

SAMYANG

TRILITE
삼양 트리라이트

Ion Exchange Resin

Ion Exchange Resin for MTBE Catalyst

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/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)

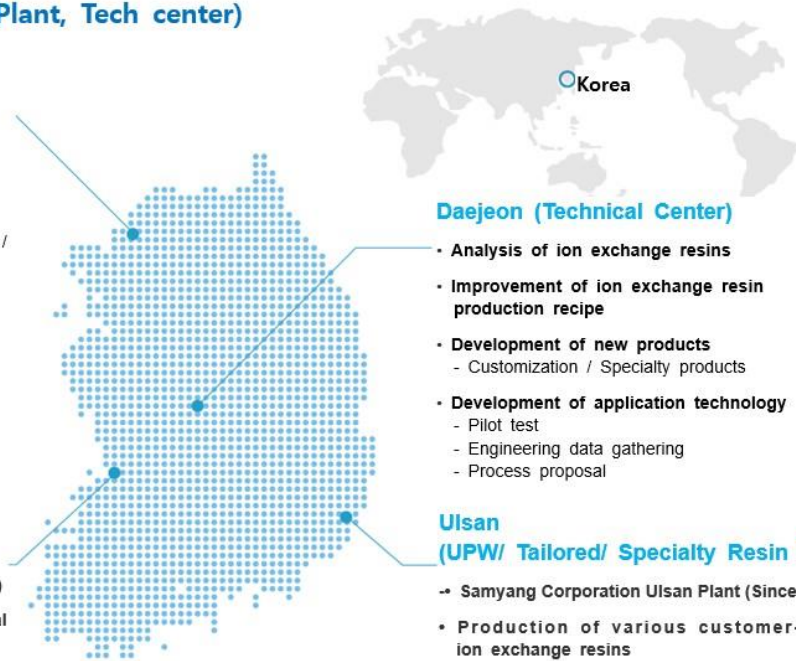
- Uniform particle sized resins
- Samyang Fine Technology (Since 2016)
- Joint venture with Mitsubishi Chemical Corporation, Japan
- Asia's largest dedicated factory for uniform particle sized ion exchange resins
- Product line
 - Uniform particle sized ion exchange resins
 - Ultrapure water resins (OLED,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

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, and GTBA, MTBE stands out as one of the representative gasoline blends due to its availability, properties, and price. Additionally, MTBE can be cracked to produce high-purity isobutene, a raw material for MMA and IIR production.

1) 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.

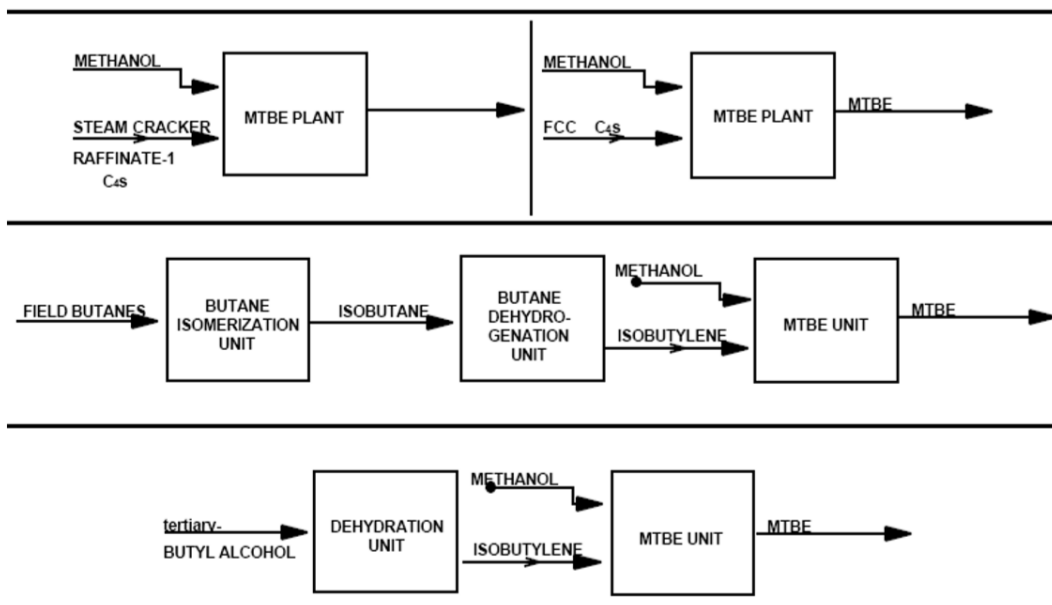


Figure 1. General MTBE synthesis process

2) 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 new participating companies. Each manufacturing process is conceptually similar, with differences mainly in the reaction system and overall heat recovery system

3) CD Tech: Fixed-Bed (downflow) Reactor and Catalytic Distillation

The CD Tech process is a well-regarded technology developed by catalytic distillation technologies which is a joint venture between ABB Lummus Crest and Chemical Research & Licensing. It allows reaction and distillation simultaneously in the CD tower, leading to cost savings in equipment and operating expenses, making it a prominent process in recent times. The C4 fractions generated in the FCCU (fluid catalytic cracking unit), C4 fractions from the steam cracker, or isobutylene produced from the dehydrogenation of isobutane, along with fresh and recycled methanol are heated using the reaction heat absorbed from the boiling point reactor (1) until vaporization is suppressed. In this case, the maximum reaction temperature is controlled by the total system pressure setting and the catalyst is a fixed bed type. The reaction effluent from the boiling point reactor is then sent to the CD reaction column and the catalytic distillation reaction column (2) is a column in which reaction and distillation are simultaneously carried out. The reaction is continued by the catalyst in the catalytic reaction part made of a structured packing style in the center of the column, and MTBE products are produced down the column. Since the CD reaction column contains a fixed bed reactor, the conversion rate of isobutylene is over 94%, so the overall conversion rate of isobutylene is over 99.8%. The effluent from the top of the reaction column separates and recirculates methanol by washing with counter-current water in the extraction tower, and the water at the bottom of the column is recirculated to the extraction tower. The CD Tech process is also known to be capable of coproducing TAME.



4) Snamprogetti: Tubular (Upflow) Reactor and Fixed-Bed (downflow) Reactor

The process, which is based on technology developed by Snamprogetti in Italy, involves a counter-current washing process to remove NMP, which is the extracted solvent of butadiene in the washing tower (1), before mixing methanol with the FCC (fluid catalytic cracking) C4 fractions, Stream Cracker C4 fractions, or the dehydrogenation product of Isobutane. The processed feed is continuously sent to the MTBE synthesis reactor, which consists of two reactors along with methanol.

The first reactor, the tubular reactor, is of the tubular type with a catalyst filled inside the tube, making it easy to control the reaction temperature. The isothermal reaction occurs inside the tube, and the reaction heat is removed by cooling water on the shell side. The reaction conditions at this stage are 45~60°C and 10~12 atmospheres of pressure.

The second reactor is a fixed bed type and consists of two beds. The first bed is designed to achieve a conversion rate of 97% for isobutylene along with the first reactor. And the additionally added second bed re-reacts the unconverted isobutylene from the product fractionation tower's upper part, further increasing the overall conversion rate. The reaction effluent from the first bed of the primary reactor and the secondary reactor is sent to the product fractionation tower (4), where MTBE product is produced in the lower part of the tower. The C4 and methanol components from the upper part of the tower undergo additional reactions in the second bed of the secondary reactor. And then the MTBE that was further reacted at the bottom of the tower in the C4 residue separation tower (5) is separated and sent to the PFT (4). The C4 and methanol at the top of the tower are separated and transported to the methanol removal tower (6).

The methanol removal tower is a liquid full tower, where C4 and methanol components and water are in by counter-current contact and C4 is separated and removed to the top of the tower. And the methanol and water at the bottom of the tower are sent to the methanol separation tower, and the methanol is re-injected into the tubular reactor (2) after being separated, and the water is re-injected into the washing tower (1) and the methanol removal tower (6).

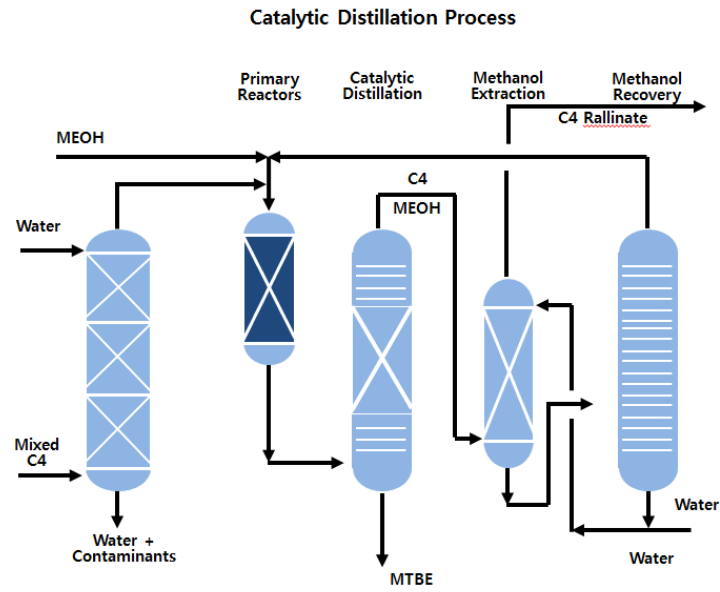


Figure 2. CDTECH MTBE process

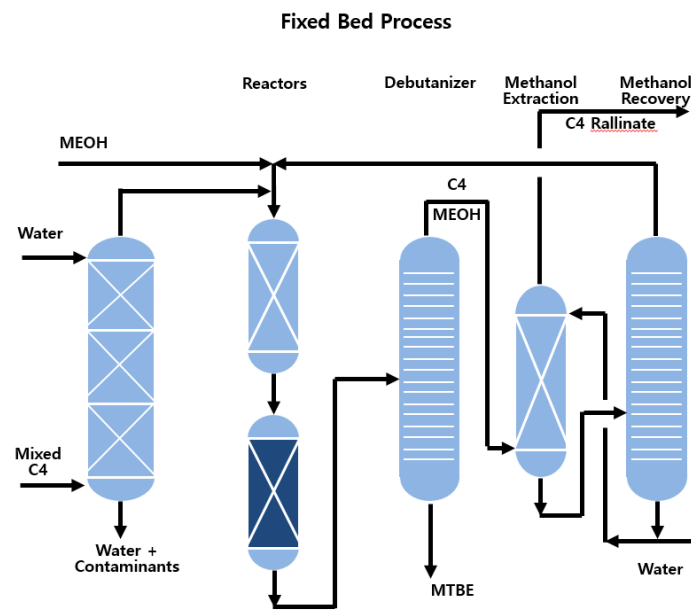
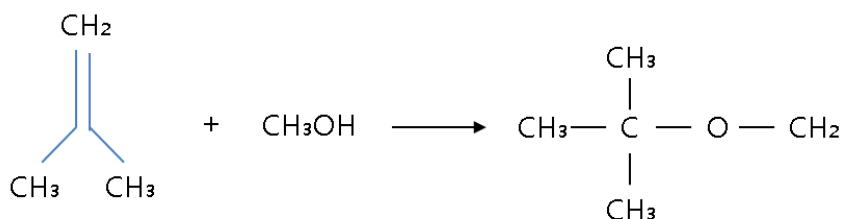


Figure 3. Samprogetti MTBE process



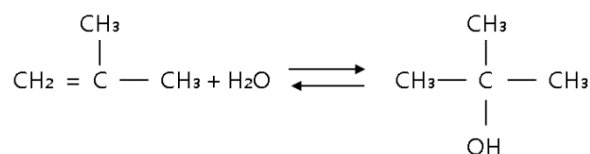
5) The synthesis mechanism of MTBE

(1) Main reaction (Etherification reaction)

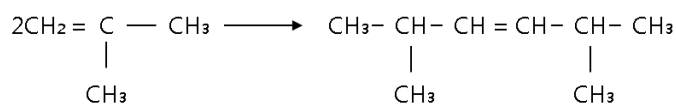


(2) Side reaction

-Addition reaction



-Bimolecular reaction



-Condensation reaction



The ion exchange resin for the catalyst should have a high conversion rate and appropriate pore size to avoid sub-reactions, and the ionic form of the R-SO₃ matrix should be H⁺.

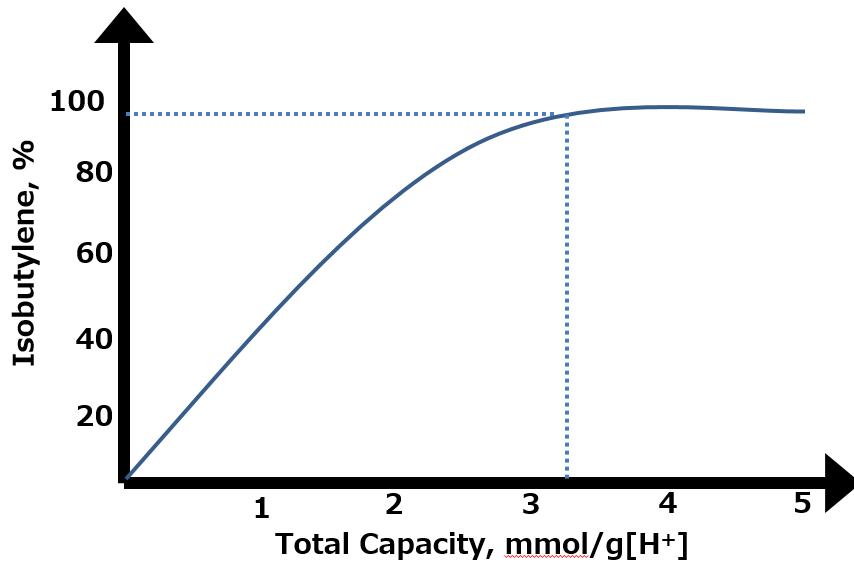
| Model | Unit | TRILITE SPC260H | TRILITE SPC280H |
|-----------------------|-------------------------|-----------------|-----------------|
| Exchange capacity | mmol/g[H ⁺] | ≥4.7 | 5.2 |
| Moisture content | % | 50~58 | 50~58 |
| Density | g/l | 0.75~0.85 | 0.75~0.85 |
| Specific gravity | | 1.15~1.25 | 1.2~1.3 |
| Particle size | mm | 0.35~1.25 | 0.35~1.25 |
| Temperature condition | °C | 120 | 120 |

Figure 4. Samprogetti MTBE process

*The theoretical operational exchange capacity for MTBE catalysis is ≥ 3.6 mmol/g [H⁺].



When the total exchange capacity exceeds 3.6 mmol/g, the conversion rate of isobutylene can be maintained at 90% or higher. The total exchange capacity is higher than this value. The catalytic starting reaction temperature of the resin catalyst starts at 28~30 degrees Celsius. Even at low



temperatures reaction, advantages such as extended operating time and reduced by-products lead to improved operation, allowing stable product production.

Figure 5. Conversion rate vs total exchange capacity

6) TRILITE SPC 260/280H temperature resistance test evaluation

(1) Experimental process conditions

Pressure: 1.2~1.5 MPa

SV: 3

(2) Temperature resistance conditions

Reaction temperature: 60°C for 10 hours, followed by heating to 120°C and operating for 10 hours (repeated 6 times)



(3) Catalytic reactivity and desulfurization status results

| Items | Unit | Normal conditions | Repeated results |
|-------------------|-------------------------|-------------------|------------------|
| Selectivity | % | 99.30 | 98.45 |
| Conversion rate | % | 96.28 | 94.87 |
| Exchange capacity | mmol/g[H ⁺] | 5.3 | 4.96 |

The experimental results show that the SPC 260/280H Series has excellent thermal stability, and even under sudden room temperature conditions during operation, it does not have a critical impact on the activity and selectivity of the resin catalyst. This process has operational advantages and can be used for an extended period.

7) Optimal operating conditions for TRILITE SPC 260/280H

(1) Alcohol to olefin ratio (mmol ratio): 1.0~1.05 :1

(2) Reaction temperature: 50~80°C (Optimal reaction temperature: 55~65°C)

(3) SV: 1~5

(4) Maximum pressure drop: ≤0.01 MPa/M bed

(5) MTBE production (per ton of catalyst dry) FCC carbon ≥ 44,500 tons, DCC carbon ≥ 46,000 tons

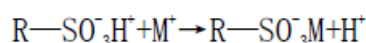
Reactor Isobutylene conversion rate: FCC carbon query 92%, DCC carbon query 95%

Catalyst distillation tower isobutylene conversion rate: ≥99%

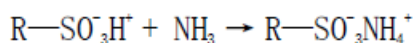
8) Affect of impurities on resin catalyst

Impurities in the raw materials (alkaline substances and metal cations) can affect the catalyst's active centers.

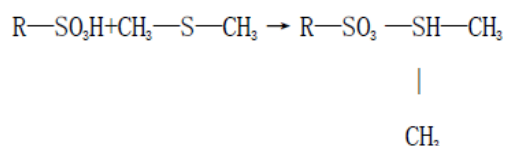
(1) Metal ions present in the raw materials undergo ion exchange reactions with the catalyst.



(2) Neutralization of alkaline nitrogen compounds:



(3) Sulfide poisoning.





2. Cautions for the use of resin catalyst

- 1) Raw material of etherification reaction (mixed carbon 4 and methanol), metal ions, and alkaline nitrogen $\leq 2\text{PPm}$
- 2) Butylene content $\leq 0.1\%$
- 3) Control the alcohol-to-ethylene ratio in the reactants to operate under conditions of low alcohol/ethylene ratio for an extended period. If isobutylene control is not achieved, the etherification reaction may generate more heat, significantly affecting the catalyst.
- 4) Strictly control the reaction temperature to achieve higher conversion rates.
- 5) Pore blockage Adhesive components and compounds generated by side reactions in the raw materials may deposit inside the pores, directly affecting the catalyst.

When the resin catalyst is in contact with water at high temperatures, the exchange capacity of the resin may decrease slowly.

To minimize side reactions, conduct the reaction under low-temperature conditions.



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>