloride (CAC):** Purified Mother liquor is chlorinated using sulfur mono chloride to obtain crude product at completion of the reaction. The crude CAC thus formed, is distilled out and collected.

**Step – 3: Chloroacetyl Chloride to crude Tri-Chloroacetyl Chloride (TCAC):** The CAC obtained in step (ii) is chlorinated further by using chlorine gas till minimum specific gravity achieved is 1.602 – 1.612 at 30°C. The catalyst from reaction mass is later separated in 4-6 hrs.

**Step – 4: Crude Tri-Chloroacetyl Chloride to pure Tri-Chloroacetyl Chloride:** Pure TCAC is obtained by refluxing the crude TCAC till the purity is reached around 99.5% and then further distillation is performed. This is final TCAC product

**Step – 5: For Pharma/fine Grade:** The product is again refluxed till the product purity is closer to 99.75% followed by another round of distillation.

The intermediate products obtained are characterized by using Gas Chromatograph (GC) Instruments. Gas chromatography is a separation technique in which the components of a sample partition between two phases, stationary phase and mobile gas phase. During a GC separation, the sample is injected and vaporized in Injector and carried by the mobile gas phase (i.e., the carrier gas) through the column. Separation of the different components is achieved based on their relative vapour pressure and affinities for the stationary phase in column. Then those separated components go into detector in which detection happens. The moisture content in ML of MCA is tested by using Automatic Karl Fisher (Auto KF) Titrator. The data obtained from various trials are presented in Table 1 (A, B, C). To obtain repeatability and reproducibility, conducted various Laboratory Experiments to optimize batch yield and the verification of Analytical method followed for Characterization of products. Detailed results are given below tables.

| Batch No | % ASSAY | % Chloroacetyl chloride (CAC) | % Dichloro acetyl chloride (DCAC) | % High boiling Impurities | % $SO_2$ |
|---|---|---|---|---|---|
| 1 | 98.35 | 0.390 | 0.310 | 0.767 | 0.168 |
| 2 | 98.40 | 0.366 | 0.224 | 0.822 | 0.181 |
| 3 | 98.38 | 0.379 | 0.250 | 0.810 | 0.170 |
| 4 | 98.41 | 0.356 | 0.260 | 0.780 | 0.180 |
| 5 | 98.34 | 0.409 | 0.244 | 0.842 | 0.171 |
| 6 | 98.47 | 0.350 | 0.200 | 0.740 | 0.180 |

**Table - 1A: Purity of Crude TCAC**

| Batch No | % ASSAY | % Chloroacetyl chloride (CAC) | % Dichloro acetyl chloride (DCAC) | % High boiling Impurities | % $SO_2$ |
|---|---|---|---|---|---|
| 1 | 99.46 | 0.084 | 0.134 | 0.168 | 0.145 |
| 2 | 99.39 | 0.105 | 0.149 | 0.173 | 0.137 |
| 3 | 99.43 | 0.098 | 0.110 | 0.187 | 0.151 |
| 4 | 99.45 | 0.120 | 0.082 | 0.138 | 0.147 |
| 5 | 99.52 | 0.092 | 0.091 | 0.140 | 0.151 |
| 6 | 99.47 | 0.109 | 0.123 | 0.148 | 0.150 |

**Table - 1B: Purity of Distilled TCAC**

| Batch No | % ASSAY | % Chloroacetyl chloride (CAC) | % Dichloro acetyl chloride (DCAC) | % High boiling Impurities | % $SO_2$ |
|---|---|---|---|---|---|
| 1 | 99.76 | 0.040 | 0.075 | 0.017 | 0.082 |
| 2 | 99.78 | 0.066 | 0.053 | 0.019 | 0.078 |

| | | | | | |
|---|---|---|---|---|---|
| 3 | 99.81 | 0.020 | 0.053 | 0.018 | 0.075 |
| 4 | 99.77 | 0.053 | 0.050 | 0.023 | 0.088 |
| 5 | 99.78 | 0.046 | 0.042 | 0.032 | 0.072 |
| 6 | 99.71 | 0.023 | 0.078 | 0.028 | 0.092 |

**Table - 1C: Purity of Double Distilled TCAC**

Products obtained from trials were analyzed by Gas Chromatography (GC) for purity. A Representative GC chromatogram of one of the trial batches is shown in Fig. 1.

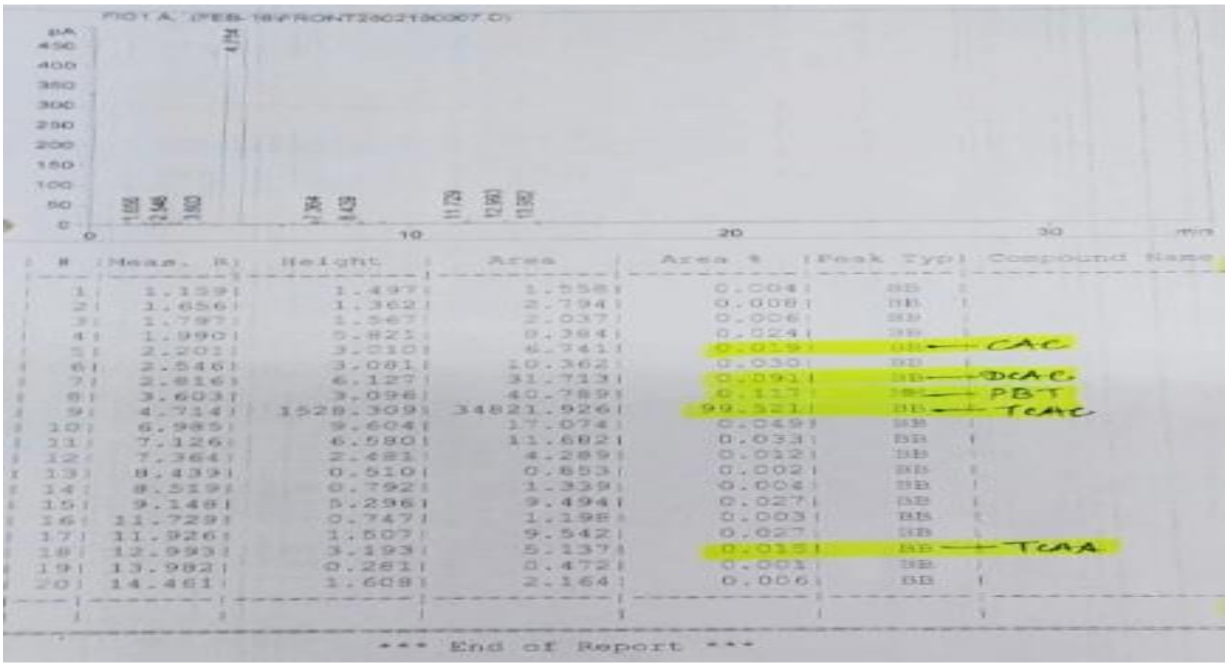


**Figure 1: GC Chromatogram of TCAC Batch No. 5**

The results presented in Table 1A are of crude TCAC obtained after step (iii) of synthesis. In all the batches tested, the purity of crude product is higher than 98 %. The side products are ~ 3.0% & while the high boiling purities are ~ 0.8 %. The purity of TCAC increases to ~99.5% after first distillation & is close to 99.7% after double distillation. The level of side products & impurities drops to less than 0.1 % after final purification step. The maximum purity achieved from earlier processes was between 97 – 98 % with higher level of impurities. The new method produces TCAC with > 99 % purity, making it fit for using in pharmaceutical industries. Additionally, the process removes the tedious efforts needed for disposing the chemical waste generated through recycling & reuse. As a result, the methods become more sustainable.

**Conclusion**

  

In this work, we have discussed the successfully manufacturing of Tri-chloroacetyl chloride from the by-product Mother Liquor (ML) of MCA obtained from the MCA manufacturing industries which they have bigger challenge to dispose off this by-product and hence, the importance of either reuse or recycling in other chemical manufacturing. We have successfully achieved the desired results and the quality of product prepared is equivalent or better than product manufactured using fresh starting materials. The new improved process allows us to use of Mother liquor (ML) of MCA in combination with acetic acid as alternative raw material. Low cost and easy availability of Mother Liquor (ML) of MCA makes this process economically viable. In conclusion, chemistry plays a pivotal role to reuse or recycle by-products into valuable chemical compound. It will help for MCA manufacturing industries for sustainable production as they will not have worry for deposition of this by-product and will also help them earn money by selling this by-product Mother Liquor (ML) of MCA to TCAC manufacturing Industries. An application of green chemistry by industry where the output of one process is the input of another one, can be viewed as a solution to promote a sustainable economy, low carbon footprint and resource efficient.

**Declaration on Conflict of Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Glossary

**TCAC-** Tri chloroacetyl chloride

**TCAA-** Tri Chloroacetic acid

**DCAC-** Di Chloroacetyl chloride

**MCA-** Mono chloroacetyl chloride

**Mother Liquor-** the liquid remaining after a substance has crystallized out

**Key starting material-** a raw material used in production of chemical molecule and is incorporated as significant structural fragment

**Crude product-** Impure product obtained immediately after synthesis

**Distillation-** action of purifying a liquid by a process of heating & cooling

**Reflux-** a technique involving the condensation of vapors & return of this condensate to the system

**Side product-** Impurities which appear during the reaction as a result of side reactions that can be alternative reaction pathways

**$SO_2$-** Sulphur Dioxide

**Agro-** Agrochemicals

**Pharma-** Pharmaceuticals