



Ion Exchange Resin for Catalyst (Overall Summary)

Technical Report



Samyang Corporation Ion exchange resin

31, Jongno 33-gil, Jongno-gu, Seoul, Korea TEL) 82-2-740-7732~7 FAX) 82-2-740-7709 <http://samyangtrilite.com>

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/Ultrapur 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. Overview

Ion exchange resins, like acids and bases used as catalysts, can also be employed as solid acid catalysts or solid base catalysts in organic reactions. In the early stages of using ion exchange resins as catalysts, they were primarily used in polar solvents for reactions such as esterification or hydrolysis of esters.

With the development of porous-type ion exchange resins, it became possible to use them in non-polar solvent systems, such as alkylation reactions. (Not applicable with the traditional gel-type resins.)

This table provides information about the types of ion exchange resins and their applications. Currently, ion exchange resins are being used as catalysts in various chemical processes.

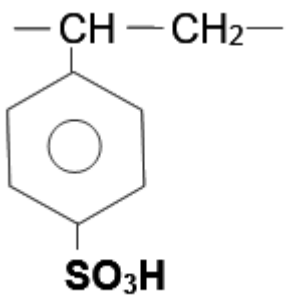
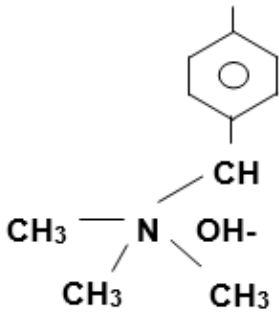
| Type | Type of reaction |
|---|--------------------------------|
| SA (Strong Acid)  | hydrolysis |
| | esterification |
| | acetal/ketal formation |
| | cyclization |
| | condensation |
| | dehydration |
| | decarboxylation |
| | hydrogenation |
| | amidation |
| SB (Strong Base)  | hydrolysis |
| | elimination of hydrogen halide |
| | condensation |
| | hydration |
| | cyclization |
| | esterification |
| | acylation |
| | phase transfer catalyst |

Table1. Ion exchange resins as reaction catalysts



2. General Characteristics of Ion Exchange Resins

When used as a catalyst, ion exchange resins can be easily separated from the reaction system and enable continuous reactions through the use of column reactors, making them economical. Ion exchange resins for catalysts do not need regeneration or reconcentration, and the reaction selectivity is high with low by-products. In addition, the low corrosiveness of the device makes material selection easy. On the other hand, compared to inorganic catalysts it has the disadvantages of lower thermal stability and slower reaction rates when the reaction materials are polymers.

Catalyst-grade ion exchange resins come in various grades depending on the type of matrix, crosslinking, and functional groups. Each grade of catalyst-grade ion exchange resin has different catalytic capabilities and selectivity. Therefore, it is essential to determine the grade of ion exchange resin based on the reaction system and reactants. The reaction system and reactants should be examined based on the following conditions.

- 1) Polarity of the reaction system
- 2) Molecular weight of the reacting substances
- 3) Reaction temperature

The reaction between the catalytic ion exchange resin and the target substance can vary depending on the reaction conditions. Therefore, it is challenging to predict the actual reaction yield and experimental testing is typically necessary for prediction. However, there are tendencies based on the general characteristics of the catalytic ion exchange resin, so they should be taken into consideration as a reference.

3. Selection of Ion Exchange Resin for Catalyst

3.1 Matrix structure

The polarity of the reaction system is an essential factor in choosing the matrix structure of the ion exchange resin.

- (1) Gel-type resins

- Gel-type ion exchange resins are used in polar solvent systems and are not suitable for non-polar solvent systems.

- (2) Porous-type resins

- Porous-type ion exchange resins can be used in polar solvent systems, and their porous structure allows for faster reaction rates compared to gel-type resins. They can also be utilized for reactions involving high molecular weight substances.



Table 2 provides examples of ion exchange resin selection for typical reactions.

| Solvent system | Reaction | PCC series | SPC series |
|-----------------------|--------------------|------------|------------|
| Aqueous solution | Esterification | ←-----→ | |
| | Hydrolysis | ←-----→ | |
| | Hydration Reaction | | ←-----→ |
| Non- aqueous solution | Alkylation | | ←-----→ |

Table 2. Selection of ion exchange resin

| | Swelling capacity (mL/g-dry resin) | | | | | | | |
|--------|------------------------------------|----------|---------|------------|---------|---------|---------------------|---------|
| | water | methanol | ethanol | 2-propanol | acetone | dioxane | Ethylene dichloride | toluene |
| SCR-BH | 2.8 | 2.4 | 2.4 | 2.5 | 2.1 | 1.1 | 1.2 | 1.2 |
| CMP08 | 4.6 | 3.7 | 3.6 | 3.6 | 2.5 | 1.2 | 1.1 | 1.1 |
| CMP16 | 2.8 | 2.5 | 2.5 | 2.4 | 2.1 | 1.2 | 1.1 | 1.2 |
| CMP28 | 2.2 | 2.1 | 2.1 | 1.6 | 1.4 | 1.2 | 1.2 | 1.2 |

Table3. The swelling capacity (25°C) of ion exchange resins in organic solvents

3.2 Crosslinking degree

The crosslinking degree of ion exchange resins is directly related to the size of micropores. Ion exchange resins with large pores and a low crosslinking degree exhibit fast reaction rates and relatively good thermal stability. Due to their large pores, larger molecules can diffuse into the interior of the ion exchange resin. However, low cross-linked resins have the disadvantage of having lower exchange capacity and reduced acid resistance. Therefore, it is crucial to choose a resin with an appropriate crosslinking degree depending on the reaction conditions.

3.3 Pore size

When dealing with large molecules as catalysts, it is important to be cautious about the difference in pore size between gel and porous types and make a careful selection. Generally, gel-type resins have pore sizes ranging from 20 to 40 Å (angstroms), while porous-type resins have pore sizes between 200 and 700 Å.



3.4 Particle size

The particle size of ion exchange resins also affects the reaction rate, similar to the crosslinking degree. Smaller particle sizes of ion exchange resins result in faster reaction rates, but the selected particle size should be such that it does not cause any operational issues during use. This is because various factors such as viscosity, flow rate, and side reactions can be influenced by the reaction system.

3.5 Counter ion

Generally, ion exchange resins used as catalysts are used in their regenerated form. (For cation exchange resins, they are typically used in the H-form.) However, in some applications, the reactor may be neutralized by the counter ion. This is done to adjust the acidity or increase selectivity and affinity with the reactants.

3.6 Product type - Commercial products

Ion exchange resins are usually supplied in a moist state. In some cases, they need to be rinsed with anhydrous alcohol to remove the moisture. Figures 1 and 2 illustrate examples of substitutions with anhydrous alcohol.

The new resin contains water-soluble substances. If these water-soluble substances could influence the reaction system, they should be removed before use. Figure 3 shows an example of ion exchange resin rinsing.

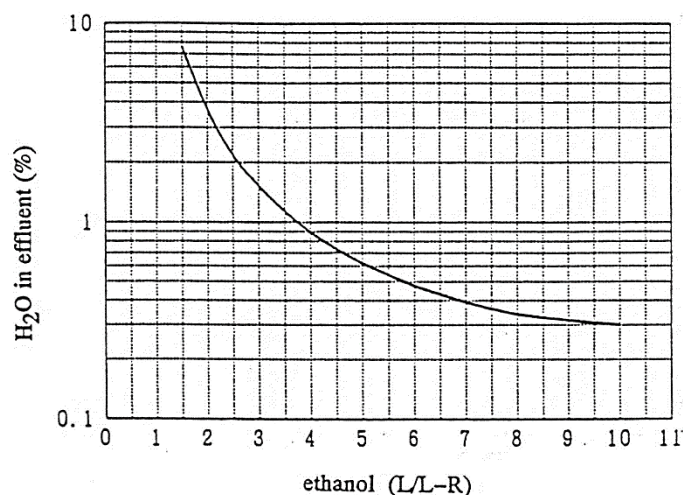


Figure 1. Substitution of water in ion exchange resin by ethanol

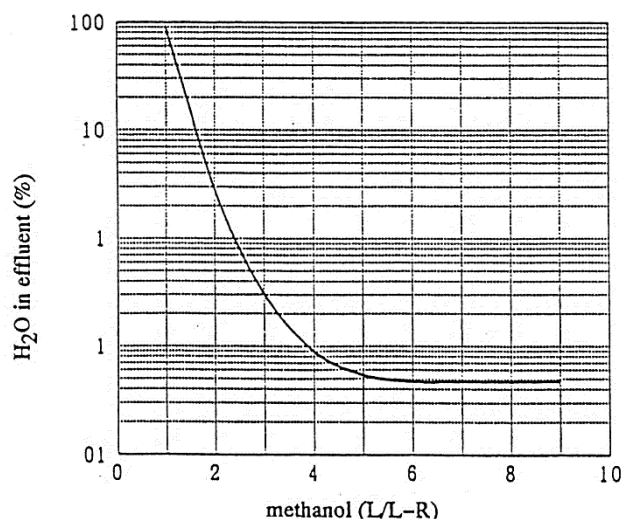


Figure 2. Substitution of water in ion exchange resin by methanol

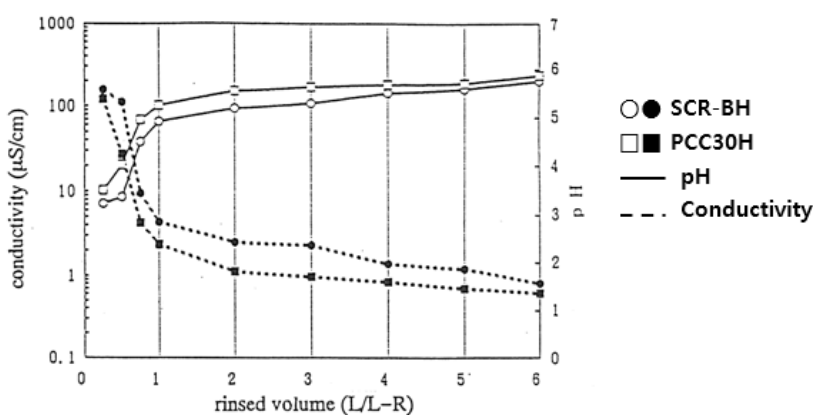


Figure 3. Cleaning of ion exchange resin with water.

4. Performance decline of ion exchange resins for catalyst

Strong acid cation exchange resins for 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 ions

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, Cl₂, and O₂), it undergoes oxidation and irreversible swelling, leading to performance deterioration. Oxidizing substances (Fe, Cl₂, and O₂) 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.

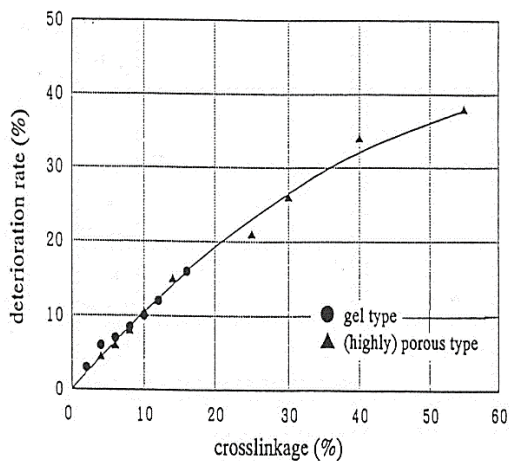
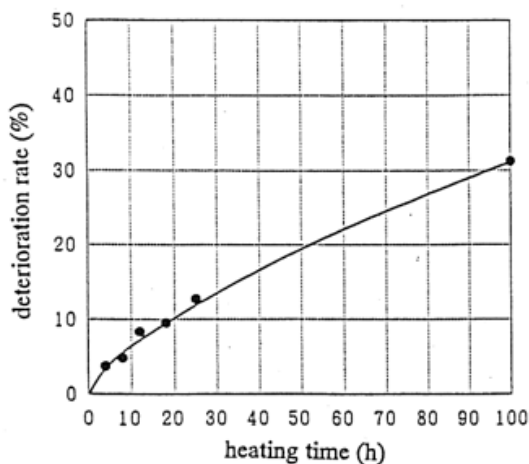
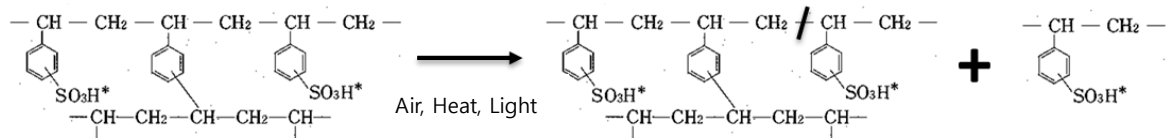


Figure 4. Degradation of ion exchange resin according to heating time and crosslinking degree



5. Application of Ion Exchange Resin for Catalyst

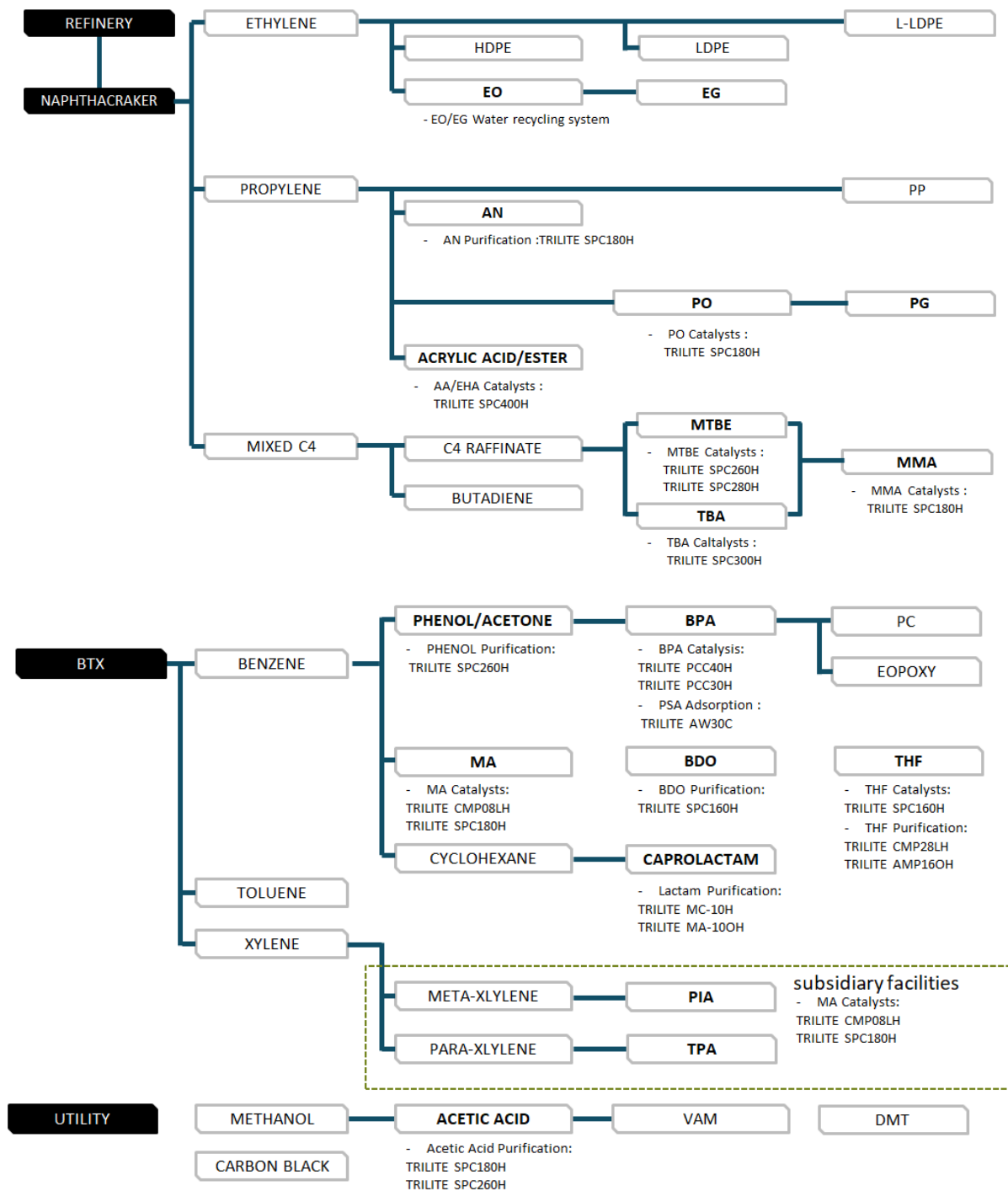


Figure 5. Application of ion exchange resin for catalyst



| Application fields | Reaction mechanism | Recommended products |
|--|---|---------------------------------|
| Synthesis of Bisphenol A | <chem>c1ccccc1O.CC(=O)C>>CC(C)(c1ccc(O)cc1)c2ccc(O)cc2</chem> | PCC20H, PCC30H, PCC40H, MC-04LH |
| Esterification reaction (MMA, EA, BA) | <chem>CC(=C)C(=O)O.RO>>CC(=C)C(=O)OR.O</chem> | SPC180H |
| Methyl tertiary butyl ether (MTBE) | <chem>CC(C)=C.CO>>CC(C)(C)OC</chem> | SPC260H, SPC280H |
| tert-Butyl alcohol (TBA) | <chem>CC(C)=C.O>>CC(C)(C)O</chem> | SPC260H, SPC300H |
| t-amyl methyl ether (TAME) | <chem>CC(C)C=C.CO>>CC(C)C(OC)C</chem> | SPC160H, SPC180H |
| Hydrolysis of methyl acetate | <chem>CC(=O)OC.O>>CC(=O)O.CO</chem> | CMP08LH |
| Alkylation of phenol | <chem>c1ccccc1O.CC=C.R>>Cc1ccccc1O.CC(R)C</chem> | SPC260H, SPC320H |
| Dehydration reaction (THF) | <chem>OCCCCO>>C1CCOC1.O</chem> | SPC260H |

Table4. Application fields and recommended products for ion exchange resin for catalyst

5-1. BPA process

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.

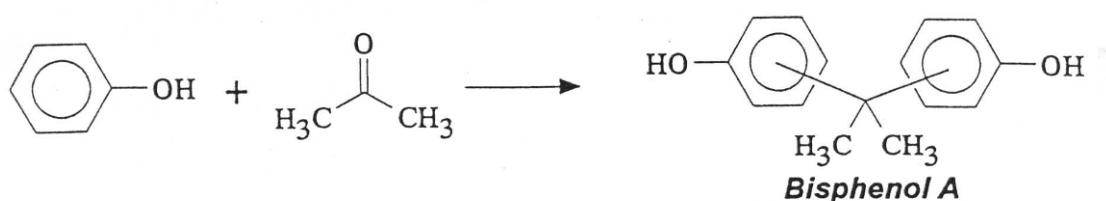


Figure 6. BPA reaction mechanism

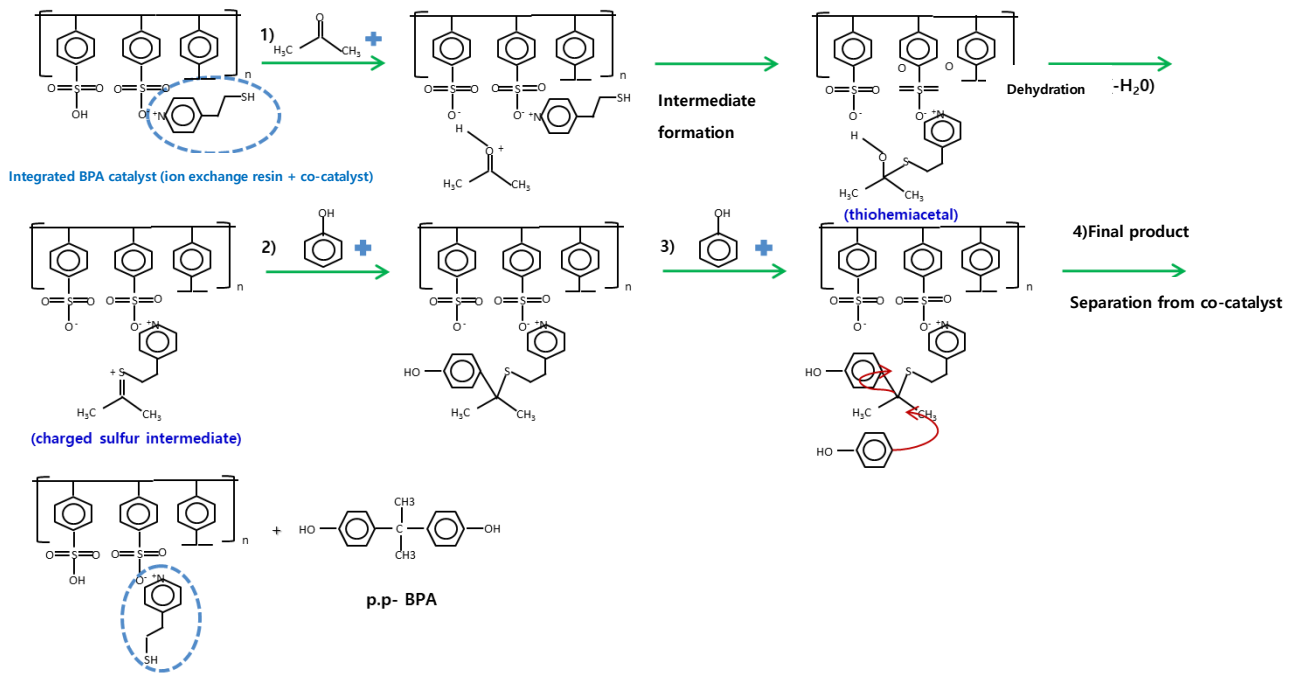


Figure 7. BPA catalyst reaction mechanism

There are several methods for manufacturing BPA, including IDEMITSU, BADGER, and SHIYODA methods. The IDEMITSU method utilizes 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. In the BADGER method, strong acid cation exchange resins are also used as catalysts, along with methanethiol and ethanethiol as co-catalysts. However, the key difference lies in the use of the upflow technique. On the other hand, the SHIYODA method utilizes a single-unit ion exchange resin as a co-catalyst, eliminating the need for a separate recovery process. Moreover, it incorporates an environmentally friendly process with a MeOH purification facility.

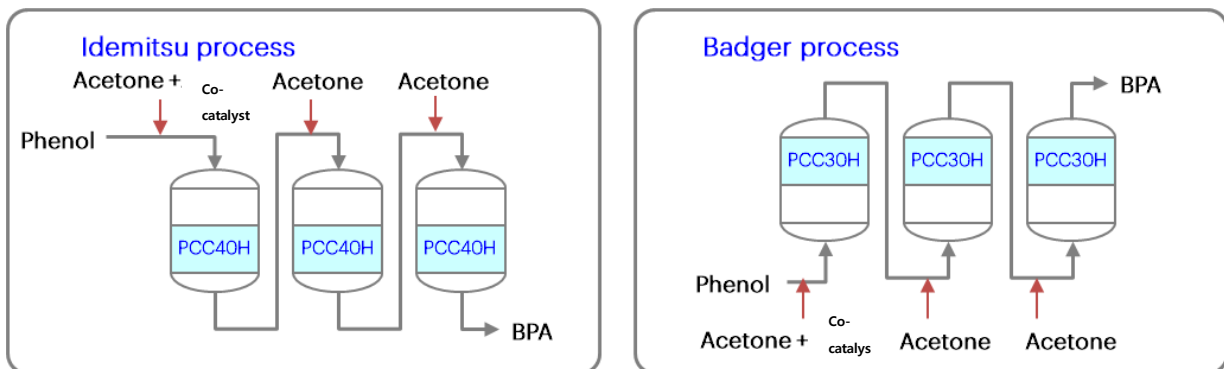
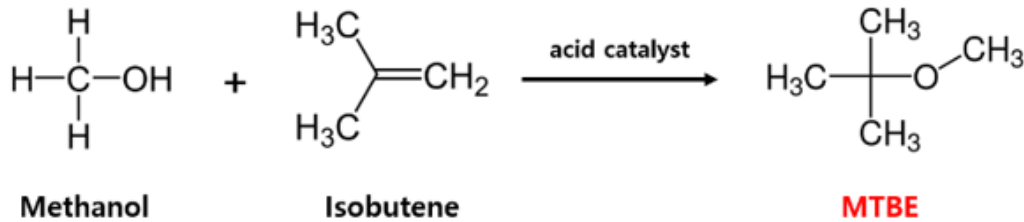


Figure 8. BPA Process



5-2. MTBE process

MTBE is an ether compound containing oxygen in its molecular structure and is widely used as an octane booster in automotive gasoline. Among various octane boosters such as MTBE, ETBE, TAME, GTBA, and MTBE stands out as one of the representative gasoline blends due to their availability, properties, and price. Additionally, MTBE can be cracked to produce high-purity isobutene, a raw material for MMA and IIR production.



- General process:

C4 residue-I, extracted from mixed C4 fractions in a naphtha cracker, contains impurities such as NMP, which is used as an extraction solvent in the BD process. Therefore, after removing impurities through water washing in the pre-treatment process, C4 residue-I is introduced into a reactor filled with ion exchange resin along with methanol. Methanol and isobutene react selectively to synthesize MTBE.

- Process: The secondary synthesis reactor is transitioning from the traditional fixed-bed reactor to catalytic distillation.

Licensors for MTBE manufacturing include Acro, Phillips, CDTech, and UOP from the United States, Snamprogetti from Italy, IFP from France, and Huls from Germany. In South Korea, the Snamprogetti process and IFP process, used by existing MTBE production companies, are commonly introduced, along with the CDTech and UOP processes, which are gaining attention globally and being considered by newly participating companies. Each manufacturing process is conceptually similar, with differences mainly in the reaction system and overall heat recovery system.

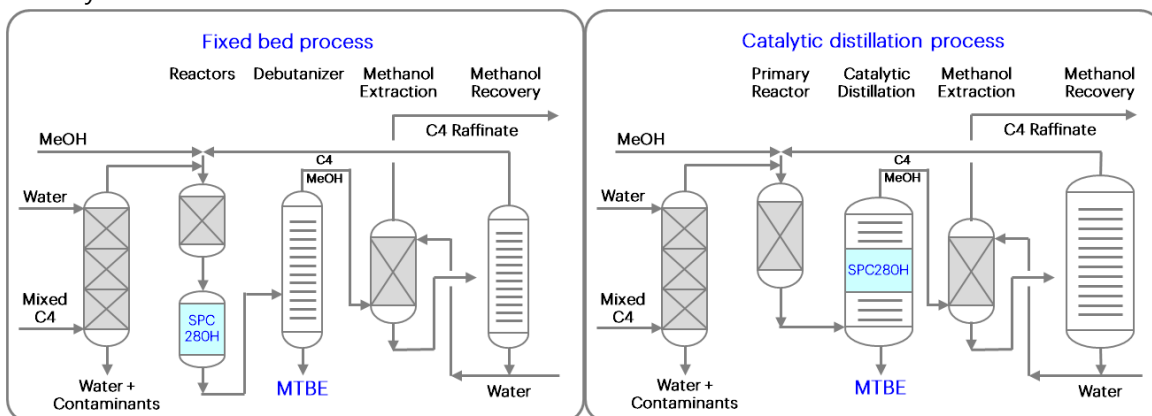
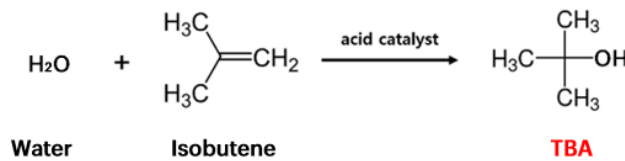


Figure 9. MTBE process



5-3. TBA process

TBA is an important intermediate produced on a large industrial scale and used as a solvent and intermediate for the production of MMA. TBA can be obtained through the acid-catalyzed reaction of water with isobutylene. Typically, in a down-flow process, isobutylene and water are mixed and introduced into the reactor with a TRILITE SPC300H catalyst for the reaction. In the up-flow process, isobutylene and water are separately introduced into the reactor through two inlet ports located at the top and bottom of the reactor, and a uniform large particle size resin is utilized.



For the TBA catalytic process, H-form strong acid cation exchange resin is used. Due to the rapid reaction rate and high-temperature/high-pressure conditions, a highly cross-linked porous-type strong acid cation exchange resin with excellent physical and chemical strength is employed. For reactors operating at high LV, large particles of ion exchange resin are used to reduce pressure drop. On the other hand, for reactors operating at low LV, small particles are used to achieve optimal conversion rates.

Using C4R1 as the raw component, TBA (85.0% ~ 87.0%) is produced through the reaction of water and isobutene. And C4R1 is recycled in the reactor to enhance the purity of TBA. Operating at pressures of 10~15 bar and temperatures of 45~70°C, the process uses a specific gravity difference in the TBA column to recover TBA from the bottom of the column and C4R2 from the top.

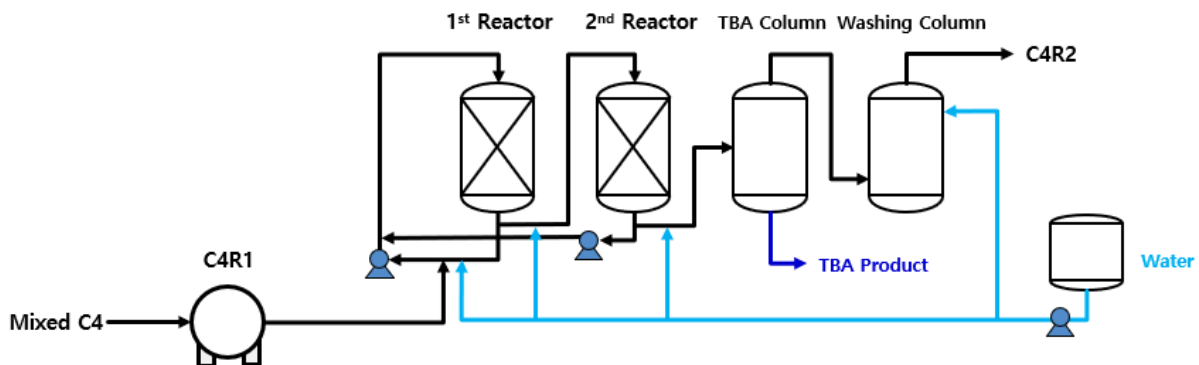


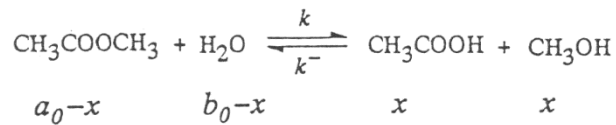
Figure 10. TBA process

5-4. Hydrolysis of Methyl Acetate

The hydrolysis of methyl acetate is a typical case where ion exchange resin is used as a catalyst on an



industrial scale. During the production of polyvinyl alcohol, methyl acetate, a byproduct, is hydrolyzed using ion exchange resin as a catalyst to produce acetic acid and methanol.



$$\begin{aligned} a_0 : b_0 &= 1 : 20 \\ \text{temperature} &= 30^\circ\text{C} \\ x &= \text{molar concentration (mol/L)} \end{aligned}$$

Primary irreversible rate constant

$$\begin{aligned} \frac{dx}{dt} &= k_1(a_0 - x) \\ k_1 &= \frac{1}{t} \ln \frac{a_0}{a_0 - x} \end{aligned}$$

Secondary reactive rate constant

$$\begin{aligned} \frac{dx}{dt} &= k_2(a_0 - x)(b_0 - x) - k_{-2} \cdot x^2 \\ k_2 &= \frac{1}{m} \cdot \frac{1}{t} \left[\ln \frac{(a_0 + b_0) - m - 2(1 - 4k)x}{(a_0 + b_0) + m - 2(1 - 4k)x} - \ln \frac{(a_0 + b_0) - m}{(a_0 + b_0) + m} \right] \\ m &= \sqrt{(a_0 + b_0)^2 - 4a_0 \cdot b_0(1 - 4k)} \\ k &= \frac{k_2}{k_{-2}} \end{aligned}$$

In Figure 11, low cross-linked ion exchange resins such as SK104H and PK208H exhibit high reaction rates. However, considering their oxidation resistance, ion exchange resins with an 8% or higher crosslinking degree are generally used in applications.

Figure 12 illustrates the variation of k_i according to the acidity of the resin (acid content), and it can be observed that high porous ion exchange resins are not suitable for this reaction. The swelling degree of the ion exchange resin is closely related to k_i , as shown in Figure 14.

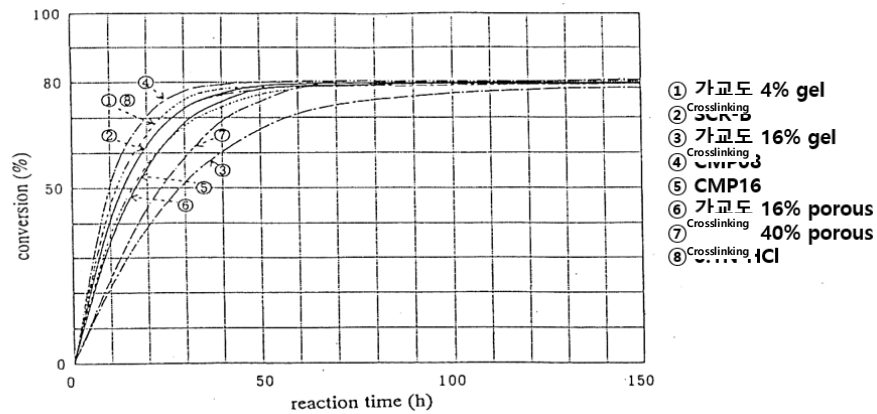


Figure 11. The reaction rate and conversion rate of methyl acetate hydrolysis

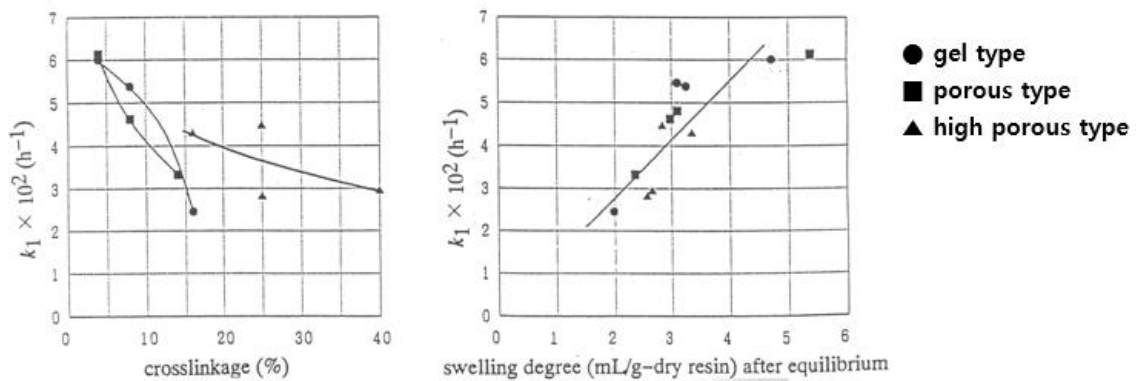


Figure 12. The relationship between the reaction rate (k_i) and crosslinking degree in the hydrolysis of methyl acetate.

5-5. Esterification reaction

Methyl esterification of acetic acid is one example of an esterification reaction. Low cross-linked ion exchange resins show high reaction rates as shown in Figure 13. Figure 14 illustrates the change in k_i with the agitation speed. It can be observed that k_i is almost unaffected when the agitation speed is above 200 rpm. From Figure 14, it can be seen that k_i is significantly influenced by the particle size of the ion exchange resin. However, in actual operation, considering factors such as ΔP , ion exchange resins with typical particle sizes (500-600 μm) are used to ensure the operability of the reaction system. Figure 14 illustrates the relationship between k_i and the carbon chain length of carboxylic acid in the esterification reaction. The length of the carbon chain in carboxylic acid influences k_i in the esterification reaction because longer chains hinder the diffusion of carboxylic acid molecules internally.

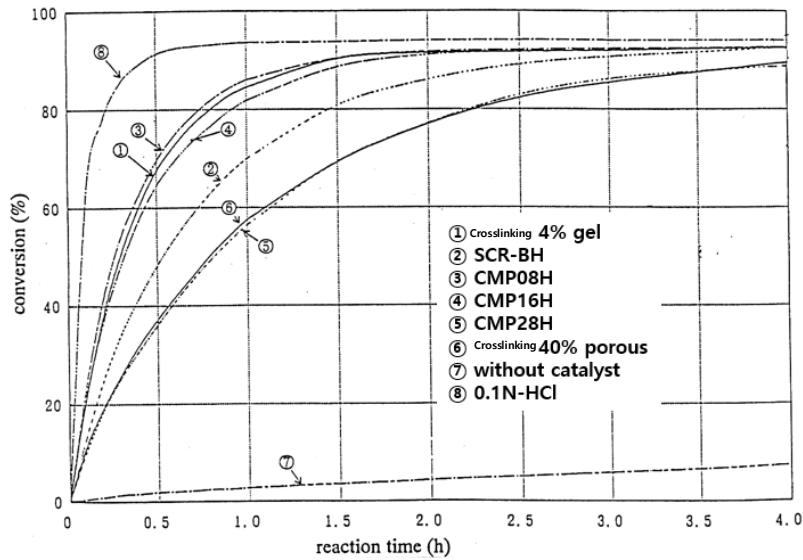


Figure 13. Figure 13 shows the relationship between reaction time and conversion rate in the esterification reaction of acetic acid.

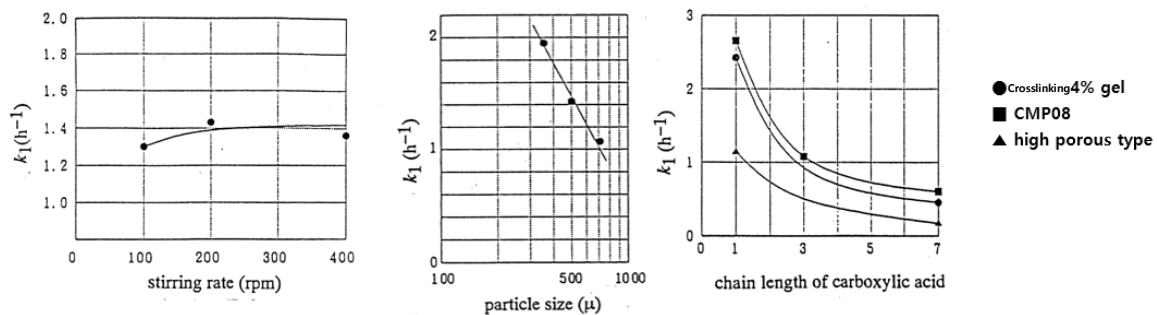


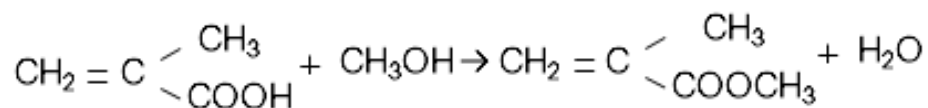
Figure 14. The effect of agitation speed, particle size, and chain length on k_i

5-6. Synthesis of methyl methacrylate (MMA)

Methyl methacrylate has traditionally been produced using the ACH method. However, due to the recent scarcity of hydrogen cyanide, an alternative approach has been devised, which involves directly oxidizing isobutylene or related C4 distillate as a precursor. In this process, ion exchange resins are used to separate isobutylene, synthesize tertiary butyl alcohol, and serve as a catalyst for the methyl esterification reaction.



① Reaction



② Reaction conditions

methacrylic acid: 27g(0.31mol)

methanol : 100g(3.1mol)

Catalyst resin: An amount of dry resin equivalent to 10mL of its volume in water

Reaction temperature: 60°C

Reaction Time: 6 hours

③ Used ion exchange resin

| Grade | Volume in water (mℓ) | Dry weight (g) | Exchange capacity (meq/g) | Total acid input (meq) (acid amount) |
|---------|----------------------|----------------|---------------------------|---|
| CMP08H | 10 | 2.2 | 5.1 | 11 |
| CMP16H | 10 | 3.3 | 5.1 | 17 |
| CMP28H | 10 | 4.3 | 4.9 | 21 |
| SPC160H | 10 | 3.8 | 4.5 | 17 |

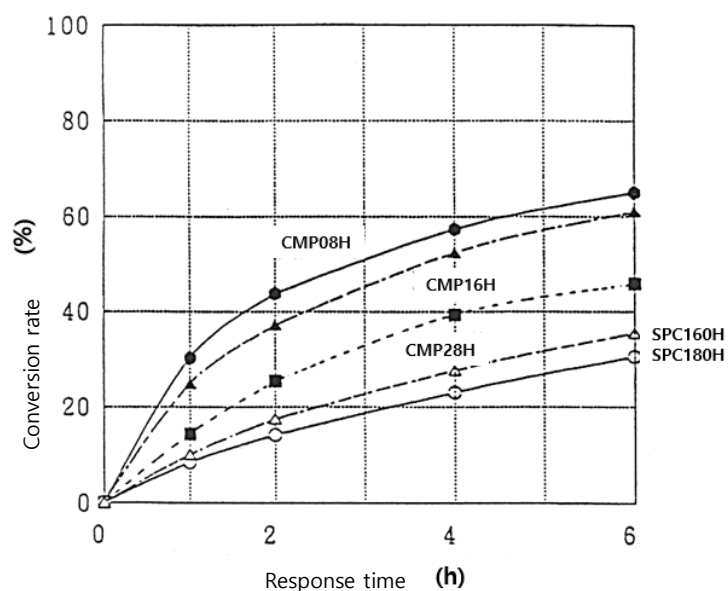


Figure 15. The relationship between reaction time and conversion rate in MMA synthesis.



5-7. Alkylation of phenol

In the past, applying ion exchange resins to non-aqueous reactions was very challenging. However, with the development of high-porous ion exchange resins with thermal stability, it has become possible.

As an example, there is an alkylation reaction of phenol using the thermal stability ion exchange resin DIAION RCP145H. The experimental results are presented below.

① Reaction

Phenol + Octadecene \rightarrow (catalyst) \rightarrow Monoalkylphenol

② Reaction conditions

Phenol: 94.1g

Octadecene: 115.5g

Catalyst resin: 10.0g

Reaction temperature: 110°C

Reaction time: 2 hours

③ Results

| Category | TRILITE CMP28 | Competitor L | Competitor D | Activated bentonite |
|-----------------|---------------|--------------|--------------|---------------------|
| Monoalkylphenol | 80 | 73 | 80 | 75 |
| Polyalkylphenol | 9 | 12 | 9 | 10 |



6. Catalyst Ion Exchange Resin Specification

| Grade | Unit | MC-04H | PCC30H | PCC40H | CMP08H | CMP28H | SPC160H | SPC180H | SPC260H | SPC280H | SPC320H | SPC400H |
|------------------------|-------|--|----------|---|--------|--------|---------|---------|---------|---------|---------|---------|
| Type | | UPS | Gaussian | | | | | | | | | |
| | | Gel | | | Porous | | | | | | | |
| Matrix | | Polystyrene + DVB | | | | | | | | | | |
| Functional group | | Sulfonic acid | | | | | | | | | | |
| Ionic form | | H ⁺ (H Conversion rate 99.9% ↑) | | | | | | | | | | |
| Shipping weight | g/l | 750 | 700 | 780 | 720 | 780 | 740 | 750 | 800 | 800 | 780 | 690 |
| Moisture content | % | 65~70 | 60~70 | 57~67 | 65~71 | 42~48 | 54~60 | 53~60 | 50~58 | 50~58 | 42~48 | 65~75 |
| Total capacity | eq/kg | 5.1 ↑ | 4.5 ↑ | 5.1 ↑ | 4.9 ↑ | 4.0 ↑ | 4.5 ↑ | 4.5 ↑ | 4.7 ↑ | 5.2 ↑ | 4.5 ↑ | 4.0 ↑ |
| Total capacity | eq/l | 1.2 ↑ | 1.2 ↑ | 1.2 ↑ | 1.1 ↑ | 1.0 ↑ | 1.5 ↑ | 1.5 ↑ | 1.75 ↑ | 1.9 ↑ | 1.9 ↑ | 1.0 ↑ |
| Effective Size | μm | UPS | 780 ↑ | 400 ↑ | | | | | | | | |
| Uniformity coefficient | | 1.1 ↓ | 1.6 ↓ | | | | | | | | | |
| Particle size | μm | 500±30 | 700~1450 | General type: 300~1200 , L-type : 425~1200 , XL-type : 700~1200 | | | | | | | | |
| Operating Temp | ℃ | 120 ↓ | | | | | | | | | | |
| Operating pH range | | 0~14 | | | | | | | | | | |



SAMYANG

Samyang Corporation Ion exchange resin

31, Jongno 33-gil, Jongno-gu, Seoul, Korea / TEL) 82-2-740-7732~7 / FAX) 82-2-740-7709 / <http://samyangtrilite.com>