

## Popcorn Polymers in Butadiene Extraction Units

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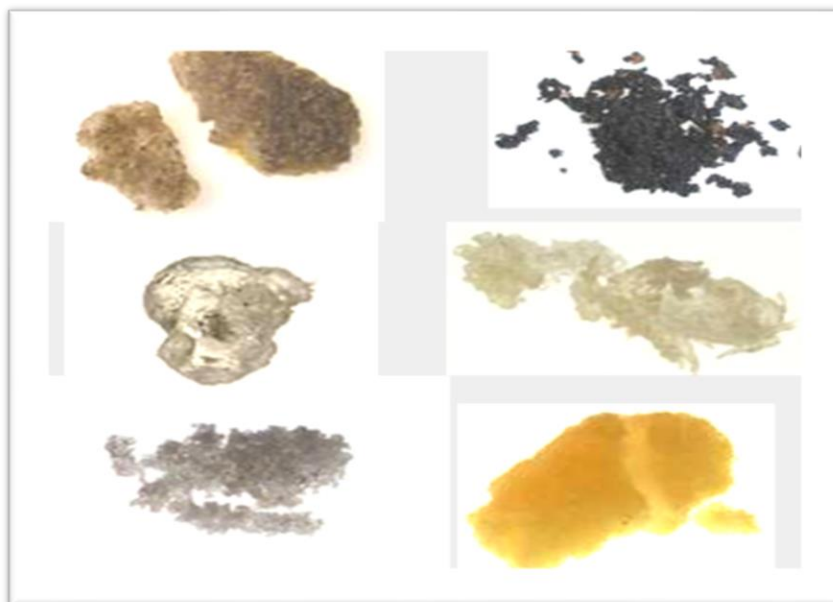
### ABSTRACT

Several aspects disturb operation of industrial facilities which can cause severe impact on their efficiency and productivity. In some cases, the impact can expose industrial facilities to serious safety concerns. Therefore, Industrial facilities should always plan to invest in reliability and sustainability of their daily operation. Polymerization is one of the unavoidable risks that can be unpredictable and cause several issues to operating facilities. On the other hand, effective proactive plans can be addressed to minimize and eliminate polymerization risks. This article provides introductory information about polymerization of butadiene “Popcorn polymers”, formation mechanism, associated hazard, control and mitigation methodologies.

**Keywords:** Butadiene, Polymerization, Petrochemical

### 1 Introduction

In petrochemical ethylene plants, 1,3-Butadiene is a major product from butadiene extraction units. It is an organic compound with a chemical formula of  $C_4H_6$  and it is colorless gas that is widely used to produce synthetic rubber, latexes, resins and plastics products. However, the most frequent issue and challenge that threaten butadiene extraction units’ productivity, reliability and safety is butadiene polymerization which is known as “popcorn polymers”. These polymers are very reactive, rigid and porous substance [1]. In addition, they can exist in several shapes and colors. The produced polymers may appear as crystalline, sheet, rubber or popcorn as shown in Figure 1 [2].



**Figure 1:** *Popcorn polymers in several shapes [2]*

Depending on many factors such as rate of growth, level and degree of cross linking, existing of air or peroxides, reaction with rust, oxygen and/or water as described in Figure 2 [3]. Refining and petrochemical industries have made significant efforts to minimize operation cost and improve productivity by reducing plants turnarounds and improving plant's reliability. Several risks and challenges need to be closely monitored and mitigated to achieve optimum results. One of the main changes in refining and petrochemical industries is linked to improve fouling control mechanism, which is a major contributor to achieve operational sustainability. In addition, it plays a main role in reducing energy costs, maintenance frequency, and emissions. The aim of this article is to raise the awareness about popcorn polymers associated risks, promote reliability and maintain operability of industrial facilities by adapting best practices and analyzing recent proven developments and technologies.

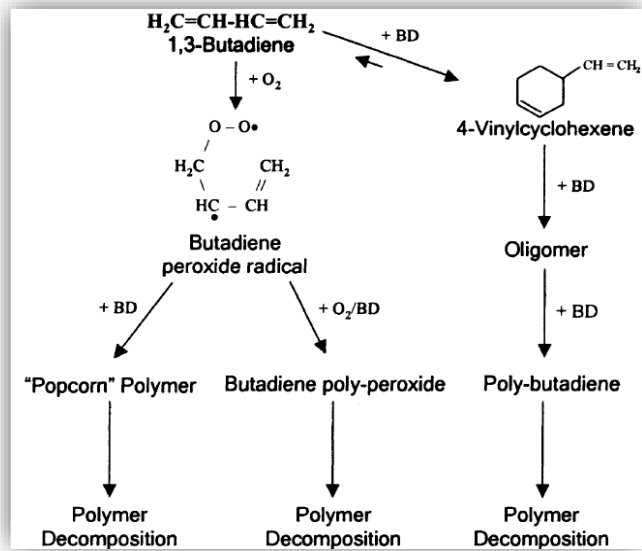


Figure 2: Reaction mechanism for 1,3-butadiene [3]

## 2 Butadiene Polymerization Mechanism

Initiation of popcorn polymers can be observed with various scenarios and conditions. Generally, existence of oxygen, rust and/or water in butadiene system led to initiation of peroxide radicals. Interaction between peroxide radicals, butadiene and polymers can generate hydrocarbon radicals. These reactions are relatively slow process and can be named as initiation phase. After that, the following step which can be called as growth phase where popcorn seeds are being formed once high concentration of butadiene is present with hydrocarbon radicals then these seeds grow up rapidly to form popcorn polymers. As a result, a phenomenon of seed generation is introduced where new popcorn seeds continue to be generated because of chains rupture due to high internal strain. Reactions and process of growth phase are relatively rapid compared with initiation phase. Polymerization process can be summarized as per the following scheme (Figure 3):

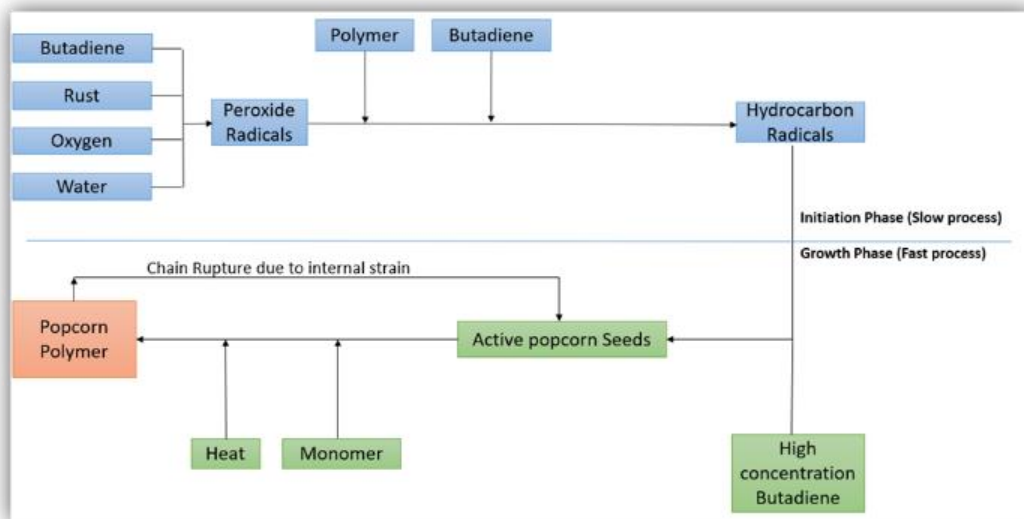


Figure 3: Butadiene polymerization flowchart

Several conditions can catalyze popcorn formation such as dead legs, butadiene concentration higher than 30%, high surface roughness, existence of water and rust [4].

### 3 Hazards And Safety Concerns

1,3-Butadiene is a chemical compound with high flammability and reactivity while popcorn polymers is an outcome of 1,3-butadiene reaction with oxygen and water, and it can tremendously grow and expand causing major risks to the industrial facilities. The influence of popcorn polymers is not limited to reduce efficiency of operating facilities, but it is also a serious safety hazard that must be closely monitored and mitigated. According to a laboratory-generated test developed by (DOW), the growth rate of popcorn polymers can be estimated by using the following formula:

$$W = W_0 e^{kt}$$

$W$  = weight of the popcorn after specific time

$W_0$  = initial weight of popcorn

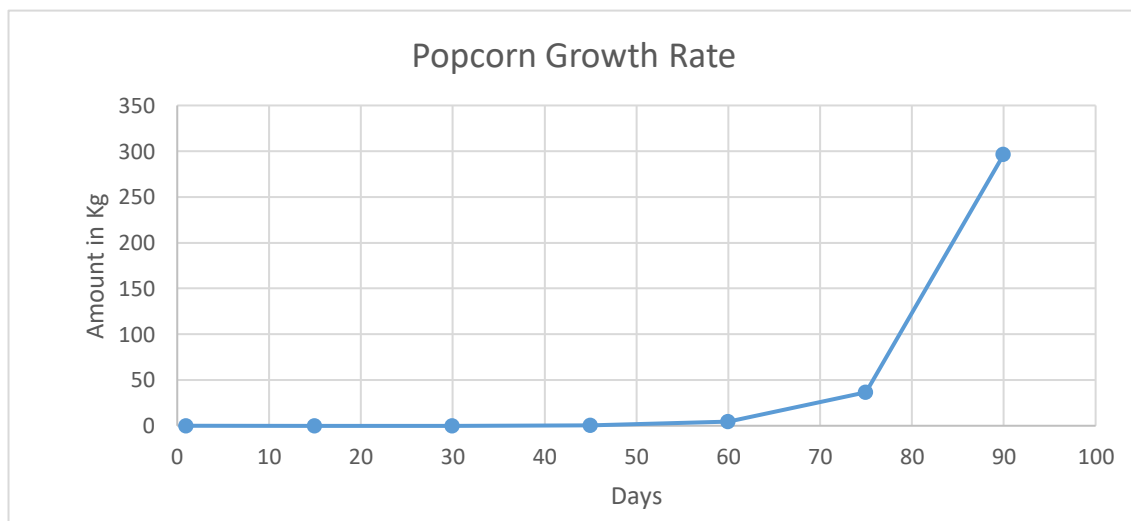
$k$  = growth rate constant

$t$  = time on stream

An example below (Table 1) and (Figure 4) is for applying the formula with a typical value for the growth rate which is 0.14/day at 45 °C. The above formula and growth rate value are according to European Ethylene Producers Committee Document [5].

**Table 1:** Popcorn growth rate in Kg per day

Days	Amount (Kg)
1	0.0012
15	0.0082
30	0.0667
45	0.5456
60	4.4471
75	36.3155
90	296.5586



**Figure 4:** Popcorn growth rate in Kg per day

As shown in the above example, popcorn polymers can expand exponentially causing serious damage and rupture to pipes and equipment if left unabated.

Several actual cases are described below:

1. Manhole of a butadiene extraction unit is blocked with popcorn polymers (Figure 5). No further details are available from the source [6].



**Figure 5:** *Popcorn polymers in a manhole of butadiene extraction unit [6]*

2. An incident occurred in TPC Group (TPC) Port Neches Operations (PNO) facility in Port Neches, Texas in 2019. The incident involved major loss of containment and multiple explosions that resulted in human injuries and an estimated property loss of \$500 Million. Popcorn polymers accumulation in a dead leg segment was the root cause of the incident as per the outcome of the investigation (Figure 6) [6].



**Figure 6:** *Explosions of PNO facility in Port Neches, Texas in 2019 [6]*

3. Heat exchanger bundles of acetylene removal section and associated pressure relief valve were found accumulated with popcorn polymers as reported by TPC Group (Figure 7) [6].



**Figure 7:** Heat exchanger bundles accumulated with popcorn polymers [6]

4. Rupture of 8” line of butadiene reboilers in Lavera Petrochemical Complex resulted in releasing 7 tons of butadiene to atmosphere. Investigation concluded that popcorn polymers were accumulated in a dead leg area (Figure 8) [4].



**Figure 8:** Rupture in butadiene reboiler in Lavera Petrochemical Complex in December 2000 [4]

#### 4 Polymerization Control

Over the years, operating facility gained and learned significant information about popcorn polymers nature and behavior. They become able to predict initiation signs and mitigate associated risks by applying best practices. Several procedures can be adapted to predict and reduce the polymerization tendency. Some of these procedures are globally in service since long time while others are still under experimental phase. Planning polymerization control can strongly contribute to enhance productivity and efficiency of producing facilities by reducing turnarounds and preventing equipment damage. This section discusses several methodologies that can be considered.

#### 4.1 Popcorn Mitigation and Industrial Best Practices

Several mitigations, procedures and best practices to reduce probability and minimize popcorn polymers risks can be considered such as:

- Passivation of unit's equipment is considered as a chemical treatment and aims to generate a protective surface area which is usually performed by circulating hot sodium nitrite solution ( $\text{NaNO}_2$ ). Passivation should be done before start-up and repeated each time after exposing unit's equipment air.
- Pickling is also considered as a chemical treatment to remove rust from the unit. It is typically performed by circulating citric acid solution with an inhibitor followed by flushing. Then, neutralization steps are taking place.
- In high butadiene concentration services, it is recommended to use vertical condensers and pad nozzles to minimize stagnant areas.
- Conduct periodic x-ray inspection in vapor lines.
- Injection of polymerization inhibitors

#### 4.2 Online Cleaning Technology

There are many ways to remove polymerization/fouling from equipment. Each methodology has its own pros and cons. The typical cleaning mechanism is performed by applying hydro blasting and mechanical scratching for the dismantled part of the unit. The typical cleaning is effective in removing unwanted fouling and polymers. However, it requires to shut down the unit and dismantle the equipment that will be out of service until the cleaning process is completed. On the other hand, one of the newly existing proprietary technologies that are still not widely used called online cleaning technology. The technology developers aimed to replace the typical cleaning mechanisms with easier procedures that don't require dismantling unit's equipment. This process is performed by pumping chemical solution through the unit in a closed loop condition for a short period of time (around 24 hours). The technology has several advantages as claimed by the developers such as: short downtime, environmental friendly and reusable chemical solution. Figure 9 shows a tray dismantled for mechanical cleaning while Figure 10 shows a similar tray after performing online cleaning without dismantling [7]. Due to unavailability of field data, it is not possible to assist the efficiency and reliability of this new technology in this article.



**Figure 9:** Dismantled tray for typical cleaning [7]



**Figure 10:** Undismantled tray after online cleaning [7]

#### 4.3 Inhibiting Formation of Popcorn Polymers by Heat Treatment (Experimental Analysis)

A published experimental invention provided promising analysis results to deactivate popcorn polymerization initiation and disable popcorn seeds growth by exposing the system to heat source. According to the experiment report, the procedure should be applied in different ranges of temperatures

between 60°C and 650°C and different ranges of time between 15 minutes to 100 hours. Heating the system can be performed by utilizing external heat sources or by-passing hot gas through the system.

The experiment was conducted to treat samples of popcorn polymer seeds that were derived from 1,3 butadiene. The seeds samples heated in an oven with different ranges of temperatures for comparisons. Each test was conducted for two samples which came with different growth rates. The tests results are shown in (Table 2) below:

**Table 2: Heat temperature vs popcorn growth rate**

Sample N.	Heat Treatment Temperature	Popcorn Polymer Growth Rate
Sample 1	25	1.2
Sample 2	25	0.9
Sample 3	90	0.25
Sample 4	90	0.22
Sample 5	150	0.10
Sample 6	150	0.15
Sample 7	260	0.0
Sample 8	260	0.0

According to the results above, a clear linear relationship between increase of treatment temperature and reduction of popcorn growth rate [8]. The result of this invention should be further studied and assessed to evaluate the possibility of applying the method to the polymerized equipment to reduce/eliminate popcorn polymer tendency.

## 5 Conclusion

Butadiene extraction units are always under threat of polymerization and fouling. In fact, popcorn polymerization is unpreventable issue which can quickly and powerfully propagate within the operating units causing extreme damage to unit equipment, reduction/suspension of production and jeopardizing plant's operators' safety. The difficulty with these kinds of polymers that they are highly reactive and act as seeds for further polymer growth. Despite the several years of fighting the popcorn polymerization, the initiation phase is still not well defined and require serious attention to be managed. On the other hand, operating facilities have learned over the years several ways to predict popcorn polymers initiation and mitigate the risks by adapting several proactive approaches, best practices and being open to apply new methodologies which can help to achieve the optimum level of safe operation.

## 6 Declarations

### 6.1 Competing Interests

I would like to certify that the authors whose names are in the paper have no affiliations with or involvement in any organization or entity with any financial interest or non-financial in the subject matter or materials discussed in this article.

### 6.2 Publisher's Note

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### How to Cite the Article:

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## References

- [1] M. Liang *et al.*, "Oxidation reaction and thermal stability of 1,3-butadiene under oxygen and initiator," *Arabian Journal of Chemistry*, vol. 15, no. 11, p. 104289, Nov. 2022, doi: 10.1016/J.ARABJC.2022.104289.
- [2] J. M. Hancock, Debby Rossana, and S. J. Korf, "Popcorn in light ends," *Hydrocarbon Engineering*, Dec. 2014. Accessed: Feb. 02, 2023. [Online]. Available: <https://www.hydrocarbonengineering.com/magazine/hydrocarbon-engineering/december-2014/>

- [3] L. Li and O. Dogu, "Mitigating butadiene popcorn formation in industrial olefin units," LABORATORY FOR CHEMICAL TECHNOLOGY, Ghent. Accessed: Feb. 02, 2023. [Online]. Available: <https://www.lct.ugent.be/sites/default/files/mastertheses/36.%20Li-Mitigating%20butadiene%20popcorn%20formation%20in%20industrial%20olefin%20units.pdf>
- [4] French Ministry of the Environment, "Butadiene leak in a petrochemical unit," Dec. 2000. Accessed: Feb. 02, 2023. [Online]. Available: [https://www.aria.developpement-durable.gouv.fr/wp-content/files\\_mf/A22062\\_ips22062\\_002.pdf](https://www.aria.developpement-durable.gouv.fr/wp-content/files_mf/A22062_ips22062_002.pdf)
- [5] EEPCC Butadiene Popcorn Issue Group, "Recommendations for Preventing Popcorn in Steam Crackers and Butadiene Plants," *European Ethylene Producers Committee*, pp. 1-34, Mar. 2019.
- [6] CSB, "Fires and Explosions at TPC Group Port Neches Operations Facility," Port Neches, Texas, 2020. Accessed: Feb. 02, 2023. [Online]. Available: [https://www.csb.gov/assets/1/17/tpc\\_factual\\_update\\_10-29-2020.pdf](https://www.csb.gov/assets/1/17/tpc_factual_update_10-29-2020.pdf)
- [7] M. FERRARA, T. KIM, and C. FERRARA, "Safe removal of polymeric deposits," Jan. 2015. <https://www.digitalrefining.com/article/1001034/safe-removal-of-polymeric-deposits> (accessed Feb. 02, 2023).
- [8] H.-N. Sun, C. C. Ingram, and J. J. Mcmanus, "Method for inhibiting popcorn polymer formation by heat," Jan. 24, 1992 Accessed: Feb. 02, 2023. [Online]. Available: <https://patentscope.wipo.int/search/en/detail.jsf?docId=WO1992013010>

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