Ethanol Dehydration
pocket size reference guide

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MOLECULAR SIEVE MANUFACTURING

All Type A molecular sieve begins as HYG04DG and needs to be treated with potassium to create HYG03C molecular sieve. A perfect and total ion exchange, however, is not feasible, so a certain amount of molecular sieve crystals will retain a HYG04DG structure; this can allow the co-adsorption of larger molecules, such as ethanol, which has a molecular diameter of less than 4 Angstroms (see*figure 1).*

THE SIGNIFICANCE OF PORE SIZE

Co-adsorption is an undesirable occurrence and refers to the amount of ethanol that is adsorbed by the molecular sieve along with the water that is intended to be adsorbed. This co-adsorption factor can indicate the quality of the HYG03C sieve and the amount of residual HYG04DG crystals in the molecular sieve beads.

HOW CAN THE QUALITY BE DIFFERENT?

The co-adsorption factor varies by product selection and by manufacturer. Quality is based on the efficiency of the potassium ion exchange during manufacturing, the clay binder used, manufacturing methods, and other factors.

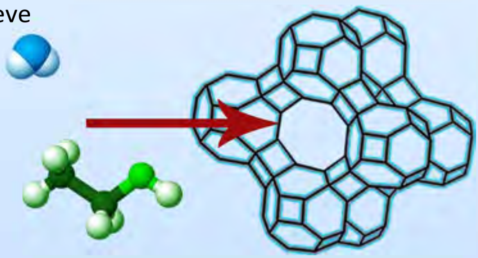
Molecular Diameters

Water = 2.8 Angstroms Sieve

Opening = 3 Angstroms

Ethanol = 3.6 Angstroms

figure 1



The Role of Co-adsorption *cont.*

LAB TESTING METHOD

Heat is released when sieve adsorbs liquids. The amount of heat released can be measured and used to determine sieve quality. Adding water to an unused HYG03C sample should result in a measurable heat increase, up to 30° or more; this can indicate the full working capacity of the sieve sample. Adding pure ethanol to an unused HYG03C sample should result in a minimal heat increase, up to around 15°F; a lower increase in heat upon the addition of pure ethanol indicates a high quality HYG03C molecular sieve.

TESTING IN AN OPERATIONAL ETHANOL PLANT

Using the Regeneration Flow rate in gallons per minute and the Regeneration Proof, we can estimate the amount of ethanol that is co-adsorbed.

Ethanol Adsorbed = RF x (RP/200)

RF = Regen Flow RP = Regen Proof
200 = a constant, representing the proof of pure ethanol

Example

RF = 87 GPM RP = 87 x (112.8/200) = ethanol adsorbed
RP = 112.8 proof = 87 x 0.564 = 49.068 gallons

In this case, for every 87 gallons of regen gas, 49 gallons consists of ethanol with the rest being water.

*Regeneration Proof should be taken from the regen tank or regen condenser around 20 psi, after switching to regen gas for the most accurate results of actual performance.

The Role of Co-adsorption *cont.*

THE IMPACT OF CO-ADSORPTION FOR ETHANOL

Loss of Capacity and Productivity

- Decreases capacity for water per cycle by adsorbing ethanol instead
- Causes less ethanol by volume to be produced during a given cycle due to adsorbed ethanol

Regeneration Proof Too High

- Loss of energy efficiency by reprocessing ethanol
- Decreased capacity for new ethanol in distillation unit due to excessive recycled ethanol

Although the working capacity and efficiency may only equate to a few gallons per minute, over the course of 350 operation days per year, these savings can quickly add up to over one million gallons. If evaluated correctly, this method can allow plants to increase their productivity and overall profitability.

What Can Molecular Sieves Adsorb?			
HYD03A	**HYD04BLU**	**HYD05C**	**HYD10A**
water	water	water	water
	ethanol ethane	ethanol ethane	ethanol ethane
		propynol propane	propynol propane
			large chain hydrocarbons

Process Optimization

TEMPERATURE AND PRESSURE

Capacity of molecular sieve is directly dependent on the operational temperatures and pressures. To increase capacity of the sieve, producers must operate the unit at the highest pressure and lower temperature possible.

1. Capacity increases as pressure increases.
2. Capacity decreases as temperature increases.

TEMPERATURE

This is strictly a vapor phase process, meaning the feed stream cannot change to a liquid at any point; thus, the lowest temperature that can be utilized would lie just above the point of a phase change. It is suggested that the inlet vapor temperature be set at 50°F above boiling point to ensure vapor phase. Boiling points can be calculated using tools on-line or by asking an engineer for assistance.

PRESSURE

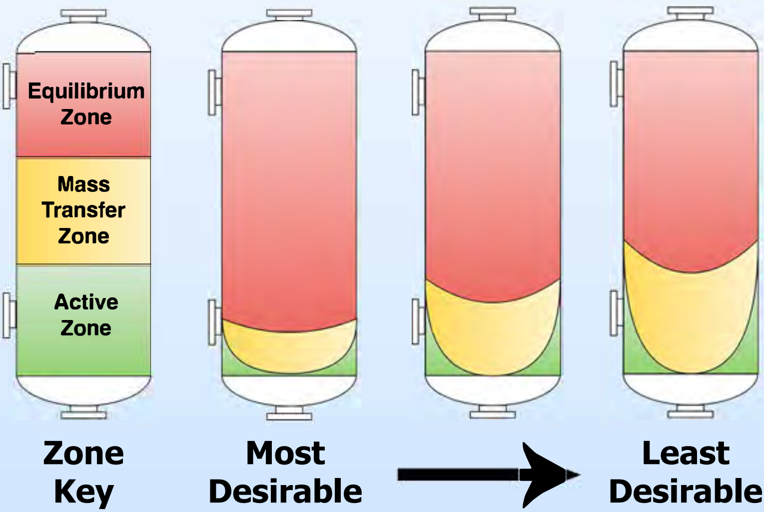
The system is limited by the maximum pressure sustainable by the system as defined by the vessel, piping, and valve ratings (consult P&ID, engineer, or construction team/manuals). Aside from avoiding overloading the system, it's important to consider the critical velocity through the molecular sieve. Extreme pressures will rapidly deteriorate the integrity of the beads and break them down quickly.

Process Optimization *cont.*

MASS TRANSFER ZONE

The Mass Transfer Zone (MTZ) describes the section of the dehydration unit that is actively adsorbing water. This zone will move from the top of the bed, downward as the cycle progresses. Undesirable vapor dynamics can cause gas to move through the bed unevenly, which can increase the height of the MTZ; the very moment that any part of the MTZ reaches the bottom of the bed, breakthrough occurs and the cycle ends. For this reason, a short MTZ can allow more sieve to fully reach capacity before the cycle ends, which leads to increased capacity, increased cycle times, and an overall boost in operational efficiency.

Three Different Mass Transfer Zone Scenarios



Process Optimization *cont.*

FACTORS AFFECTING WORKING CAPACITY

An ideal balance between temperature, pressure, and feed rate is the key to having the most optimized system.

- Temperature should always ensure vapor phase maintenance under given temperature and pressure.
- Consider the distribution of vapors on the inlet relating to the shape and velocity of the Mass Transfer Zone.
- Maximize the difference between the adsorption pressure and regeneration vacuum.
- Choose the right 3A molecular sieve.
- Compare specification sheets and request to review recent Certificates of Analysis.

Compare molecular sieve products from multiple manufacturers.

Crush strength - a higher number indicates a more durable product

Attrition - the tendency to dust, which can lead to inefficiency in the dehydration unit

Ethanol co-adsorption - the quality of 3A can largely affect the efficiency of the dehydration unit

Talk to us when you have questions about why any of this should matter to you. We work with dozens of ethanol plants and can help clarify and give perspective from a different angle.

Commodity or Investment?

INVALUABLE INVESTMENT

Many plant managers and operators view molecular sieve as an invaluable investment - a choice that plays a critical role for the plant's productivity for the next decade. This is due to the high product and labor costs that are associated with installing new sieve material. Operating with this mindset requires relentless care and control over the ethanol dehydration units to ensure the longevity of the molecular sieve beads.

The Invaluable Investment theory requires ethanol producers to monitor and care for the molecular sieve constantly, with numerous preventative maintenance procedures. Very quickly and easily, overlooked top off maintenance, rapid pressure changes, and bed fluidization can break down sieve, which will begin a decline of efficiency and productivity for the plant, overall.

CONSUMABLE COMMODITY

When an ethanol plant is focused on increasing output as a means of increasing overall profitability, one might reconsider how molecular sieve is valued. Some ethanol producers view molecular sieve as a Consumable Commodity that can be pushed to the limits to increase overall ethanol production by twenty percent or more. The Consumable Commodity theory of operation aims to maximize output by operating under extreme conditions.

Invaluable Investment

HOW NOT TO KILL YOUR SIEVE BEADS

Like all processes in an ethanol plant, careful attention is required in ethanol dehydration units to care for molecular sieve:

- Proper preventive maintenance
- Proper care during the actual operating process
- Knowing what can cause long term damage to the sieve beads and dehydration unit

Proactive monitoring is imperative to ensure a long, efficient lifespan, which could offer more than five years, up to a possible ten years of service life.

DON'T FLUIDIZE THE BEDS

Excessive pressure can damage beads and even cause them to lift and shift within the dehydration unit. Broken beads can quickly tum to dust and can cause a quicker break through, which results in decreased cycle times. The presence of dust will also require more pressure during operations, so the problem tends to only become worse once the initial damage has begun. We strongly recommend that you consult with your design and engineering team for assistance in calculating the appropriate operating pressures that won't damage your ethanol dehydration system.

Invaluable Investment *cont.*

BEWARE OF CONTAMINENTS

Extreme Acids and Bases

• An ideal pH range is 4.5 - 9.0.

• Concerns for extreme pH levels can arise when using Cleaning-in-Place chemicals that may be accidentally carried over into the dehydration unit.

• Strong acids, such as sulfuric acid, and strong bases, such as caustic soda, can damage the structure of the clay binder and cause beads to melt and fuse together.

Light Hydrocarbons and Others

• Organic plant material can cause beads to coke and turn black, which prevents the bead from adsorbing water in that spot (image on Page 8 shows black coke formation).

• Coke is formed when hydrocarbons are physically burned onto a sieve bead.

• Installing demister pads or coalescing filters can help prevent the formation of coke.

SUCCESS THROUGH PREVENTION

The best way for Ethanol Producers to increase their success when treating sieve as an invaluable investment is to persistently train the team how to properly care for sieve and to also know what to avoid. One false move can devastate a dehydration unit beyond use and require an early change out.

Consumable Commodity

SAFETY CONSIDERATIONS

Some upgrades might be required to ensure that sieve vessels can handle higher pressures and the addition of more durable valves and pressure gauges that can accurately measure the higher values of these extreme operating conditions.

OPERATIONAL CONSIDERATIONS

In cases where plants are operating at extreme temperatures and pressures, molecular sieve will quickly be worn down due to rapid pressure change, which causes the sieve to move inside the vessel, crack, and degrade to dust. The occurrence of this rapid degradation of material is caused by the natural law of fluid dynamics and not by the strength or quality of the molecular sieve beads.

Keep in mind that the return on investment for operating in such a manner can justify the added costs of more frequent change outs. A cost analysis and some discussions amongst plant operators can help you determine if this method could be beneficial for your individual situation.

BENEFITS

Production capacity can increase by up to 20% or more when sieve is running at optimal capacity. Even with added costs from frequent sieve change outs, the increase in overall profitability of a hard-working dehydration system can offset added maintenance and labor costs.

Consumable Commodity *cont.*

FLUIDIZATION

Beware of avoiding excessive fluidization while running at extreme pressure:

- the lifting of sieve material within the bed
- caused by rapid surges in vapor velocity.

High crush strength will not do much to increase the lifespan of fluidized beads because they're crashing into other beads that are equally as strong.

PRESSURE DROP

Realize what's happening inside your system to help control its degradation:

- the difference in pressure of the feed stream compared to the product stream
- operations will constantly require more pressure to push the feed stream through the bed

THEORETICA L VELOCITIES

Know the specific limitations of your plant and consult with your design and engineering companies before changing your output. Always put safety first before increasing the pressure inside your vessels and ensure your system can handle the extremes.

300 F, 70° PSIG Pristine 4x8 Beads	
GPM	**Theoretical Velocity, ft/min**
325	87.53
350	94.27
375	101.00
400	107.73
425	114.47
450	121.20
475	127.93

Preparing for Unloading

SAFETY CONSIDERATIONS

Vessels should never be entered if they contain used molecular sieve. While working around used molecular sieve, be aware that the sieve may allow chemical compounds to be desorbed, even after regeneration, when exposed to the open atmosphere - particularly in the presence of high humidity. It is the responsibility of the operator to be aware of the chemicals that may be desorbed in this manner and what hazards or toxins may be encountered. It's highly recommended to wear proper eye protection, skin protection, and an approved breathing mask or respirator while unloading molecular sieve.

UNLOADING PROCEDURE

1. Begin by regenerating the bed, following normal bed regeneration operating conditions.

2. Once the bed is completely heated, depressurize then cool the bed with gas and send to flare.

3. Once purged with process gas, purge a second time using inert gas at ambient temperature. The gas flow rate needs to be a balanced flow that allows a fairly equal or even distribution inside the bed.

4. Continue to purge the bed until the outlet gas is free of toxic materials and at least 50% below the LEL. Once this has been achieved, the bed is ready for dumping.

Loading a Dehydration Unit

SAFETY CONSIDERATIONS

Molecular sieves are inert and pose no significant health hazards when used in the proper manner.

ALWAYS review Safety Data Sheets before and while handling molecular sieve.

1. Molecular sieve generates heat when adsorbing water. This heat can be significant enough to reach boiling point and cause injury or bums if handled improperly.

2. There is a small amount of residual dust on the sieve that can be released during its handling. This dust can be an irritant to the eyes, nose, throat, lungs, and skin. It's recommended to wear a dust mask, proper eye protection, skin protection, and gloves when handling sieve.

VESSEL INSPECTION

Make sure your vessels are free from physical damage and no cracks are present.

1. Ensure all support material in properly secured if your unit requires screen and ceramic balls.

2. Notate the condition of sample taps, thermal wells, etc. Confirm proper insertion and working conditions.

3. Check the calibration of the hygrometer probe or replace the probe before startup.

4. If the vessel is internally insulated, check for surface defects. These should be properly repaired before proceeding to prevent gas bypass around the sieve bed.

Loading a Dehydration Unit *cont.*

PACKAGING

HYG03C molecular sieve for ethanol dehydration, is packaged in 2,205 pound Super Sacks and 330 pound Drums (net weight).

MATERIALS INSPECTION

Molecular sieves undergo quality control testing prior to shipment to ensure that material meets the specification sheet and matches the quality, strength, and performance as designated.

- Ensure that the packages, product code, description, mesh size, are all correct and that there is enough material to fill the bed.
- Packages should be sealed and in fair condition without any major tears or punctures and should be dry without any wet spots.

Super Sacks

- Untie the inner liner and outer top spout of the Super Sack, reseal after inspection.

Drums

- Be cautious when removing the lid of the Drum as it can pop off abruptly, potentially causing injury.
- Follow instructions on the lid, be sure to release any pressure valves before unbolting the rim.
- Once the lid is removed, inspect the product in the drum, then replace lid and bolt.

Loading a Dehydration Unit *cont.*

LOADING INSTRUCTIONS

It's recommended to use a chute to minimize the vertical drop; typically, molecular sieves may be allowed to free fall a distance of up to 25 feet. Super Sacks by crane to the top of the vessel, where the two bottom chutes of the Super Sack are opened and the sieve unloaded.

NOTE

Super Sacks have an inner liner that is not attached to the outer shell of the Super Sack. It is possible for the weight of the sieve to pull the liner from the Super Sack and into the vessel. If this should happen, it is necessary that the liner be retrieved from the vessel to prevent damage to the sieve and the vessel.

TRADITIONAL UNITS

It is generally recommended that there be 1.5 feet or more of open vessel space below the inlet gas nozzle and the sieve bed. The bed topping recommended consists of a 6-12 inch depth of support balls. This layer helps with flow distribution and also helps to keep the bed secure and level, minimizing the possibility of sieve movement.

LATERAL UNITS

These units need to remain topped off at all times. See article Following Top Off Schedules on Page 20 for more information.

Starting a Dehydration Unit

SAFETY CONSIDERATIONS

During initial start up, the bed can get very hot when the first feed is sent to the dehydration unit. In extreme cases, gauges, thermometers, valves, and the vessel itself can become damaged or even melt from intense heat. Steps must to be taken to prevent the beds from getting too hot and causing damage to personnel or equipment.

OPERATIONAL PRECAUTIONS

Every plant builder has their own version of a startup procedure and every plant is unique, so these should just be considered as some basic tips that work in most situations.

In every case, the objective is to preload the molecular sieves with water and ethanol, without getting any violent temperature runaways, while keeping the beds hot enough that the ethanol stays in vapor phase. The process is generally safe and simple when performed with a bit of patience.

- Avoid rapid pressure changes that could cause the material in the bed to fluidize or lift.
- Avoid an uncontrolled raise in temperature from the heat of adsorption when adding fluid to fresh sieve.
- Most pressure vessels are rated at 600°F, so we suggest that temperatures must never exceed 600°F at any time.

Starting a Dehydration Unit *cont.*

1. The easiest way to start is by using 200 proof ethanol because it has the lowest water content and should only begin by charging the HYG03C crystals since the residual HYG04DG won't adsorb ethanol. The 200 proof ethanol is vaporized (310-320°F, 20-40 PSIG) and sent to the beds at slowly increasing rates up to 75% of the design feed rate.

2. The 200 proof ethanol is then condensed, fed back to the vaporizer, and recycled back through the beds, until the bed temperatures have stabilized around 350°F.

3. Once the bed has stabilized, continue to recalculate start up by adding 190 proof at 10-20% of the normal feed rate. Start slowly, to help ensure that temperatures are maintained at 500°F or less. See the Temperature Control Tips section on the next page for keeping temperatures within safe, manageable ranges.

4. Continue to recirculate vaporized wet feed, diluted with 200 proof recycle, until the bed temperature has again stabilized around 350°F.

5. Repeat this procedure on the other beds. It may be a good idea to keep a small amount of hot feed flowing through the first bed to minimize condensation and allow for an easy startup with wet feed.

Starting a Dehydration Unit *cont.*

TEMPERATURE CONTROL TIPS

Keeping the temperature in a safe range is crucial for the safety of operators and for preventing damage to the newly loaded material. Below are some tips on how to keep temperature in control.

- Control the feed addition; some liquids will need to be drained from the loop.
- Adjust wet feed rate. Less water means less heat added.
- Lastly, pressure can be dropped to lower temperature.
- Recirculating feed rate should always be high enough to maintain turbulent flow through the molecular sieve beads to prevent hot spots.
- To ensure turbulent flow, measure the pressure drop across the sieve beads - it must be at least 0.01 psi per foot of bed.

DON'T HAVE 200 PROOF?

If there is no 200 proof ethanol available for start up, 190 proof ethanol can be used, but it's recommended to utilize the 200 proof produced from the first feed that exits the dryer. This process requires extra caution until a low water content stream is available for recirculation as the bed will be more actively adsorbing a saturated feed stream and will be more susceptible to rapid rises in heat.

Lateral Top Off Schedule

GENERAL GUIDE TO LATERAL TOP OFFS

Lateral beds MUST be topped off regularly to prevent sieve bead degradation such as excessive attrition, abrasion, and more. There is no one correct schedule, you may need to top off more frequently, but this guide will give a good idea of what to do in each phase:

1: During the first week, plant operators will want to check once per shift to help fill any empty space that appears as the material settles in from initial loading.

2: After for the first week, operators can begin checking for top offs once per day for the next 3 weeks.

3: After the first month, operators can begin checking for top offs once per week for months 2 and 3.

4: After the third month, operators can begin checking for top offs twice per month for months 4 - 6.

5: After the first six months, operators can begin checking for top offs needs during the regularly scheduled Plant Maintenance, but **no less** than once per month.

Month 1		**Months 2 and 3**	**Months 4 - 6**	**Month 7 and Beyond**
Phase 1 **1 week**	Phase 2 **3 weeks**	Phase 3 **8 weeks**	Phase 4 **12 weeks**	*Phase 5* **Week 25 and beyond**
once per shift	once per day	once per week	twice per month	During regularly scheduled Plant Maintenance **NO LESS** than once per month

Disposal of Molecular Sieve

SAFETY CONSIDERATIONS

No special precautions need to be taken for the molecular sieve itself, as the zeolite and binder mixture is inert and is classified as synthetic clay. The only reason for analysis would be the possibility of controlled waste substances (special wastes, hazardous substances, metals, sulfur or nitrogen compounds, etc.) being picked up by the sieve from the process stream. In this case disposal would be predicated by these substances, not the synthetic, zeolite based molecular sieves.

DISPOSAL CONSIDERATIONS

In the United States, material can be disposed of in a licensed landfill. The material is normally analyzed to meet the regulations for proper chemical waste management.

NOTICE

All information contained in this booklet is for the sole purpose of sharing general knowledge and ideas about ethanol production. Hengye does not accept or imply any responsibility for actions taken by ethanol plant operators or staff. Hengye ALWAYS recommends consulting your engineering and design companies, upper management, technical manuals, P&ID, vendors, and members in your ethanol community before making decisions about ethanol dehydration units and operational procedures.

A Global Manufacturer

In 2014, Hengye Inc. was established in the USA to offer the flexibility and reliability required to meet the growing, dynamic needs in the American Ethanol market. From beginnings as a molecular sieve manufacturer, we have grown to offer full-service dehydration unit services for the ethanol community.

We Provide

- HYD03C and HYD03A molecular sieve
- Inventory in Omaha, Nebraska for quick access
- Technical guidance and industry knowledge
- On-site and remote troubleshooting support
- Full change-out services to ease your tum-around duties
- Process optimization assistance
- Product testing and remaining lifespan analysis

Feed streams are unique and Hengye is able to manufacture and select the ideal product to meet specification requirements and maximize the value of product streams. Paired with our engineers and industry experts, our sales and service team will provide the data and technical education to support and bring confidence to those who use our products.

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Hengye currently provides molecular sieve and services for more than 60 ethanol plants.

Our mission is to help ethanol plants flourish and increase profitability with the equipment already in use.

HYD03C molecular sieve is specially designed and manufactured for use in ethanol dehydration units and offers ideal selectivity, capacity, and durability.

Our goal for HYD03C is to optimize existing bed capacity, extend cycle times, and increase productivity in ethanol dehydration units, thus boosting the overall operational efficiency to offer an attractive return-on-investment.