CHEMICALS

De-calcification of Beet Sugar by Tulsion® Resins

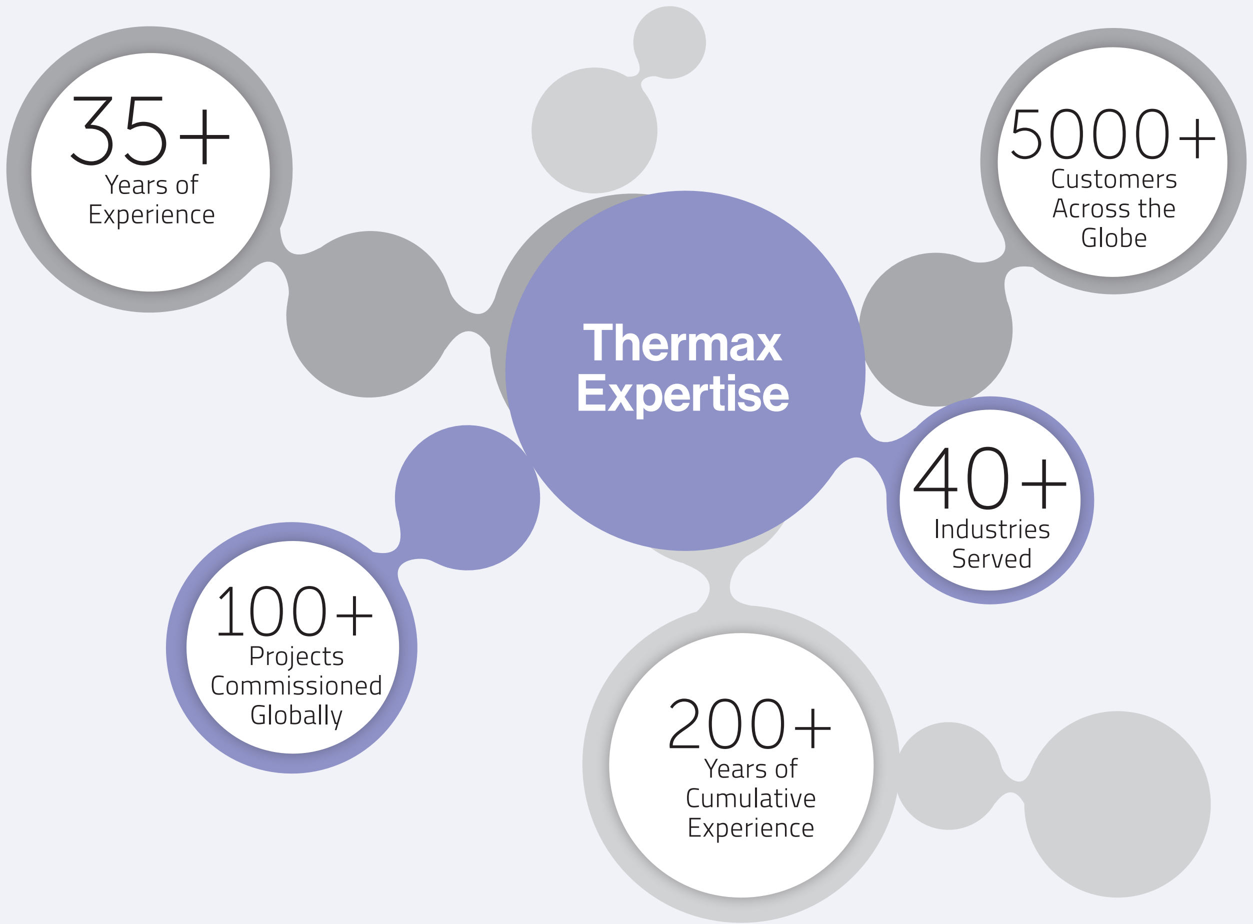
Welcome to Thermax - an engineering company providing sustainable solutions in energy and environment. The company's vision for the future is firmly anchored in the belief that to stay competitive, companies need to adopt sustainable development practices.

The systems, products and services developed by Thermax help industry achieve better resource productivity and improve bottom lines, while maintaining a cleaner environment. Even as we convert costs to profits, we help to protect the environment in our own ways. A win-win for industry and the society at large.

Thermax's business portfolio includes products for heating, cooling, water and waste management, and specialty chemicals. The company also designs, builds and commissions large boilers for steam and power generation, turnkey power plants, industrial and municipal wastewater treatment plants, waste heat recovery systems and air pollution control projects.

Thermax Chemicals is Asia's leading manufacturer of Tulsion® ion exchange resins.

Our business is about providing 'effective customer solutions' through innovation and development, service and co-operation, reliability, commitment, and customer-centricity. Our dynamic teams focus their energy and resources to offer the very best solutions for customers' needs.



Why Tulsion® Ion Exchange Resins?

Better Quality at Cost-Effective Value

Water treatment is traditionally one of the largest applications in the field of ion exchange resins; however, it has now evolved to various speciality applications. Hence, we believe in developing and offering customised solutions to our customers, which are efficient, economical and provide value for money.

To date, a number of customers seeking solutions for industrial, municipal, domestic and wastewater related problems have benefited from Thermax products and services.

Product Customisation

Our research and development team consists of highly experienced professionals in the field of ion exchange resins and speciality polymers, who can understand the depth of customer requirements and provide customised solutions in complete accordance with customer expectations.

On Time Technical Support

Our technical support team ensures quick response time to our customers and connects them to our product management team, who can understand their problems, troubleshoot and provide optimal solutions.

Manufacturing Excellence

Our resin manufacturing plant at Dahej, Gujarat, India is a fully automated plant with state-of-the-art DCS system and latest digital technologies. We use clean fuel and modern air scrubbing units that are environment friendly. Every batch of Tulsion® ion exchange resins is manufactured under carefully controlled process parameters and follows a rigorous quality assurance protocol. We have already commenced the Phase–II of our Dahej facility to cater to the growing global market demand.

Thermax has two other manufacturing facilities at Paudh, Maharashtra, India and Jhagadia, Gujarat, India for ion exchange resins and performance chemicals respectively.

Value Added Services

At Thermax, we offer free-of-cost plant audits, design proposals, post sales technical support, and a very efficient and experienced research and development team that understands customer requirements to the last detail.

Thermax Chemicals is committed to complying with stringent global quality standards and respects the environment. Ion exchange business unit is ISO 9001: 2015, ISO 14001: 2015 and ISO 45001: 2018 certified. Many of the Tulsion® resins are also certified for Halal, Kosher and REACH.

Overview

Reducing hardness from beet sugar following the juice purification process is one of the essential operation in the beet sugar processing industry. To optimize the alkalinity in primary carbonation, pH adjustment is performed to reduce or optimize the soda ash which is being added before the second carbonation. This reduces the hardness in thin sugar juice and also minimize the load on ion exchange softening equipment. Thin juice ion exchange softening is a well established proven process and offer benefits at various stages of sugar processing such as evaporation or vacuum pan drying due to increased heat transfer, reduction in color formation, lower temperature exposer, and decrease in turbidity, etc.

Beet Sugar De-calcification by Tulsion® Resins

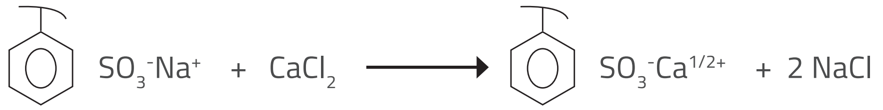
Ion exchange in general is insoluble solid materials that carry exchangeable cations or anions. Thus, any typical ion exchange consists of a polymer matrix and a functional group that contains exchangeable ions.

To increase brix and form sugar crystals, the raw beet sugar juice has to go through evaporation and crystallization. This raw beet sugar juice contains different amount of undesirable impurities which is necessary to remove before forwarding it to evaporation and later for crystallization. Many such impurities are removed in the initial step of precipitation and filtration where lime is added. After this step, the thin juice only contains a variable concentration of hardness (depending on different regions from where beet is sourced) which has to be removed in order to avoid scaling in the evaporator.

To remove this Ca^{2+} in exchange with Na^{+}, Tulsion® resin is used; which is the most suitable technique to remove the said impurities. This resin is a Strong Acid Cation (SAC) resin in Na^{+} form, which is generally supplied in gel type.

Hard Juice Softening process

Objective of any beet sugar factory is to maximise the sugar recovery from molasses by separating the non-sugar content from sugar. The sugar separation is gradual and accomplished in several steps of sugar processing. At each step of process, the sugar content is improvised and expressed as purity as % of dry substance in sugar syrup. By conventional technology, the maximum sugar recovery is possible up to 80% However, with advanced MDC process (molasses desugaring by chromatography) which make use of ion exchange resins for chromatographic separation as downstream process of conventional sugar separation, the sugar recoveries are >90%. MDC is mostly preferred by many beet sugar manufacturers because of its efficiency. It uses soft molasses as feed which can be obtained only if the thin juice softening process is carried out to lower the hardness to < 25 mg/100 DS. Several juice softening processes have been adapted by sugar factories such as gryllus process and NRS (New Regeneration System). The gryllus process though is most common but do not produce the desired quality of juice and molasses.



Na^{+} - Sodium ion for exchange Ca - Cationic impurity in juice Cl - Exchangeable chlorides

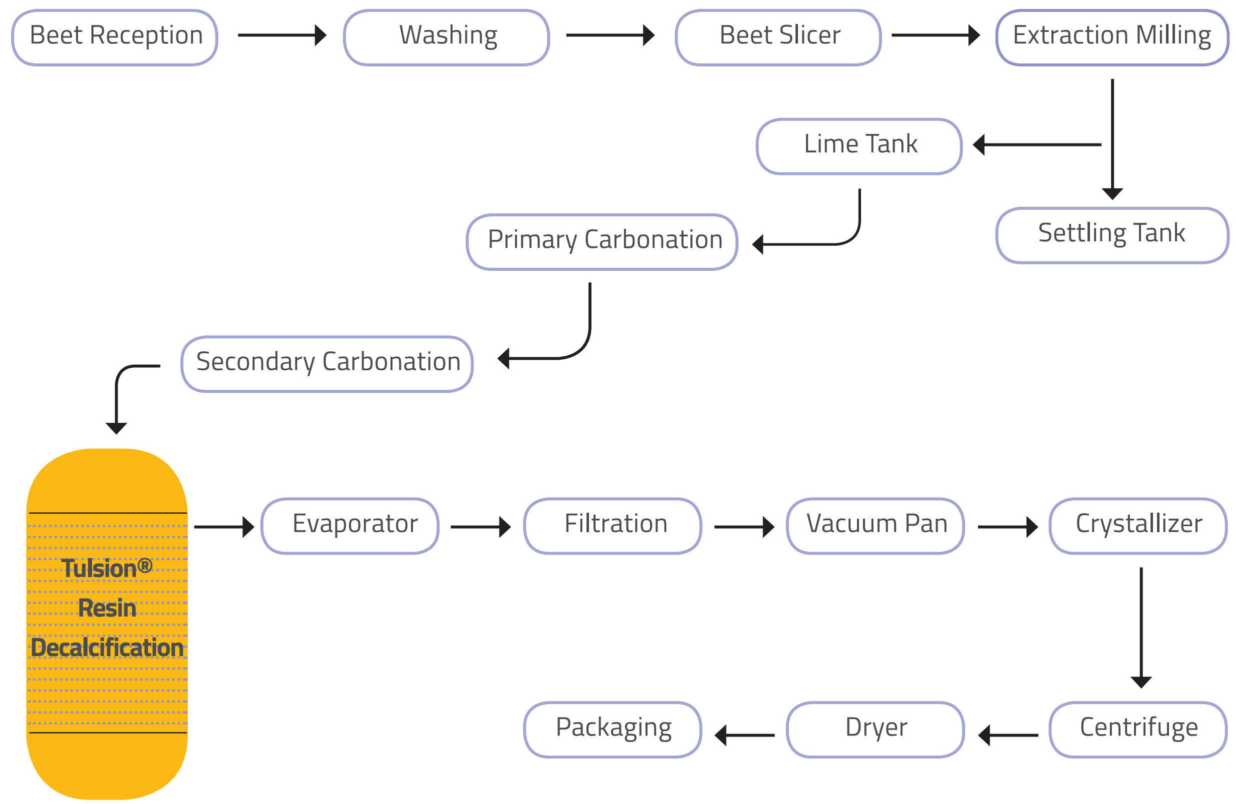
Typical quality of soft beet sugar juice after strong acid cation resin:

Sugar	Calcium	Brix	Polarization
Decalcified beet Sugar	< 25 ppm	16 %	9.5

The values depends on inlet feed quality. Brix, polarization and colour remains same as inlet.

Typical Refining Process

Upon arrival at the processing plant, the beets are tested for quality and sucrose content. Then, it is thoroughly washed to remove soil and other impurities. The clean beets are forwarded to beet slicers. In the beet slicing process, beets are sliced into thin chips to increase the surface area of the beets so that sugar can be easily extracted. At this stage, pressing is executed to extract the remaining amount of sugar. The sugar syrup, or 'raw juice' is moved on to the purification process, where impurities are removed using the carbonation process. During carbonation, the juice contains a high amount of calcium, which is treated using Tulsion® Resin. This process is also called juice softening. After this step, the 'thin juice' is concentrated using Multiple Effect Evaporators (MEE) and put through another filtration process. This filtered juice is taken for the last stage treatment where it is crystallized, dried, and packed for domestic or industrial use.



Regeneration Process

Ion exchange with very few exceptions is a reversible process. Due to this reversibility, it is possible to regenerate the exhausted resin to its original form. Same can be applied for the process of beet sugar decalcification. When resin beads are completely loaded with the calcium ions, they will be regenerated using soft thin juice and NaOH. For regeneration, thin juice is cooled down to 40°C so that the calcium is removed from the resin beads. This low temperature will allow removed calcium to form a soluble complex of calcium saccharate. The caustic juice containing calcium saccharate produced is recycled to the lime milk preparation, or to the 1st/2nd carbonation, where the saccharate complex is split, calcium gets precipitated as $CaCO_3$ and sucrose goes back to the juice.

After NaOH injection, there are other operations involved in regeneration. These are briefly discussed below:

Sweeten Off → Backwash → Settling Down of Resin Bed → Regeneration → Rinse

1.) **Sweeten off:** This is the step to displace syrup from the bed to make it ready for regeneration. It is continued until the brix reaches some low level. This facilitates easy and proper backwash.

2.) **Backwash:** Water is injected from the bottom in the upward direction to expand the bed to about 60 to 80%. Thin beet syrup is used for backwash. It can be carried out for 30 to 60 minutes. The main purpose of backwash is loosening & reclassifying the bed. It also helps in removing dirt and filtered matter.

3.) **Settling Down of Resin Bed:** After backwash, the bed is allowed to settle down. In this step, the resin beads which are classified after backwash again get compacted.

4.) **Regeneration:** NaOH (5%) along with thin juice is injected from the top, replacing calcium ions with sodium ions. Approximately 40% of the NaOH quantity used for regeneration is recycled back to the carbonation stage which is a huge improvement in terms of regenerant cost savings.

5.) **Rinse:** This is the last step of regeneration, wherein excess regenerant is washed from the bed, and during fast rinse, regenerant which is trapped in resin beads is also removed. Now, the resin Column is ready for another cycle of operation.

Recycling of Regenerant

To be more environmentally friendly, an innovative regeneration process (NRS process) has been developed on the fact that in alkaline conditions, the calcium saccharate is soluble in water. So, the regenerant is a mixture of decalcified thin juice (cooled) and NaOH. The spent regenerant and backwash water are fully recycled in the process without waste disposal, the rinse is using hot decalcified juice.

Introduction of NRS

Originally the resins were regenerated with a brine solution. Due to the waste handling cost, the industry has developed environment friendly alternatives such as the NRS process. This New Regeneration System (N.R.S.) has been installed worldwide in more than 100 beet sugar factories.

Typical Characteristics of Tulsion® Resins

Tulsion® T-4213 MP Na is a strongly acidic, macroporous and polymer-based resin with a sulphonic acid functional group. It exhibits the following properties:

- Excellent physical and chemical characteristics & supplied in sodium form.
- The product is designed to have a large pore structure, with high capacity, facilitating the kinetics of adsorption and desorption, which enables this catalyst to be used in polar and non-polar media.

Characteristics	Tulsion® T-4213 MP Na
Screen size USS (wet)	16 - 40
Particle size	0.4 to 1.2 mm
Total exchange capacity	1.80 meq/ml (min)
Moisture content	50 ± 3%
Effective size	0.45 - 0.55
Swelling (Max)	Na^+ -> H^+ :10%
Backwash settled density	670 to 720 g/l
Temperature stability	120°C
pH range	0 to 14

Typical Operating Conditions for Tulsion® Resins

Parameters	Unit	Values
Resin bed depth (minimum)	mm	1000
Operating temperature (Max)	°C	120
Service flow rate	BV/hr	2 to 5
Regenerant		NaOH + Soft juice
Regeneration level	g/l	80 -100
Regenerant concentration	%	4-5% NaOH
Regeneration time	minutes	30-40
Regeneration temperature	°C	<40
Slow rinse		With soft juice
Slow rinse	BV	2
Fast rinse	BV	5 (max)

Case Study

Case:

One of the prestigious beet sugar manufacturers in Europe approached Thermax to look upon their process of beet sugar, and provide a solution for their ongoing operational problems. Thermax resin technical team audited customer's plant and found out that during the carbonation process in sugar refining, the juice contained a higher amount of calcium which was creating problems like turbidity, loss of sugar, a larger mass of molasses, and scale formation in evaporators.

Solution:

Thermax team proposed Tulsion®T-4213 MP Na FG resin which was employed to remove calcium & other alkaline earth metals from the juice.

Result:

Tulsion®T-4213 MP Na FG was found suitable for the process and helped in the removal of the significant amount of calcium leading to many advantages like higher output, reduced maintenance cost and lower water consumption. Customer was delighted with the improvement in their plant operations and with the added benefits of using Tulsion ® resin; partnered with Thermax for many years and continues to do so.

Benefits of Hard Juice Softening

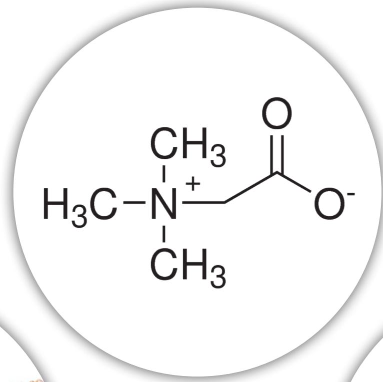
- Reduces the scale forming in evaportors and juice heaters
- Provides effcient cystalisation and sugar recovery
- Reduces or eliminates the use of antiscalent during the evaporation
- Energy saving on cleaning cost of evaporators
- Enables the use of energy efficient downstrean equipment like plate evaporators and the process like molasses desugering by chromatographic process

Do's and Don't's

S.No	Parameter	Do's	Don'ts
1	Temperature	120°C	Should not be >120°C
2	Regenerant concentration	4-5% NaOH	Not to <4%
3	Regeneration temperature	<40°C	Should not be >40°C
4	Backwash	After every cycle backwash for 60 minutes (minimum) Backwash water temp <50°C	
5	Regenerant hardness	Should be <0.01%	
6	Influent suspended solids	Nil	
7	Regenerant recycle	In case the recycled regenerant is being used for regular regeneration, it is recommended to use fresh regenerant after every 30-50 cycles.	

Applications of Beet Sugar

Beverages



Betaine

Confectionary products

Bio-fuel production

Advantages

The main advantage of ion exchange is increased extraction due to the elimination of impurities and by the same token, decreased production of molasses. Since, the price of sugar as sacked white sugar is greater than that in the form of molasses, this is the main economic justification for the process. Other advantages are lesser scaling of heat transfer surfaces in evaporators, heaters, and pans due to a substantial decrease in mineral content in the juices.

Advantages Offered Over Gel-Type Cation Resins	
Low residual hardness	< 25 mg / 100 g DS
High volume of treated thin juice per softening cycle	Depending on inlet load
Low chemical consumption and effluent generation	< 10 BV per cycle effluent generation
Low resin fouling and therefore continuous efficient operation	Continuous operation for > 300 cycles of regeneration
Low rinse volume and therefore low juice dilution	< 6 BV
Better fuel economy	>95 % hardness removal

Glossary of Beet Sugar Processing

Sediment in Sugar
Water insoluble and suspended substances particularly not visible to naked eyes

Ash Content
Water soluble salts of inorganic and organic compounds

Conductivity Ash
Ash determined by conductivity

Moisture Content of Sugar
Moisture content of sugar usually maintained @< 0.03 %

GR Sugar
Granulated refined sugar -a product of centrifuging white massecuite

RDS of Sugar (Brix)
Refractometer dry solid content or refractometric dry substances which is the dry substance measured by the refractometer, which is also called as brix applicable for pure sugar solution as the RI

Massecuites
Sugar crystal surrounded by syrup

Standard Liquor
Product of melting high raw sugar and low raw sugar in thick juice to produce feed for the first crystallisation

High Green High Wash Syrup
Mother liquor from centrifuging the white A massecuites

Low Green Syrup
Mother liquor from centrifuging high raw B massecuites

Thick Juice
Product of the evaporating station

Thin Juice
Product of the purification station

Carbonation Lime Residue
Product of the first carb operation (lime cake)

Hardness (Lime Scale)
Total water soluble salts of calcium and magnesium

Alkalinity
Alkalinity produced by alkali metal salts like sodium, potassium , calcium & magnesium salts

Diffusion Juice
Product of the diffusion station

Cossets
Product of the slicing station

Polarimeter
Instrument that measures the optically active substances like sugar

Refractometer
Measures the dry substance(DS) content in a solution

BOD
Amount of oxygen required by organisms to consume dissolved organic matter

COD
Amount of oxygen necessary for chemical oxidising agent to oxidise all the reduced species required by organisms to consume dissolved organic matter

TOC
Amount of organic carbon in the given amount of waste water

VOC
Volatile organic compound's - compounds of carbon and hydrogen that often contain oxygen, sulfer, nitorgen, fluorine and chlorine

Nox
Oxides of nitrogen (NO and NO_2)

PCC
Precipitated calcium carbonate

MDC
Process of molasses de-sugaring by chromatographic process

Remelt Liquor
Liquor produced from raw sugars from different sugar of crystallisation melted in remelt syrup

Remelt Syrup
Raw or affined sugar is melted in melter with high purity water to produce the syrup of 60% DS

Purification
Remelt syrup purified to remove insoluble solids, gums, polysachrides, colorants by precipitation methods combine with purification by phosphoric acid (phosphating) and lime (carbonation)

Affination
Process of mixing the raw sugar or low purity massecuite with high purity sugar syrup to increase the purity of the mother liquor

PAC
Powdered activation carbon

Recovery
% of the refined sugar produced per unit of raw sugar process on mass base

Mother Liquor
Sucrose crystal covered with low purity sugar syrup

Extract Processing
Products of MDC process, processed in to GR (Granulated refined) sugar

Continuous SMB
Continuous simulated moving bed chromatographic process in which the resin remains fixed and the and input and output moves around the resin

Sequential SMB
Sequential simulated moving bed chromatographic process in which input and output operates sequentially moves around the resin

HFCS
High fructose corn syrup

Hard Molasses
Molasses having hardness > 3 meq

Molasses
Runoff syrup from final stage of crystallisation

NRS Juice Softening
New regeneration system that consist of regeneration of resin bed by NaOH and sugar syrup

Garrulus Juice Softening
Low green syrup with high Na, & K is used to regenerate the resin.

Soft Juice
Juice that can be processed to generate soft molasses

Thin Juice
Product of purification having some hardness and feed to the evaporators

Betaine
One of the nitrogenous compound present in sugar beet that ends up in molasses

Raffinate (CMS)
Raffinate (concentrated molasses solid) molasses with high mineral and low amount of sucrose

CSD
Crustal size distribution

CV Value
Coefficient of variation in sugar crystal characterises the uniformity of the crystal size.

Floc
Cloudy and turbid precipitates

Speecks
Material in sugar that can be seen without microscope like caramelised sugar, hardness and rust particles

Saponin
A colloidal material that produces flocs on beverages comes from beet scene carried to sugar

Liquid Invert Sugar
Solution of sugar and invert sugar in water

MA
Mean aperture- average crystal size of the sugar

Seeding
Process of adding of the fine particle that serve as base for crystal growth in super saturated liquor

Second Carbonation
Process in which the carbonation gas is added to the filtered first carb juice to adjust the ph of 9-9.2 and alkalinity of 0.02-0.03% as CaO)

First Carbonation
Process in which carbonated gas is added to the heated limed juice until the pH 10.8 to 11 and alkalinity of 0.08 to 0.11 % as CaO is reached

Pre-liming
Which small amount of lime is added to the juice

Diffusion Juice
Product of diffusion station -juice has DS about 15% and purity is 85 to 90 %

Diffusion Process
Movement of sucrose and noon-sucrose substances from higher concentrated side (Inside the beet cells) to lower concentrated side through protoplasm

Customer Reach

EUROPE & CIS

Germany, UK, Netherlands, Sweden, Austria, Belgium, Denmark, Poland, Czechoslovakia, Italy, Spain, Portugal, Luxembourg, Norway, Russia

ASIA

India, China, Japan, Thailand, Malaysia, South Korea, Saudi Arabia, Indonesia, Singapore, Malaysia, Vietnam, Taiwan, Bangladesh, Indonesia, Philippines, Qatar, Turkey

NORTH AMERICA

USA & Canada

AUSTRALIA

AFRICA

Kenya, Nigeria, South Africa

SOUTH AMERICA

Argentina, Brazil, Mexico

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Sustainable Solutions in Energy & Environment

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