

SAMYANG

TRILITE
삼양 트리라이트
Ion Exchange Resin

Ion Exchange Resin for BPA Catalyst

Technical Report



Samyang Corporation Ion exchange resin

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TRILITE in numbers

1 First & Only



Korea's only ion exchange resin maker

+2 Factories



Our factories in Ulsan and Gunsan, OEM factory abroad

+200 Products



Over 200 types of products for power plants, ultrapure water, food, pharmaceuticals, and catalysts

+400 Partners



Collaborate with 400 partners worldwide

+50 Sales networks



Sell in 50 countries worldwide

1.1↓ Uniformity coefficient



High-quality UPS IER with a uniformity coefficient of 1.1 or lower

Locations (Headquarter, Plant, Tech center)

Seoul (Headquarter)

- Possession of specialized technical sales personnel in three fields
 - Water treatment/Ultrapure water/ Condensate polishing/ (Condensate polishing) Catalysts
 - Starch / Nucleic acids / Amino acids / Pharmaceuticals
 - Wastewater treatment / Chelates / Specialty purification
- Providing one-stop total solutions
 - Ion exchange resin analysis
 - Equipment diagnosis
 - Design support
 - Technical seminars
 - Trouble shooting

Gusan (UPS Resin Plant)

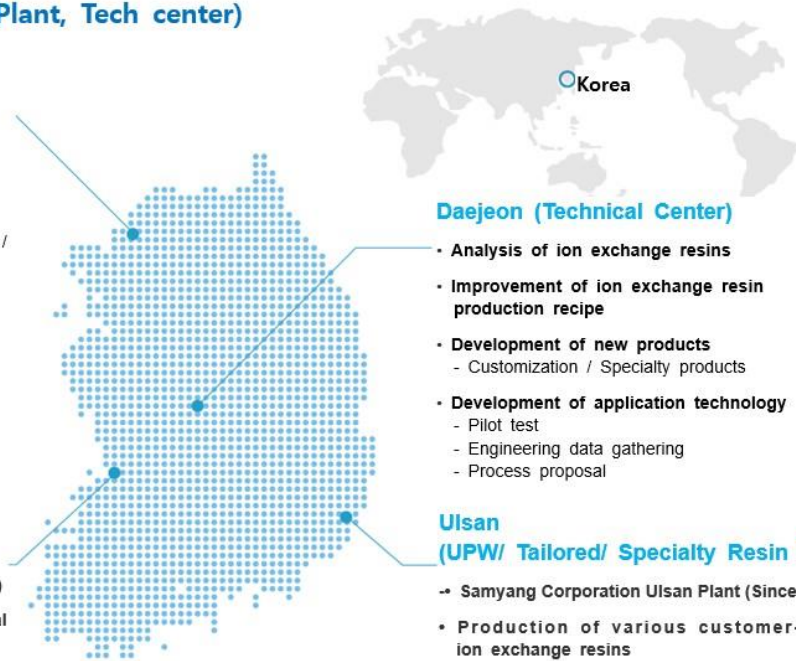
- Uniform particle sized resins
- Samyang Fine Technology (Since 2016)
- Joint venture with Mitsubishi Chemical Corporation, Japan
- Asia's largest dedicated factory for uniform particle sized ion exchange resins
- Product line
 - Uniform particle sized ion exchange resins
 - Ultrapure water resins (OLED, LCD)
 - Chromatography resins

Daejeon (Technical Center)

- Analysis of ion exchange resins
- Improvement of ion exchange resin production recipe
- Development of new products
 - Customization / Specialty products
- Development of application technology
 - Pilot test
 - Engineering data gathering
 - Process proposal

Ulsan (UPW/ Tailored/ Specialty Resin Plant)

- Samyang Corporation Ulsan Plant (Since 1976)
- Production of various customer-tailored ion exchange resins
- Product line
 - Ultrapure water resins (semiconductor)
 - Customization resins (starch, nucleic acids, catalysts, etc.)
 - Specialty resins (chelate, synthetic adsorbents, etc.)



1. Synthesis of BPA

Polycarbonate, one of the engineering plastics, is produced from high-purity bisphenol A (BPA). Ion exchange resins are used as catalysts in the synthesis of bisphenol A. The catalyst reaction mechanism for BPA is shown as follows.

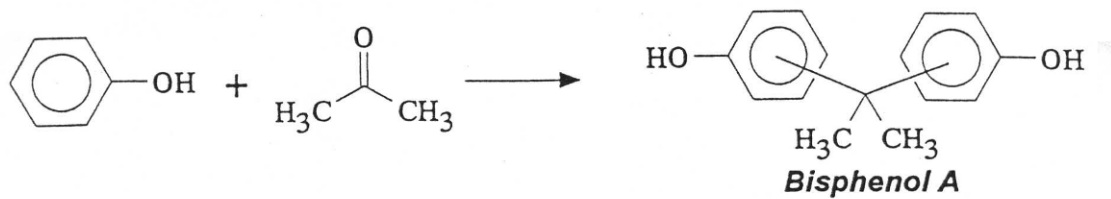


Figure 1. BPA reaction mechanism

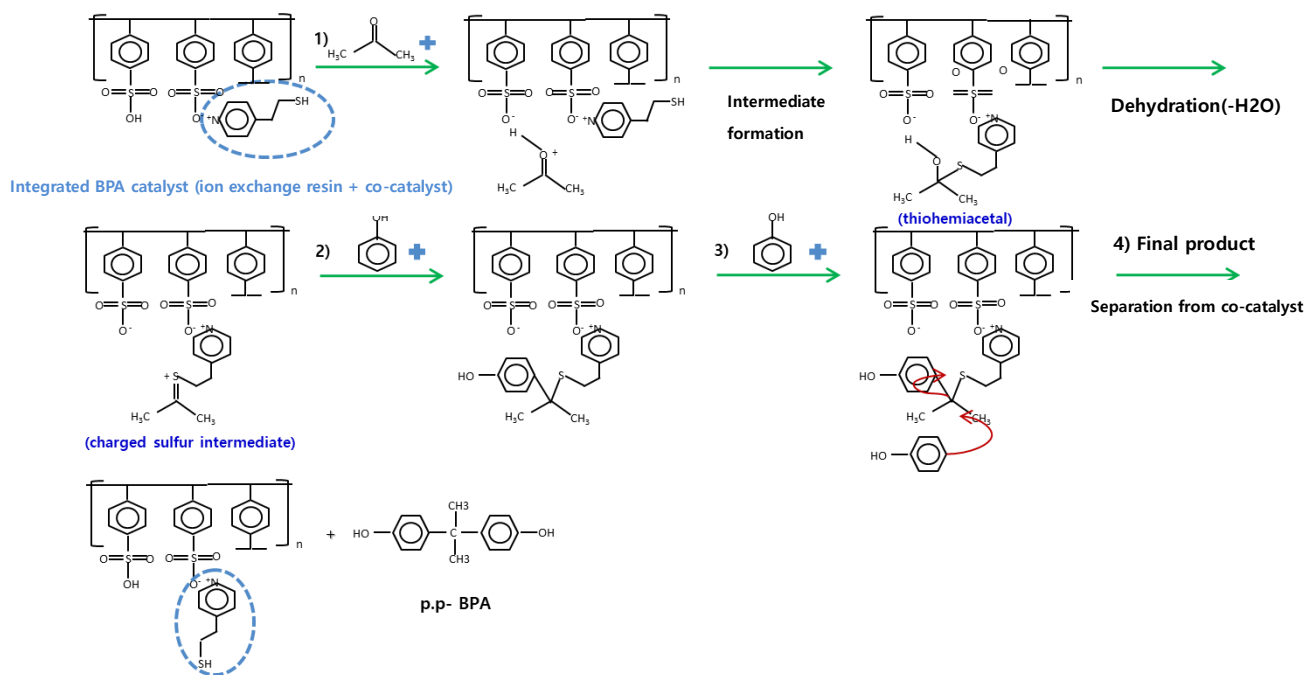


Figure 2. BPA catalyst reaction mechanism

There are several methods for manufacturing BPA, including IDEMITSU, BADGER, and SHIYODA methods. The IDEMITSU method uses strong acid cation exchange resins as catalysts and employs methanethiol and ethanethiol as co-catalysts. Due to the use of co-catalysts, a separate recovery



process is required. The BADGER process is similar to the IDEMITSU process in that it uses a strong acid cation exchange resin as a catalyst and methanethiol or ethanethiol as a co-catalyst, but it is different in that it uses up flow. On the other hand, the SHIYODA method uses a co-catalyst integrated ion exchange resin. Therefore, it does not require a separate recovery process and is an eco-friendly process because it has a MeOH purification facility.

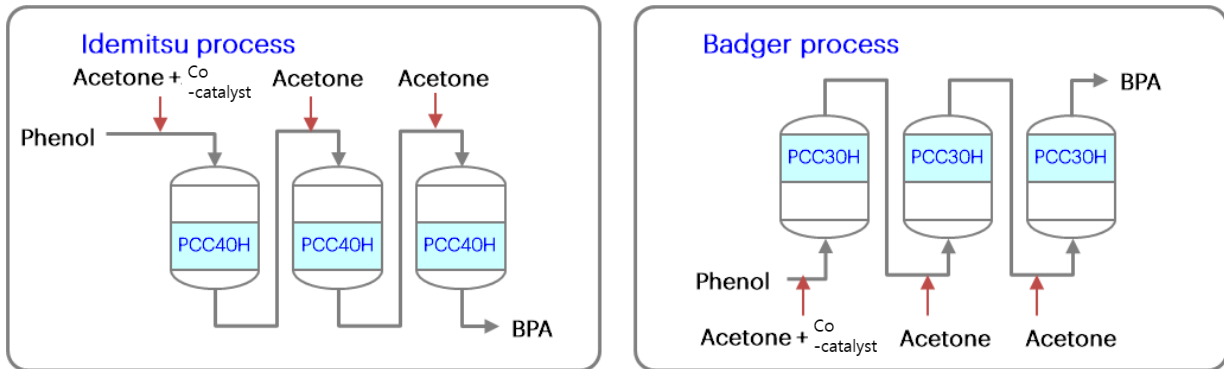


Figure 3. Idemitsu and Badger process schematics

2. Performance decline of ion exchange resins for catalyst

Strong acid cation exchange resins as catalysts generally have a long service life as they do not participate in the reaction. However, the lifetime may vary depending on the process, and the reasons for performance degradation are as follows.

1) Reduced H conversion rate by ion exchange resin for metal ion

The fresh strong acid cation exchange resin for the catalyst typically exhibits an H conversion rate of 99.9% or higher, with most functional groups converted to H form. However, during use, various metal ions from the raw solution may be introduced, leading to the exchange of H ions with other metal ions, resulting in a decrease in the H conversion rate and a reduction in the number of reactive sites. In cases where regeneration facilities are available, treatment with hydrochloric acid or sulfuric acid can partially restore the resin. However, catalytic resin towers, which often lack regeneration facilities, and are often contaminated with other foreign substances at the same time, so it is often economical to replace them.



2) Loss of functional groups

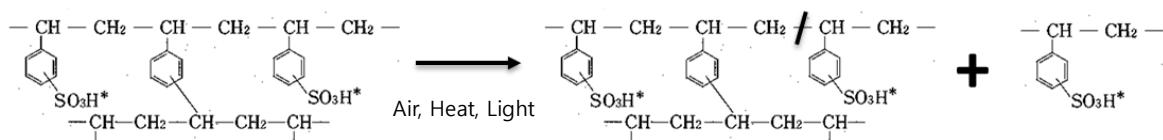
The functional group of the strong acid cation exchange resin used as a catalyst is chemically stable and exhibits high thermal stability. However, long-term exposure to chemicals and heat can lead to the loss of some functional groups.

3) Pore blockage by polymer

The functional groups in the ion exchange resin exist not only on the surface but also internally. When pores for ion diffusion become clogged, internal ion diffusion is impeded, leading to performance decline. Such cases, which occur and accumulate in small amounts as side reactions other than catalytic reactions, are generally unavoidable when generated through normal reactions. However, if there is room for improvement through changes in reaction conditions, they should be addressed.

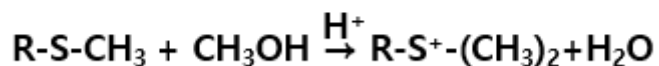
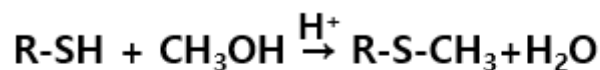
4) Oxidation of ion exchange resin

When the ion exchange resin comes into contact with oxidizing substances (Fe , Cl_2 , and O_2), it undergoes oxidation and irreversible swelling which leads to performance deterioration. Oxidizing substances (Fe , Cl_2 , and O_2) play a catalytic role in the oxidation process. As oxidation progresses, irreversible swelling occurs in the ion exchange resin. Although the overall exchange capacity does not increase, the crosslinking is severed, leading to a decrease in apparent density and an increase in moisture content. As the process continues, the resin's strength weakens, and the crosslinking is severed, resulting in the release of substances containing weak acidic groups, which can contaminate the effluent.



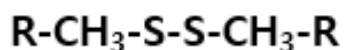
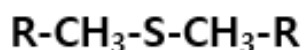
5) Influence of impurities (MeOH)

When the influent water contains impurities such as alkyl alcohols, SH (thiol) groups are transformed into SC (sulfide) groups, leading to the inhibition of catalytic activity.



6) Influence of reaction heat

Heat (exothermic reaction) can transform SH (thiol) groups into SC (sulfide, disulfide) groups, leading to the inhibition of catalytic activity.



3. Byproducts of BPA Reaction

During the synthesis of BPA, various byproducts are generated. To increase the yield of p,p-BPA, isomerization reactions, and scavenger reactions are added during the BPA process to maximize the yield. Through the isomerization reaction, o,p-BPA, and Trisphenol are produced from p,p-BPA. Additionally, the scavenger reaction leads to the production of p-Isopropenylphenol.

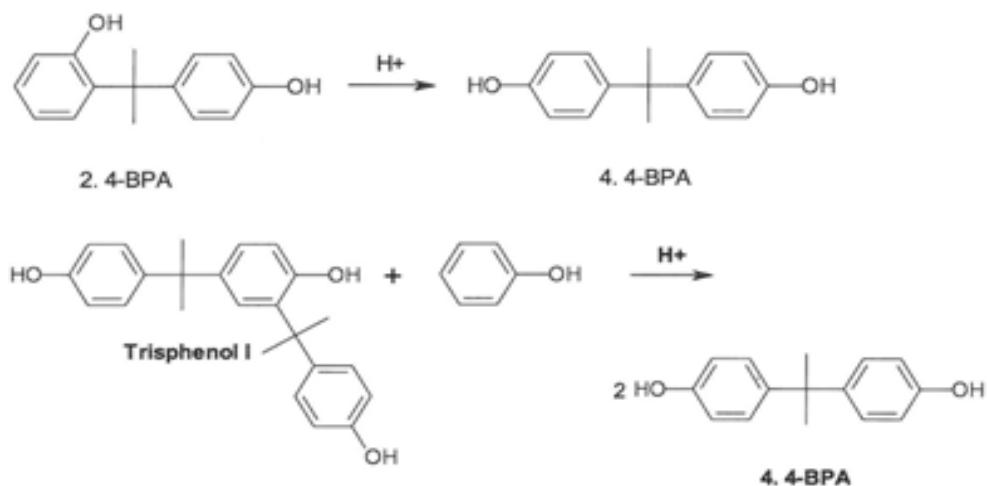


Figure 4. BPA Isomerization reaction

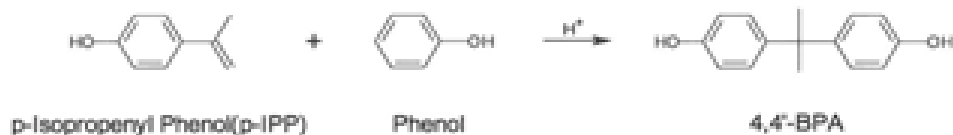


Figure 5. BPA Scavenger reaction

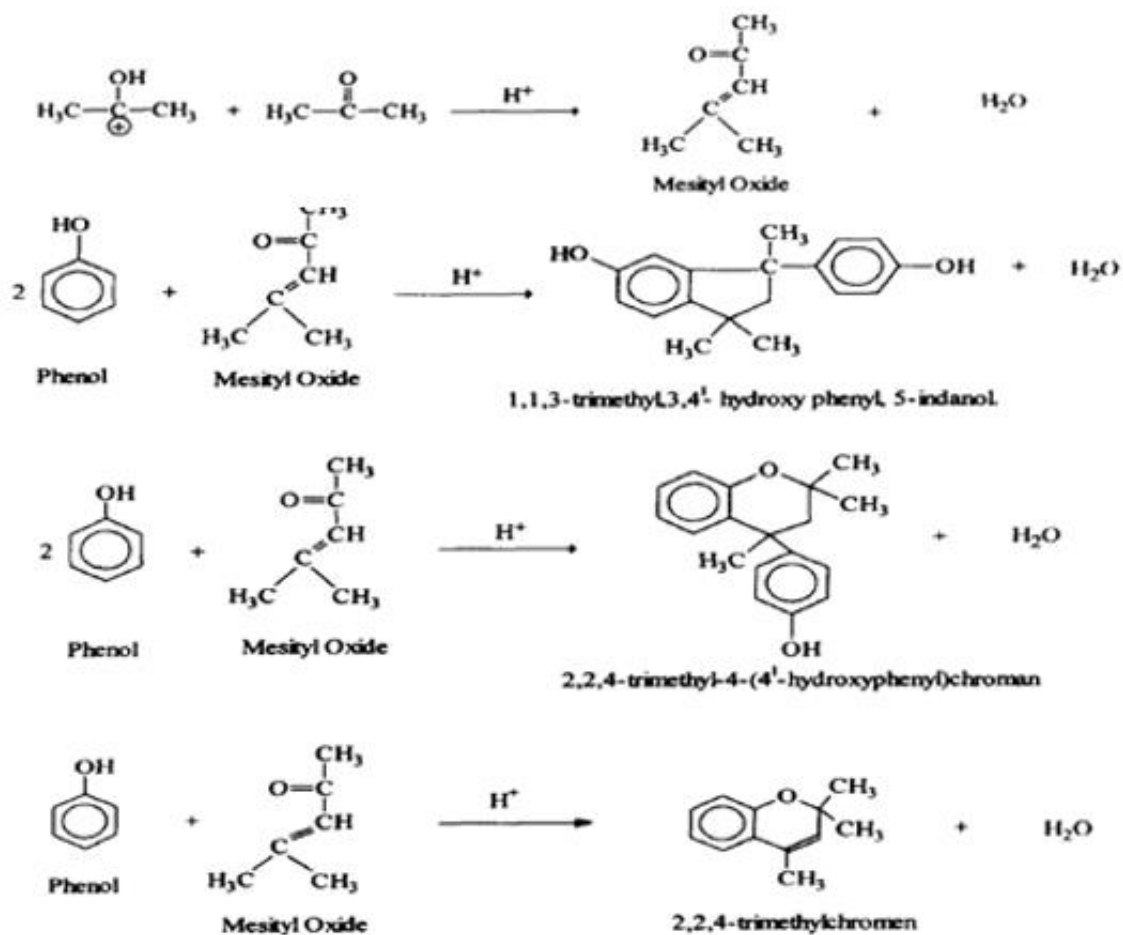


Figure 6. BPA Synthesis byproducts



4. Key Performance Indicators for BPA Catalyst

1) Conversion rate

The conversion rate of acetone as it passes through the catalyst layer during the reaction of phenol and acetone in a fixed-bed continuous reactor for BPA production.

2) p,p-BPA + o,p-BPA selectivity

The ratio of p,p-BPA, and o,p-BPA among the products produced, excluding unreacted phenol and unreacted acetone.

3) p,p-BPA/o,p-BPA molar ratio

The ratio of the conversion to p,p-BPA, and o,p-BPA in the products.

4) Catalyst lifetime

The continuous operating time of the catalyst in a fixed-bed, continuous liquid-phase reaction for BPA production without the need for catalyst regeneration.

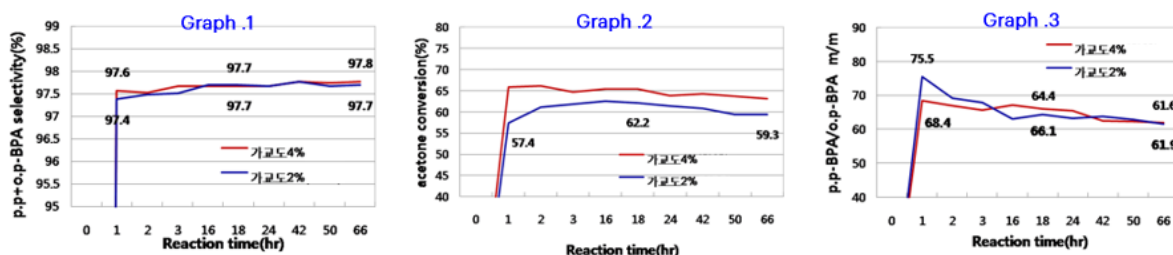
5. BPA Catalyst Reaction According to Ion Exchange Resin Crosslinking

Degree

1) Test conditions

In the Micro Reactor, 3ml of catalyst resin was filled, and phenol and acetone were introduced in a ratio of 8.5:1 at 60°C for the test. TRILIRE PCC30H (crosslinking degree of 4%) and TRILIRE PCC20H (crosslinking degree of 2%) were compared.

2) Test result





The low cross-linked ion exchange resin (2%) has the advantage of a faster reaction rate compared to the high cross-linked ion exchange resin (4%). However, it has the disadvantage of lower exchange capacity, lower oxidation resistance, and higher shrinkage, resulting in weaker chemical strength of the ion exchange resin.

The selectivity of 4,4-BPA+2,4-BPA (Refer to Graph.1) was at an equivalent level, while the acetone conversion rate (Refer to Graph.2) was superior in the high cross-linked ion exchange resin (4%). (With higher exchange capacity, there is more R-H, resulting in a higher acetone conversion rate.)

The molar ratio of 4,4-BPA/2,4-BPA production (Refer to Graph.3) initially showed a higher value in the low cross-linked ion exchange resin (2%), but over time, it reached an equivalent level to the high cross-linked ion exchange resin (4%).

6. TRILITE Ion Exchange Resin for Catalyst

Grade	Unit	TRILITE MC-04LH	TRILITE PCC30H	TRILITE PCC20H
Type		UPS	Non-UPS	Non-UPS
		Gel	Gel	Gel
Matrix		Polystyrene + DVB		
Functional group		Sulfonic acid		
Ionic form		H ⁺		
Shipping weight	g/l	795 ↓	795 ↓	795 ↓
Moisture content	%	60~72	60~70	75~85
Total capacity(M)	eq/kg	4.5 ↑	5.0 ↑	5.0 ↑
Total capacity(V)	eq/l	1.2 ↑	1.2 ↑	0.6 ↑
Particle Size	μm	700±50	300~1200	700~1600
Uniformity coefficient		1.1 ↓	1.6 ↓	1.6 ↓

※ The data for Shipping weight is for reference.



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