UOP Adsorbents

Purification of olefin and polymer process streams

A Honeywell Company

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UOP Adsorbents for the Purification of Olefin and Polymer Process Streams

As catalyst technology for the production of polymers advances, the need for high-purity olefin process streams has become even more critical. Whether their source is off-gas from an FCC unit or the final product of an olefins manufacturing facility, adsorbents provide the olefin producer with the ability to remove many contaminants and meet the high-purity requirements of their customers. Polymer manufacturers also use adsorbents to ensure feedstock purity and to treat recycle streams within their processes. All of these process areas can benefit from the full array of adsorbents UOP has to offer.

Introduction

It is well known that polymer manufacturers require high-purity feedstocks and process streams. Impurities in these streams detrimentally affect catalyst activity and functionality, lowering polymer yield and quality. Common impurities found in these streams are water, carbon dioxide, methanol and carbonyl sulfide. These impurities and others have been effectively removed using regenerative adsorption processes for decades. UOP adsorbents used for the removal of these contaminants include zeolite molecular sieves, modified activated aluminas, AZ-300 hybrid adsorbent and non-regenerable metal oxide/sulfide products. Adsorbent selection will depend on the specific impurities to be removed and the process stream in which they are contained.

Contaminants Removed Via Adsorption

Contaminant Family	Contaminant	Ethylene	Propylene	α-Olefin Co-Monomers	Solvents*
Oxygen Compounds	Water	X	X		X
	CO_2	X	X	X	
	Alcohols	X	X	X	X
	Aldehydes		X	X	X
	Ethers		X	X	X
	Carbonyls		X	X	X
	Ketones		X	X	X
	Peroxides		X	X	X
	Oxygen	X	X	X	
Sulfur Compounds	COS	X	X	X	X
	H_2S	X	X	X	X
	Sulfides		X	X	X
	Mercaptans		X	X	X
Nitrogen	Ammonia			X	X
	Amines	X	X	X	X
	Nitriles		X	X	X
Other	Arsine	X	X		
	Phosphine	X	X		
	Mercury	X	X		

*Fresh, recycle and/or catalyst preparation

While the proper choice of adsorbent is important to successful purification, so is the operation of the unit. Misapplication of an adsorbent can not only lead to off-specification product or process streams, but also can cause potentially hazardous and negative effects. Adsorbents release heat upon adsorption. If an inappropriate adsorbent is used, or if this heat of adsorption is not carefully factored into the design or operation of the unit, it may trigger the formation of by-products and can, under certain circumstances, initiate high temperature run-away polymerization reactions. In less extreme cases, reactions can create coke formation on the surface of the adsorbent thereby shortening adsorbent life.

Zeolite Molecular Sieves

Zeolite adsorbents are synthetically produced molecular sieves that are microporous, crystalline, metal aluminosilicates. The uniform crystalline structure of molecular sieve adsorbents provides very predictable and reliable adsorptive properties. Metal cations contained in the crystalline structure of molecular sieve adsorbents balance the negative charge of the framework. These metal cations create an electrical field, hence their strong affinity for polar molecules. Depending on the type of crystalline structure and the occupying cation of the molecular sieve adsorbent, molecules may be readily adsorbed or completely excluded according to their relative molecular size. For example, a 3A molecular sieve is particularly useful for the dehydration of olefins. It will adsorb water, but will exclude an olefin molecule.

Molecular Sieve Critical Diameter, Å

Water	2.6
Carbon Dioxide	3.3
Methanol	3.6
Hydrogen Sulfide	3.6
Ethylene	3.9
Propylene	4.5

Molecule Sieves: Molecules Adsorbed and Excluded

Type	Molecules Adsorbed**	Molecules Excluded
3A	Molecules with an effective diameter <3 angstroms including H_2O and NH_3	Molecules with an effective diameter >3 angstroms (ethane)
4A	Molecules with an effective diameter <4 angstroms including ethanol, H_2S, CO_2, SO_2, C_2H_4, C_2H_6 and C_3H_6	Molecules with an effective diameter >4 angstroms (propane)
5A	Molecules with an effective diameter <5 angstroms including nC_4H_9OH, n-C_4H_{10}, C_3H_8 to $C_{22}H_{46}$ and R-12	Molecules with an effective diameter >5 angstroms (propane) (iso compounds and all 4-carbon rings)
13X	Molecules with an effective diameter <8 angstroms including benzene and toluene	Molecules with an effective diameter >8 angstroms $(C_4F_9)_3N$

* Chart depicts basic molecular sieve types only. In all applications, these basic forms are customized for specific use.

** Each type adsorbs listed molecules plus those of preceding type.

Zeolite molecular sieve adsorbents have a strong affinity for polar and polarizable molecules and even exhibit a selective preference for various polar molecules

Molecular Sieve Order of Selectivity
(high to low)

Water
Methanol
Hydrogen Sulfide
Carbon Dioxide
Propylene
Ethylene

based on their degree of polarity. Water is the most polar molecule known, and is therefore the most preferred and strongly adsorbed onto zeolite molecular sieves. Physical adsorption by molecular sieve adsorbents, including zeolites, causes the release of heat, which is known as the heat of adsorption. A preload step may be required if the olefin being processed can be adsorbed by the zeolitic adsorbent. If not properly accounted for, the processing of olefin streams with larger pore zeolitic adsorbents can create unwanted contaminants or lead to hazardous situations due to the adsorbent's high affinity for olefins (which are polar molecules). A preload step is used to control this heat release by the controlled addition of olefin onto the large pore zeolite prior to the adsorption step. During this preload step, olefin is slowly metered into the regeneration stream and is adsorbed by the zeolite. In this controlled manner, the olefin's heat of adsorption is carried away by the regeneration stream, and the zeolite is now ready for the adsorption step. Since the contaminant molecules are generally preferred by the zeolite over the occupying olefin molecule, the contaminant will displace the olefin molecule and thus be safely and effectively removed from the olefin stream. UOP offers recommendations and guidelines for preload procedures if they are required in your particular application.

The combination of selective preference for polar molecules and high adsorption capacity at very low contaminant concentrations, makes zeolite molecular sieves especially suited for the preparation of high-purity polymer process streams. While zeolite molecular sieves have a high capacity for polar molecules, other adsorbents may be more effective in removing less polar molecules from olefin streams.

Molecular Sieve Heat of Adsorption, BTU/lb

Water	1,800
Methanol	809
Hydrogen Sulfide	554
Ethylene	509
Propylene	438
Carbon Dioxide	349

Modified Activated Aluminas

Modified activated alumina adsorbents are synthetically produced, transitional phase aluminas. Unlike zeolites, activated aluminas are less crystalline and have a pore system that is not uniform. An activated alumina's ability to act as an

Activated alumina chemisorption relies upon the adsorptive force provided by a weak chemical reaction, which may be reversible during the high temperature regeneration step.

adsorbent is largely determined by the functionality of its surface, which can be modified during manufacturing. Without modification, activated alumina adsorbents rely on weak molecular forces for adsorption and, therefore, are inefficient at adsorbing polar contaminants at low concentrations. However, with modifications, an activated alumina's chemisorption properties can be enhanced, thus transforming it into an efficient and effective adsorbent. In general, the addition of an inorganic compound to the activated alumina can cause it to act as a weak base.

In olefinic streams, light acid gases such as CO_2, H_2S and COS are common contaminants that can be most effectively removed with these modified activated aluminas. As these aluminas rely on chemisorption to remove CO_2, H_2S and COS, they exhibit high capacities for these contaminants even at very low concentrations.

Comparative Product Configurations for Contaminant Removal

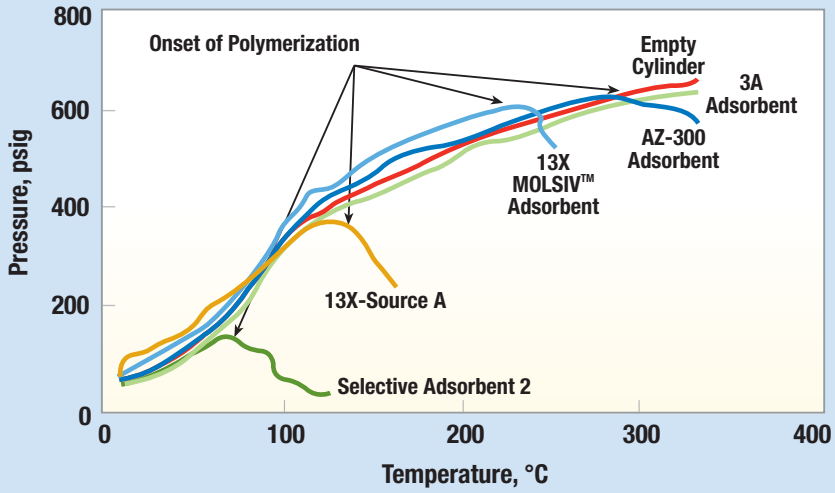
Contaminant Family	Contaminant	Product Configuration	Adsorbent Capacity	Olefin Preload?
Oxygen Compounds	Water	UOP MOLSIV™ 3A-EPG Adsorbent UOP MOLSIV 13X-PG Adsorbent UOP A-201 Alumina UOP AZ-300 Adsorbent	High High High* Moderate	No Yes No No
	CO_2	UOP CG-734 Alumina UOP CG-731 Alumina UOP AZ-300 Adsorbent Selective Adsorbent 1	High High Moderate Moderate	No No No No
	Alcohols, Ketones, Aldehydes, Ethers, Carbonyls, and Peroxides	UOP MOLSIV 13X-PG Adsorbent UOP AZ-300 Adsorbent Selective Adsorbent 2	High Moderate Moderate	Yes No Yes**
	O_2	UOP GB Series Adsorbents ***	High	No
Sulfur Compounds	H_2S	UOP SG-731 Alumina UOP AZ-300 Adsorbent UOP GB Series Adsorbents *** Selective Adsorbent 1	High Moderate High Moderate	No No No No
	COS	UOP SG-731 Alumina UOP AZ-300 Adsorbent UOP GB Series Adsorbents *** Selective Adsorbent 1	High Moderate High High	No No No No
	Mercaptans, Sulfides and Disulfides	UOP MOLSIV 13X-PG Adsorbent UOP AZ-300 Adsorbent Selective Adsorbent 2	High Moderate Moderate	Yes No Yes**
Nitrogen Compounds	Ammonia, Amines and Nitriles	UOP MOLSIV 13X-PG Adsorbent UOP AZ-300 Adsorbent Selective Adsorbent 2	High Moderate Moderate	Yes No Yes**
Arsine & Phosphine	AsH_3, PH_3	UOP GB-238 Adsorbent***	High	No
Mercury	Hg	UOP HgSIV™ Adsorbent UOP GB Series Adsorbents***	Low High	No No

* Under conditions >60% relative humidity
** Preload recommended
*** Non-regenerative material

UOP's Accelerated Reactivity Test (ART)

Liquid isobutylene is heated in an autoclave in the presence of adsorbent. Pressure is monitored as the temperature is raised. The pressure will decline at the onset of the oligomerization reaction. More reactive adsorbents will see onset of oligomerization at lower temperatures. These more reactive adsorbents will tend to produce green oil and deactivate more quickly when used in process plants.

Isobutylene ART on selected adsorbents



Modified activated alumina adsorbents do not have the extremely strong affinity for polar contaminants demonstrated by zeolites. With little or no capacity for olefins, the heat of adsorption of olefins with modified activated aluminas is negligible, and a preload step is not required. In addition, these adsorbents exhibit very low reactivity with regard to the main stream. The formation of contaminants, such as olefin oligomers, is practically excluded even under upset process conditions.

UOP AZ-300 Hybrid Adsorbent

By combining high selectivity and capacity for light acid gases with low reactivity and heat of adsorption, modified activated aluminas are suitable for the purification of olefin streams. Correspondingly, molecular sieves have a high capacity for polar molecules. Ideally, one adsorbent would exhibit the properties of both zeolitic and modified activated alumina adsorbents. AZ-300 adsorbent, a homogenous combination of modified activated alumina and molecular sieve adsorbents takes advantage of the complementary performance characteristics of both materials. AZ-300 adsorbent has high capacity for light acid gases and a broad range of polar molecules.

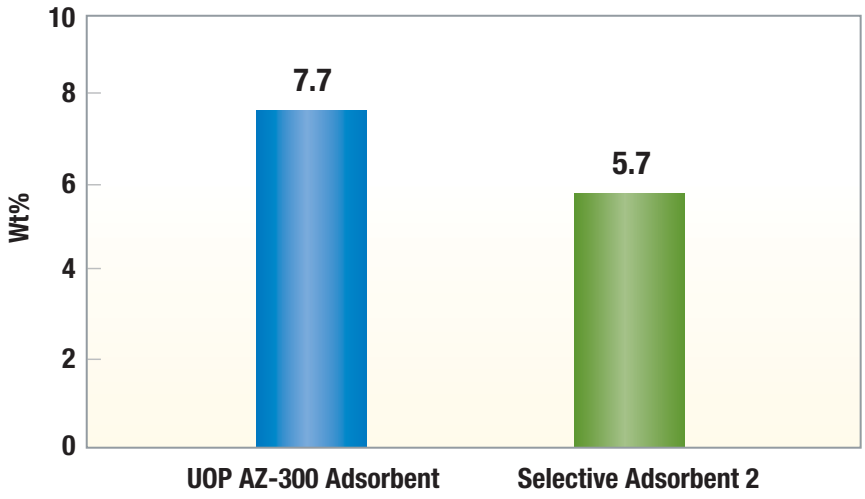
Though AZ-300 adsorbent contains zeolite, it typically does not require a preload step when processing unsaturated streams. The elimination of the preload step, while retaining the effective removal of polar compounds, provides the olefins producer and polymer manufacturer with tremendous process and competitive advantages. The unique properties of AZ-300 adsorbent enables the processor to use a single product for the adsorptive removal of a broad range of contaminants. The broad capability of AZ-300 adsorbent offers extra benefits during periods of intermittent and fluctuating levels of unanticipated contaminants.

UOP tested AZ-300 adsorbent against a similar product offered in the market (Selective Adsorbent 2). The data shows AZ-300 adsorbent's superior regenerative capacity for methanol in propylene. The tests also measured the excellent mass transfer characteristics of AZ-300 adsorbent.

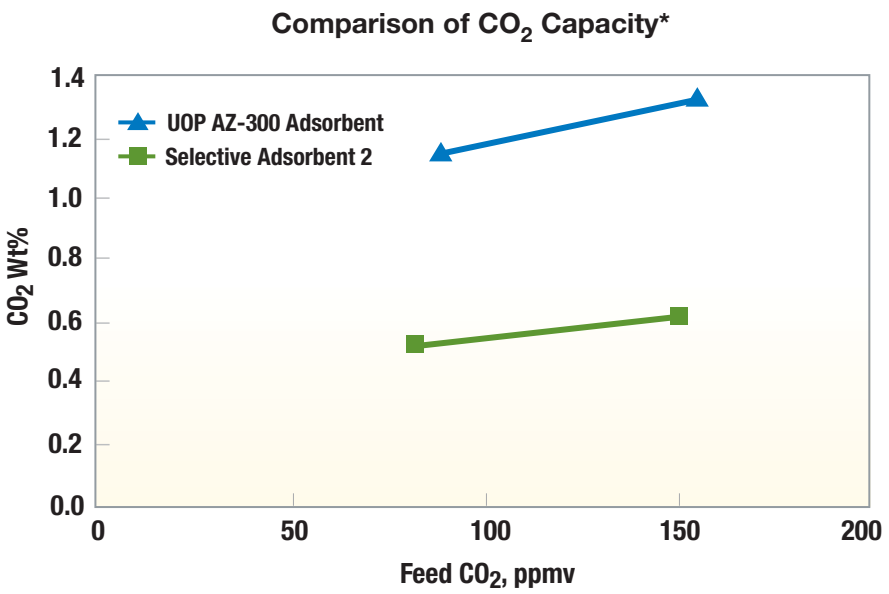
UOP AZ-300 adsorbent eliminates the preload step and offers a single-product bed without sacrificing unit performance or adsorbent capability.

Propylene Stream	Case Study
Feedrate, lbs/hr	155,000
Temperature, °C	50
Pressure, psig	300
Contaminant Profile, ppm(w)	
Water (H_2O)	20
Carbonyl Sulfide(COS)	5
Methanol (CH_3OH)	15
Total Oxygenates	30
Breakthrough Cycle Time, Days, for	
Single Product	
AZ-300 (No preload)	6
Compound Bed 1	
3A-EPG and SG-731(No preload)	3
Compound Bed 2	
13X-PG and SG-731 (Preload required)	6

Comparison of Dynamic Removal of Methanol from Propylene*

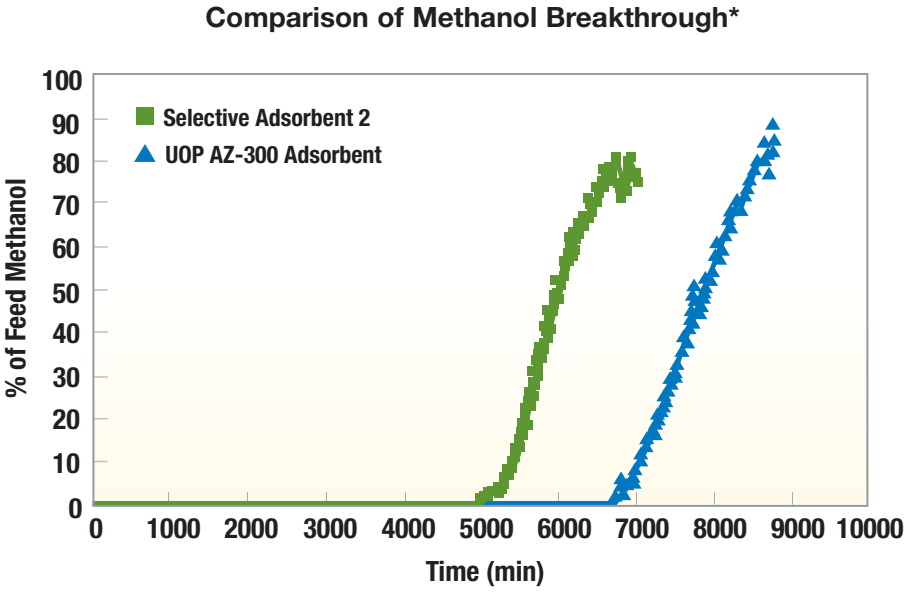


*Test conditions: 65 ppmw methanol in propylene



*Test conditions: 40°C

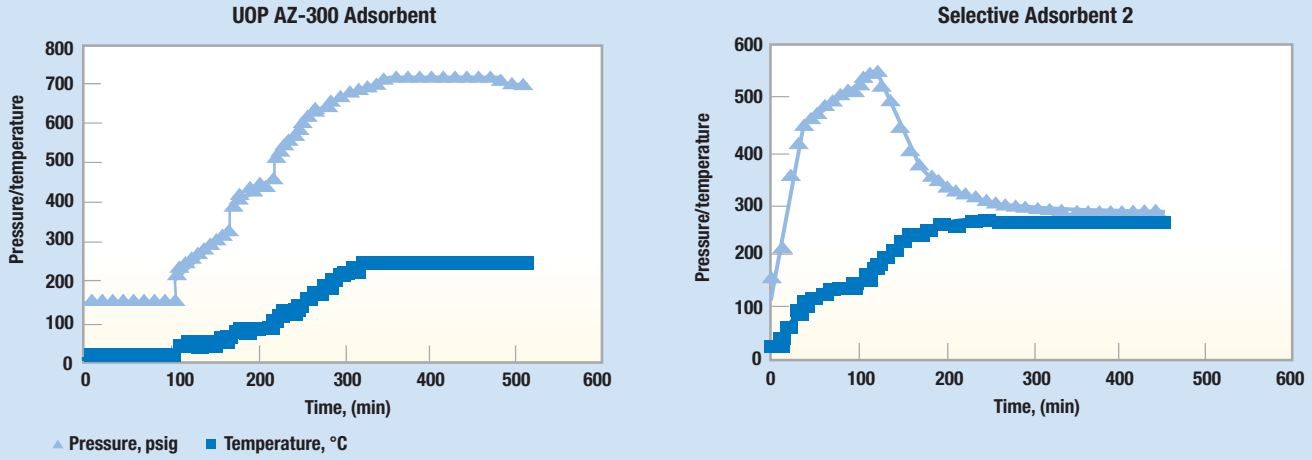
UOP evaluated a number of other potential contaminants under cycled test conditions. The testing shows that AZ-300 adsorbent has a 50% greater capacity for CO_2 compared to Selective Adsorbent 2 (also recommended for removal of oxygenated hydrocarbons). This extra CO_2 capacity, which also applies to COS and H_2S, is of particular benefit during upset conditions that can result in elevated levels of light acid gases.



* Test conditions: 65 ppmw methanol in propylene

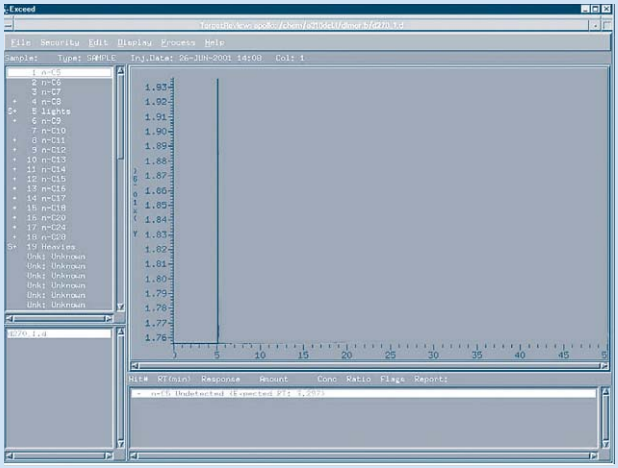
UOP also evaluated the reactivity of these materials. The data clearly demonstrate the lower reactivity of AZ-300 adsorbent. In the test, propylene liquid was charged into two test cylinders. One cylinder contained AZ-300 adsorbent, and the other cylinder contained Selective Adsorbent 2. The temperature was raised while the pressure was monitored. In the absence of any adsorbent, the pressure rises with the temperature. In our test, a decline in pressure indicates a chemical reaction is taking place. This reaction is the formation of oligomers from propylene. In addition to producing potential contaminants, this oligomerization reaction generates heat, which can lead to a runaway process. The AZ-300 adsorbent did not demonstrate any reactivity at 250°C. By comparison, the competitive adsorbent initiated reactions beginning around 150°C.

Comparison of Reactivity

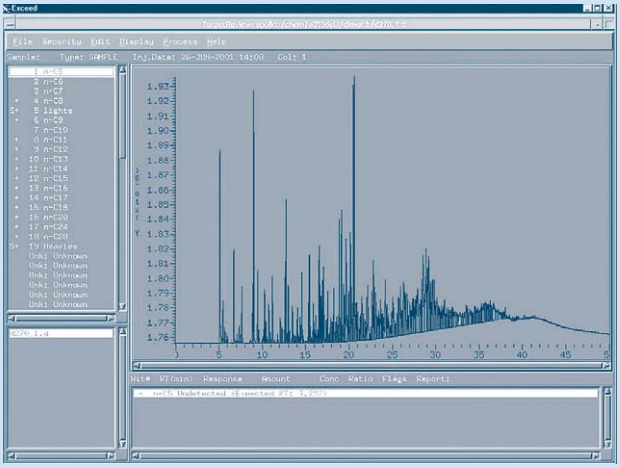


Gas chromatography analysis demonstrates that the propylene with UOP AZ-300 adsorbent has not reacted as seen by the single C_3 peak (left). The GC of the contents in the cylinder with the competitive material shows that the C_3 has reacted to make a mixture of higher molecular weight hydrocarbons (right).

UOP AZ-300 Adsorbent



Selective Adsorbent 2



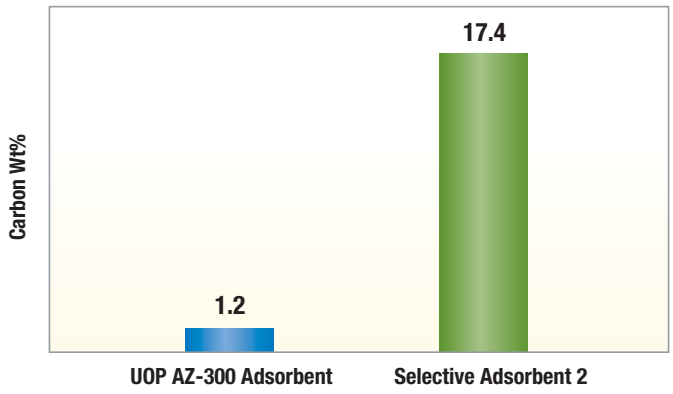
Over time, even if there is no catastrophic heat release and polymerization, carbon residue will build up on the surface of the more reactive adsorbent, thus shortening its effective life. After our tests, the competitive material contained significantly more carbon residue than AZ-300 adsorbent.

The next time you are considering adsorbents for contaminant removal, remember AZ-300 hybrid adsorbent. Its ability to adsorb a broad range of contaminants coupled with low reactivity in olefin streams puts it in a class by itself.

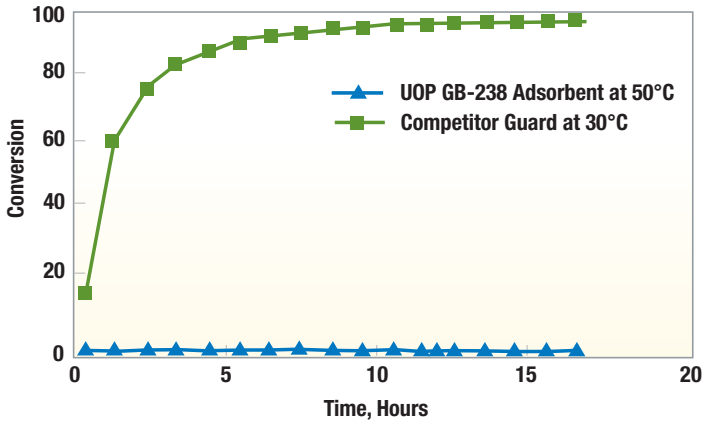
UOP GB Series Adsorbents

This class of adsorbents are high capacity, non-regenerative metal oxides or sulfides used for the removal of trace contaminants such as AsH_3, PH_3, COS, Hg, and O_2 to low parts per billion (ppb) levels from various hydrocarbon gases and liquids. They have high contaminant capacity combined with low reactivity toward the carrier stream. The pore structure has been optimized in order to minimize diffusional resistances which increases the dynamic capacity for contaminant removal. Accelerated testing at LHSV 40 hr-1 in a commercial propylene stream shows the benefit of an optimized pore structure for UOP GB-238 Adsorbent. The sharp breakthrough profile of the GB-238 adsorbent, compared to the competitive materials, demonstrates significantly better mass transfer characteristics. This results in smaller, more economical vessel designs or longer adsorbent life in existing vessels.

Residual Carbon on Selective Adsorbent Samples after Cyclic Testing

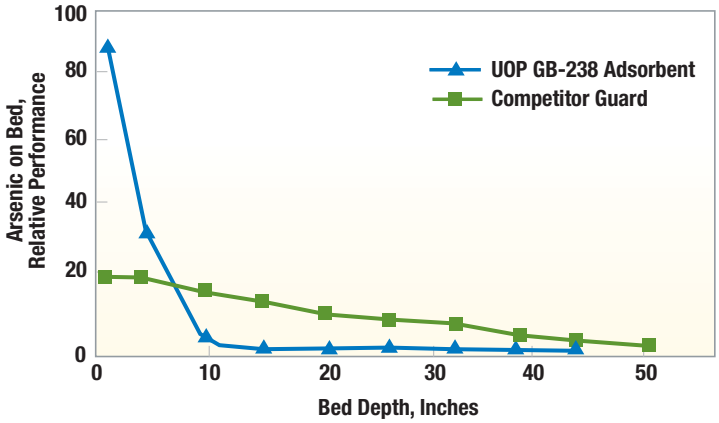


UOP GB-238 Adsorbent Reactivity Testing in Iso-butylene



Dynamic Testing in Commercial Propylene Stream

22 Days on Stream



Conclusion

UOP has developed a full array of adsorbents for the removal of many of the contaminants found in olefin and polymer plant process streams. These processes have benefited from the successful application of molecular sieves, modified aluminas, AZ-300 hybrid adsorbent, and metal oxide/sulfide containing GB series adsorbents.

The range of applications and feed conditions can vary greatly and so can the proper selection and combination of adsorbents. This brochure helps you identify the classes of contaminants that can be effectively treated with adsorbents. Please call UOP's dedicated technical staff to discuss how UOP adsorbents can help you meet your contaminant removal needs.

Find out more

If you are interested in learning more about our UOP adsorbents please contact your UOP representative or visit us online at www.uop.com.

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