

SELECTION OF A NOVEL MANUFACTURING PROCESS AND CATALYST FOR THE PRODUCTION OF DIACETONE ALCOHOL

¹Dhanashree S. Jagtap, ²Varad V. Joshi, ³Shruti G. Jadhav, ⁴Manoj B. Mandake

¹⁻³Undergraduate Students at Bharati Vidyapeeth College of Engineering,

⁴Assistant Professor at Bharati Vidyapeeth College of Engineering,

¹Department of Chemical Engineering,

¹Bharati Vidyapeeth College of Engineering, Navi Mumbai, India.

Abstract: Diacetone alcohol (DAA) is an industrially useful and important product with several applications. DAA is used as a solvent for the purification process, adhesives, paints, thinners, and household cleaners. The conventional process of manufacturing DAA from acetone by base-catalyzed aldol addition reaction is by homogeneous catalyst which is methanolic NaOH which results in so many undesired side products such as mesityl oxide, isophorone, etc. also the catalyst is not regenerated after the reaction. Due to the wide applications of DAA, the conventional process must be replaced by some other process that can overcome the limitations of the conventional process. By studying alternative processes, we get an idea about an optimized process for the production of DAA. The goal of this review paper is to do a comparative study of various processes being used in the industry or under research and developmental studies and showcase an optimal process from those. Reactive distillation is an industrially novel way of production of organic compounds which reduces the number of unit operations to synthesize them. RD has several advantages over conventional fixed-bed reactors since acetone conversions that exceed the equilibrium limit can be obtained. The present process integrates several functions into one unit, i.e., the basic catalysis of anion-exchange resin, self-aldol addition reaction of acetone, instant distillation separation of the condensates.

Keywords- diacetone alcohol, acetone, aldol addition reaction, reactive distillation.

INTRODUCTION

Diacetone alcohol is used as a solvent in varnishes, paints, cellulose acetate lacquer, thinners, and cleaning compounds and is an environmentally friendly alternative to other materials such as acetone due to its much lower volatility [3]. It is also an intermediate to other industrially important products. The dehydration of diacetone alcohol yields mesityl oxide, a useful compound with various applications, but primarily it's the precursor of methyl isobutyl ketone (MIBK), a well-liked solvent used mainly in the paint and coating industry [4]. To optimize the yield of the desired product DAA, further condensation reactions must be prevented without shifting the equilibrium towards the dehydration product mesityl oxide. A high-performance catalyst that not only gives high DAA yields but also a high selectivity is required and thus, much attention has been given to the catalyst. Conventionally, the aldol condensation of acetone is conducted using a homogeneous base catalyst such as methanolic NaOH or KOH [2,5]. Some major drawbacks are associated with the basic nature and homogeneity of the catalysts. The strong bases require specific measures to prevent corrosion problems which lead to high capital costs. In the conventional process, citric acid is added to neutralize the catalyst and stabilize DAA, after which DAA is recovered by evaporation, and by stripping off the acetone, it is then recycled [1,6]. This neutralization step must be accurately controlled as an excess of acid causes facile dehydration of DAA to MO [7]. Besides improving the catalyst, some research also focuses on a special reaction technique rather than conventional batch reactors or fixed-bed reactors, like Reactive distillation. RD has several advantages over conventional fixed-bed reactors since acetone conversions that exceed the equilibrium limit can be obtained, and no cooling of the acetone feed is required [8].

Diacetone alcohol

Diacetone Alcohol (DAA) is a clear, colorless liquid with a faintly pleasant odor with a chemical formula of $C_6H_{12}O_2$. It serves to be an industrially important product. It is usually used as a solvent in industries. The end uses of DAA are in industrial coatings, household cleaners, inks, paints, paint removers, paint thinners, pharmaceutical preparations, sealants, primer, and pesticides. DAA is used as a chemical intermediate in the preparation of Methyl Isobutyl Ketone and Hexylene Glycol. The normal boiling point of DAA is 167.9°C and its molecular weight is 116.16 kg/kmole. Dehydration of DAA results in the formation of Mesityl oxide (MO) and water (H_2O). DAA is synthesized by a simple self-aldol addition reaction using Barium Hydroxide ($Ba(OH)_2$) as a catalyst.

Raw material for the production

Only one raw material acetone is used for producing diacetone alcohol. Acetone is an organic liquid with the chemical formula C_3H_6O . Acetone is a flammable, volatile, and colorless liquid. Acetone is also majorly used as a solvent in industries. The normal boiling point of acetone is 56°C and its molecular weight is 58.08 kg/kmole.

Catalysts used for production

Ba(OH)₂: This is usually used as the catalyst for synthesizing DAA. It is fed to a Soxhlet extractor column. But it takes 72-120 hours to complete the reaction. The yield is about 70-72%. [9]

Amberlyst 15: The catalyst used in the experiments was commercial strong-acid cation-exchange resin Amberlyst 15. [10]

Amberlite IRA-900: It is an anion exchange resin. This strongly basic resin is based on a styrene-divinylbenzene copolymer, and the active sites are quaternary ammonium groups. [11]

CaC₂: It is well known that the aldol condensation is a base-catalyzed process, and the stronger the basicity of the catalyst is, the higher the catalytic activity is. Therefore, to understand an efficient aldol condensation under mild conditions, we've to explore new catalysts with much stronger Lewis basicity than the metal oxides. In this regard, calcium carbide might be an excellent candidate

due to its extremely strong Lewis's basicity, as justified by our previous research. The catalytic activity of CaC_2 is superior to all basic catalysts reported in terms of the conversion of acetone. [12]

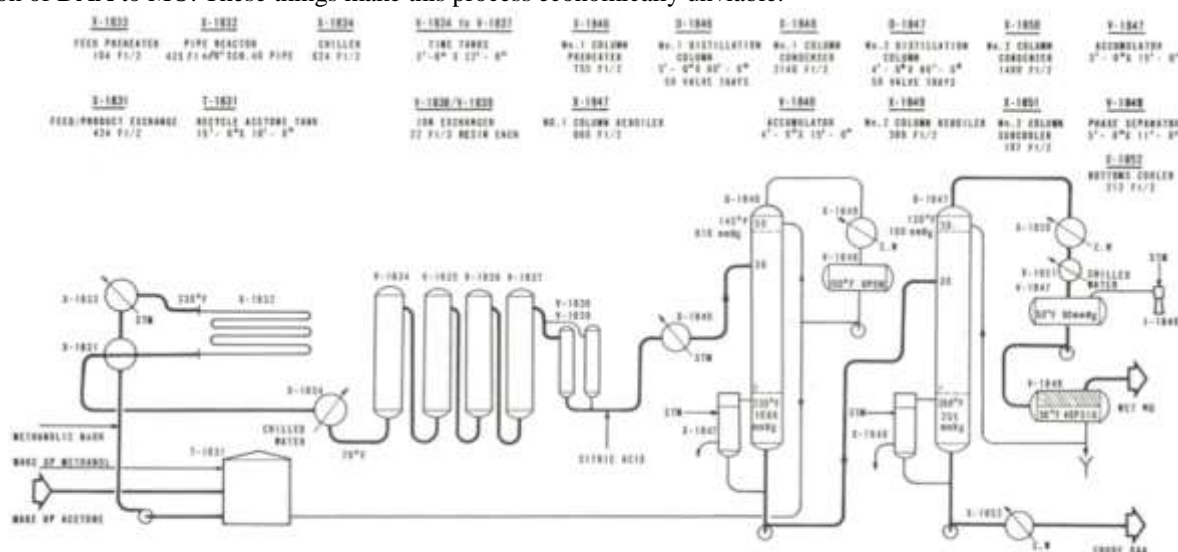
MgO/ Al_2O_3 -Al: The structured solid base catalyst, $\text{MgO}/\text{Al}_2\text{O}_3$ -Al catalyst packing, was prepared and used for the condensation of acetone to diacetone alcohol. The layer of MgO was coated on Al_2O_3 -Al by a sol-gel method. [13]

Methanolic NaOH: Sodium hydroxide pellets are dissolved in warm methanol by constant agitation to form an alcoholic NaOH solution. Being the strong base, the material of construction of the process equipment must be designed carefully to avoid corrosion and after the reaction, the catalyst must be neutralized using some acid.

PROCESSES FOR THE PRODUCTION OF DIACETONE ALCOHOL

1. Conventional Process-

The aldol condensation of acetone is conducted using a homogeneous base catalyst such as methanolic NaOH or KOH. The fresh feed of Acetone is first mixed with methanolic NaOH. After preheating this mixture, it is passed through a Plug Flow Reactor (PFR) then the pH of the reaction mixture is reduced using citric acid. Now this neutralized mixture is fed to a distillation column which recovers the unreacted acetone and recycles it back to the fresh feed. The bottom product of this column is fed to a sub-atmospheric distillation column which separated the crude DAA formed at the bottom and wet MO at the top under reduced pressure achieved by steam jet ejectors. Some major drawbacks associated with the homogeneity and basic nature of the catalysts are extremely low yield even though they have a higher conversion. The homogeneity of the catalyst requires intense purification afterward in which the catalyst is destroyed. In this process, the neutralization step must be accurately controlled as an excess of acid causes facile dehydration of DAA to MO. These things make this process economically unviable.



Conventionally, the aldol condensation of acetone is conducted using a homogeneous base catalyst such as methanolic NaOH or KOH giving acetone conversion of around 12%. In the conventional process, citric acid is added to neutralize the catalyst and stabilize DAA, after which DAA is recovered by evaporation, and by stripping off the acetone, it is then recycled.

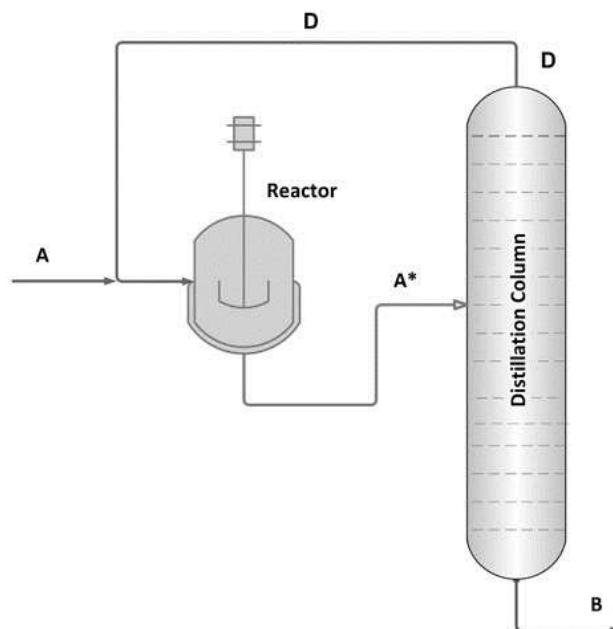
Drawbacks:

The homogeneity of the catalyst requires intense purification afterward in which the catalyst often is destroyed. This neutralization step must be accurately controlled as an excess of acid causes facile dehydration of DAA to MO.

The neutralization process and subsequent purification steps by distillation entail a high cost and produce large amounts of waste streams. Also, the catalyst NaOH is not regenerated by neutralization with citric acid.

2. Reactor-Distillation column- Recycle (RDR) Process-

In this process, acetone is charged in a fixed bed reactor (FBR) where the catalyst is loaded on the fixed bed of packing. The reactor mixture outlet is fed to a distillation column where most of the unreacted acetone is recovered from the top and recycled back to the reactor and produced DAA and by-products are collected at the bottom of the column which needs further separation. Here, the size of the fixed bed reactor, distillation column needed for the separation of acetone then DAA from by-products increases the capital cost of the process. Also, operating the condensers, reboilers, pumps and other auxiliary equipments increases the operating costs. Regeneration of catalyst loaded in the FBR is time-consuming and requires a standby FBR for the continuous operation of the plant. More unit operations and processes effectively increase the area required for the plant, total cost, net investment, and ultimately the cost of production of DAA. [14]



RDR process consists of two main units namely Reactor and a distillation column. Barium Hydroxide $\text{Ba}(\text{OH})_2$ is used as the catalyst. The diacetone alcohol is accumulated in the distillation still until the required concentration is reached.

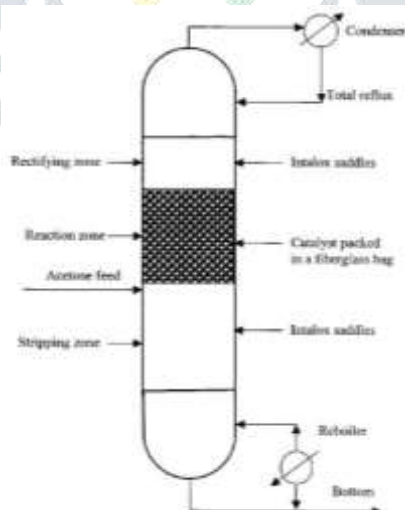
Drawbacks:

The heat released by exothermic reactions cannot be directly used in the distillation column.

The DAA formation reaction is only slightly exothermic and due to the low equilibrium conversions, there are difficulties in controlling the temperature in the reactor of the RDR process.

3. Reactive Distillation (RD)-

A specialized distillation column having a reactive section in the middle of the rectifying and stripping section composed of catalytic packing loaded with the catalyst is fed with acetone. Upcoming vapours of acetone are partially condensed using a partial condenser and refluxed (recycled) back to the column i.e., total reflux condition. The mixture of products coming out of the reboiler is fed to a vacuum distillation column to recover pure DAA and side products such as MO and Water at the top. Replacing the reactor and distillation column with a single reactive distillation column reduces the operating costs and area requirement of the plant considerably. Although though initial investment for the RD column will be huge, the amount is recoverable due to low operating costs and effectively lowers the total cost in comparison with the other two processes. Also, side product formation is comparatively lower in an RD column due to higher selectivity achieved towards DAA. This effectively reduces the cost of production of DAA. [15]



Reactive distillation has emerged as a novel technique of process intensification in which reaction and separation of product take place simultaneously in a single column. [16]

Benefits of reactive distillation include:

- Increased speed of operation
- Reduces the use of various equipment, requires less energy and handling is easy. These factors lower the capital cost.
- Fewer by-products are formed and very little or no waste is generated.
- The opportunity of degradation of the product is reduced due to reduced energy requirements, thereby improving the quality of the product.

Some reactions which show potential for RD are Esterification, Transesterification, Etherification, Alkylation, Aldol Condensation, Dehydration, Acetylation, Isomerization, etc. [17]

PROCESS SELECTION

Based on the literature survey, it was observed that in the conventional process, due to the use of a homogeneous catalyst which is methanolic sodium hydroxide and its inability to be regenerated and gets destroyed in the process while neutralization it with citric acid makes the conventional process pretty inefficient. Also, side-product formation such as mesityl oxide, isophorone, and further higher polymeric products are higher in the conventional process which decreases the overall yield of diacetone alcohol. Furthermore, inaccuracy in the addition of citric acid during the neutralization step can make the resulting solution too alkaline or even too acidic which will corrode the downstream equipment, increasing the maintenance costs.

In the case of the Reactor-Distillation-Recycle (RDR) Process, the use of the fixed bed reactor followed by a distillation column which would have to separate a mixture of four or even five components, mainly acetone, water, mesityl oxide, diacetone alcohol, and some quantity of isophorone, makes the process so much complicated. Also, the energy requirement for running the fixed bed reactor and the distillation column is significantly higher. Considering the deactivation of the catalyst, the need for a standby fixed bed reactor increases the fixed capital investment. In this process, unnecessarily too many unit operations are required, where each of them consumes a lot of energy.

The Reactive Distillation process greatly overcomes all of the limitations of the above two processes. Here, a reactor followed by a distillation column is replaced by a single multi-functional reactive distillation (RD) column. The efficient use of the heat of reaction to decrease the load on the reboiler duty is achieved inside an RD column. As the reaction occurs in the reactive section only, side reactions that occur due to undesired longer residence time in the reactor are suppressed. RD is often used when the products of a reaction are less volatile than the reactant. In such a case the reactant is kept in the RD column by operating the column at total reflux. The heavier product separates from the light reactant and is removed at the bottom of the RD column.

In the RDR process, Ba (OH)₂ was used as a catalyst where the process took almost 50-120 hours to give around 34% conversion, after that further separation needed a series of distillation columns to separate the DAA from unreacted acetone, side products such as mesityl oxide, isophorone, and water.

After required the reaction time the deactivated catalyst is to be unloaded and the fresh activated catalyst is to be loaded. This loading and unloading are time-consuming.

The deactivated Ba (OH)₂ catalyst is then landfilled which causes harmful Ba⁺² ions to leach out in the soil and groundwater bodies.

The total volume of reactor required will be less when resins are used as they can provide tremendous surface area and being more compact and denser than the Ba (OH)₂.

Resin regeneration is a process used by many industries which can regenerate the exhausted resins and by this process, although the resins being more expensive than Ba (OH)₂, can be used multiple times and there is no harm to the environment with less load on fresh resin supply.

Barium hydroxide being an alkaline earth metal hydroxide can cause corrosion issues to the material of construction whereas resins are inert towards metals.

Reactive distillation gives out only the mixture of DAA and some MO and Water which can be separated easily by using a sub-atmospheric distillation column downstream the RD column.

COMPARATIVE STUDY OF THESE PROCESSES

Parameter	Conventional Process	RDR Process	RD Process
Raw materials	Acetone	Acetone	Acetone
Catalyst used	Methanolic NaOH / KOH	Ba (OH) ₂	Amberlite IRA 900
Conversion (%)	12.20 %	24.34 %	7.4733 %
Yield (%)	35.62 %	30.12 %	83.98 %
Selectivity	0.55	0.43	5.24
Utilization of heat of reaction	No	No	Yes
Number of Distillation columns required	More than 3	More than 3	Less than or equal to 2
Side Product formation	Considerable	Considerable	Minimum
Catalyst Regeneration	Not possible, as it is neutralized	Not possible, due to permanent loss of active sites	Possible, due to ion-exchange characteristic of the catalyst
Capital cost	Higher, due to a greater number of equipments used	Comparatively less than conventional process but more than RD	High-cost of RD column is compensated due to minimum number of equipments used
Area required for Plant	Greater	Moderate	Less

Hence, Reactive Distillation is the process selected for the production of Diacetone Alcohol from Acetone.

CONCLUSION:

Based on the above discussions, although the conventional process and the RDR process being used industrially, the Reactive distillation process is an optimal approach for the large-scale production of Diacetone alcohol. Amongst several other catalysts, Amberlite IRA-900 anion-exchange resin catalyst stands out due to its selectivity towards DAA. More research and pilot-plant level study are suggested from this review to maximize the feasibility of carrying out the production on an industrial scale. Further scope is to enlighten some essential parts of the reactive distillation column, like the selection of the material of construction for catalytic packing along with its design with packing pressure drop, resin-catalyst regeneration, and proper disposal of the wastes produced after regeneration.

REFERENCES:

- [1] G. S. Salvapati; K. V. Ramanamurty; M. Janardanarao. 1989. Journal of Molecular Catalysis, 54: 9-30.
- [2] K. Weissmermel; H.-J. Arpe. 2003. Industrial Organic Chemistry, Wiley-VCH, 3.
- [3] E. M. Kirschner. 1994. Chemical & Engineering News, 72: 13-20.
- [4] W. K. O. Keefe; M. Jiang, F. T. T. Ng; G. L. Rempel. 2005. Chemical Engineering Science, 60: 4131-4140.
- [5] F. A. Carey; R. J. Sundberg. 2007. Advanced Organic Chemistry, Springer, 5.
- [6] J. Braithwaite, in M. Howe-Grant (Ed.). 1995 Kirk-Othmer Encyclopedia of Chemical Technology. Wiley, 4: 485-506.
- [7] N. B. Lorette. 1954. Journal of Organic Chemistry, 22: 346-347.
- [8] W. NICOL. 2003. Trans IChemE, 81 (A).
- [9] Hossein Dabbagh; Burtron H. Davis. 1988. Condensation of Acetone using metal hydroxide and hydrous metal oxide catalysts. Journal of Molecular Catalysis, 48: 117 - 122.
- [10] Suman Thotla; Vishal Agarwal; Sanjay M. Mahajani. 2007. Aldol Condensation of Acetone with Reactive Distillation Using Water as a Selectivity Enhancer. Ind. Eng. Chem. Res., 46: 8371 - 8379.
- [11] Yuxiang Zheng; Flora T. T. Ng; Garry L. Rempel. 2007. Process Analysis for the Production of Diacetone Alcohol via Catalytic Distillation. Ind. Eng. Chem. Res, 42: 3962 - 3972.
- [12] Xuebing Xu; Hong Meng; Yingzhou Lub; Chunxi Li. 2018. Aldol condensation of refluxing acetone on CaC₂ achieves efficient coproduction of diacetone alcohol, mesityl oxide, and isophorone. RSC Adv., 8: 30610 - 30615.
- [13] Changhai DU; Yan SHEN; Linping SUN; Xiangchun MENG. 2012. Condensation of Acetone to Diacetone Alcohol over Structured MgO/Al₂O₃-Al Catalyst Packing, Advanced Materials Research: 347 – 353.
- [14] W. Nicol. 2003. Comparing catalytic distillation to separate reaction and distillation for the production of diacetone alcohol. Trans IChemE, 81: 1026 - 1032.
- [15] G. G. Podrebarac; F. T. T. Ng; G. L. Rempel. 1998. The production of diacetone alcohol with catalytic distillation Part I: Catalytic distillation experiments. Chemical Engineering Science, 53 (5):1067 - 1075.
- [16] G. G. Podrebarac; F. T. T. Ng; G. L. Rempel. 1998. The production of diacetone alcohol with catalytic distillation Part II: A rate-based catalytic distillation model for the reaction zone. Chemical Engineering Science, 53 (5): 1077 - 1088.
- [17] Anton A. Kiss; Megan Jobson; Xin Gao. 2019. Reactive Distillation: Stepping Up to the Next Level of Process Intensification. Industrial & Engineering Chemistry Research, 58 (15): 5909 - 5918.

