

SHELL INTERNATIONAL CHEMICALS B.V.
AMSTERDAM - THE NETHERLANDS

SHELL EO/EG PROCESS MEMORANDUM 107

SUBJECT : PROCESS MATERIALS AND FEEDSTOCK
PURIFICATION

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INTRODUCTION

The EO catalyst is sensitive to many different chemical compounds, which may be present in the feedstocks. Therefore, feed clean-up facilities are required whenever these impurities could exceed, either on a steady-state basis or as a brief excursion, the feed specifications in this document.

This document discusses the effects impurities will have on catalyst performance.

Several vendors and contractors offer guaranteed solutions to clean up the various feed stocks.



FEEDSTOCK SPECIFICATIONS

ETHYLENE

Ethylene	min 99.95 % mol
Ethane + Methane	max 500 ppm mol
Total C3 and heavier hydrocarbons	max 10 ppm mol
Acetylene	max 1 ppm mol
Hydrogen	max 5 ppm mol
Carbon monoxide	max 0.1 ppm mol
Carbon dioxide	max 0.1 ppm mol
Oxygen	max 0.1 ppm mol
Total combined sulphur	max 0.5 mg/kg
Total sulphur after sulphur guard bed	max 0.01 mg/kg
Methanol	max 0.5 mg/kg
Oxygenated organics	max 0.5 mg/kg
Water	max 0.1 ppm mol
Total combined nitrogen	max 0.2 ppm mol
COS	max 0.02 ppm mol
Mercaptans	max 0.3 ppm mol

OXYGEN

Oxygen	min 99.8 % mol
Nitrogen + Argon	max 2000 ppm mol
Trichloroethylene + trichloroethane	max 0.001 ppm mol
Others	zero

EFFECTS OF IMPURITIES ON EO CATALYST

Certain impurities are commonly found in EO reactor feeds and some of their effects on catalyst selectivity and activity have been reported. Feedstock specifications for these impurities have been established to protect the catalyst. The feed stock composition is to be continuously monitored and if necessary controlled. Analytical methods for those feed impurities that are given in the feed stock specifications are provided.



For those impurities that are not shown in the feedstock specifications, but which in some cases have been detected and that have been known to effect catalyst performance, analytical methods have been published in the technical literature.

The licensee should check for the presence of feed impurities prior to start-up or when an effect on catalyst performance is suspected. Analytical methods to detect impurities not listed in the feed specifications will need to be derived from the open literature or from the licensee's own methods file.

Some impurities are particularly undesirable because they impair catalyst performance with no recovery after the impurity is removed from the feed. Other impurities cause temporary decline and partial or nearly total recovery occurs after the impurity is removed. Despite the fact that in some cases the effect has in the past been reported as reversible, one must pay extreme care to feed stock purity and contamination issues and be aware of potential irreversible effects under different conditions.

SATURATED HYDROCARBONS

Methane is inert to the catalyst and is not involved in the oxidation process. Ethane and heavier saturated hydrocarbons affect the moderator concentration on the catalyst surface and may cause sub-optimal performance of the catalyst. The heavier the hydrocarbon, the greater the effect on moderator equilibrium and the greater the effect on catalyst performance. 1% m C₃^o in the feed would result in the drop of about 6% selectivity at 15 ppm Cl level and about 9% selectivity at 7 ppm Cl level, 1 %m C₄^o would result in a drop of about 10% selectivity at 15 ppm Cl. Very heavy hydrocarbons, such as lubrication or absorption oils, hydrocarbon solvents or kerosene, might have a profound effect even at very low concentration levels. They also may result in carbon deposition on the catalyst and thus cause deactivation.

ACETYLENES

In low concentrations in the reactor feed (10 to 100 ppm) acetylene temporarily deactivates the catalyst because of carbon deposition, however selectivity is usually not affected appreciably. After acetylene is removed from the feed, the carbon burns off and the catalyst will be reactivated. Higher concentrations of



acetylene (> 100 ppm) can coke up the bed so badly that a permanent effect will be established.

PROPYLENE AND HIGHER OLEFINS

Propylene and higher olefins depress conversion and affect ethylene oxide selectivity. 1 %m $C_3=$ leads to a reduction of about 10% selectivity at 15 ppm Cl level. The catalyst should recover when the olefins are removed from the feed.

SULPHUR, SELENIUM, TELLURIUM AND ARSENIC COMPOUNDS

Sulphur is by far the most common contaminant found in the feedstocks and therefore should be monitored closely. Pilot plant observations with reactor feeds containing 1 ppm sulphur indicate a progressive top to bottom bed deactivation in a one day period as denoted by the peak temperature shift. When after a short time sulphur returned to specification levels, the profile slowly started to return to normal shape. During this period the selectivity decreased noticeably. If sulphur addition is allowed to continue, its effect on the catalyst becomes permanent. In this case it has been found that selectivity loss is proportional to the sulphur concentration by weight on the catalyst.

The general effect of any of these contaminants is to first deactivate the catalyst. This will be noticed by the need to raise the coolant temperature to hold conversion. If the contaminant in the feed is not removed, the catalyst will begin to show loss of selectivity. In some instances, a catalyst can be regenerated with partial success after being poisoned modestly by the above contaminants.

Arsenic has been found in ethylene originating from refinery gas streams. In plants with no special guard beds this impurity can be carried through with the finished ethylene.

EO REACTION PRODUCTS

Recycle gas with 0.1 %m of EO suppresses the reaction rate slightly. Hence higher coolant temperatures are required and a portion (about 10%) of the EO in the



recycle gas is destroyed. No permanent effect on the catalyst is apparent. A massive EO breakthrough from the EO absorber (>0.5%) can deactivate the catalyst and produce a yield loss of up to 2 selectivity units.

Water in the reactor feed has a strong impact on catalyst selectivity and activity. When water increases from, for example, 0.7% to 1.4%, the catalyst activity and selectivity deteriorate severely. At high levels it can become impossible to operate the catalyst in a stable optimum condition. For high selectivity catalyst, water in the feed gas has a small effect on activity but a significant effect on selectivity.

Increasing the CO₂ concentration in the reactor feed gas decreases activity. Thus, in holding a constant oxygen conversion, the temperature must be increased and the selectivity is therefore lowered.

Carbon monoxide, hydrogen and aldehydes burn rapidly at EO reaction temperatures. Levels of up to 500 ppm of CO in the reactor feed have had no apparent effect on activity or selectivity.

OTHER COMPOUNDS

Below table summarises the effect of a number of other compounds on EO catalyst performance.

INFORMATION RELATING TO EO CATALYST PERFORMANCE



Compound	Reactor feed molar %	Effect on catalyst activity	Effect on catalyst selectivity	Permanency of effect on performance	Other remarks
Argon	15%	minor to none	minor to none	none	Inert to the reaction
Nitrogen	75%	minor to none	minor to none	none	Inert to the reaction
Ammonia	6%	reduces	lowers	temporary	Causes exothermal reaction
Hydrazine	40 ppm	none	none	none	Decompress rapidly
Nitrogen oxide	20 ppm	none	none	none	Above 20 ppm poisonous
Methanol	10 ppm	reduces	lowers	temporary	-
Acetic acid	-	lowers	lowers	temporary	Can be burnt off
Ethylene glycol	50 ppm	increases	lowers	temporary	Can be burnt off
Hydrogen	<0.5%	lowers	none	temporary	Burns and raises catalyst temp
Ethylene oxide	> 0.5%	lowers	lowers	-	-
Silicone-base antifoam	100 ppm	lowers	lowers	permanent (1)	Poisonous contaminant
Mercury	3 ppm	lowers	lowers	temporary	-
Potassium carbonate	50 ppm	lowers	lowers	permanent (1)	Concentration on catalyst
Potassium chromate	50 ppm	lowers	lowers	permanent (1)	Concentration on catalyst
Rust	50 ppm	lowers	lowers	permanent (1)	Concentration on catalyst

(1) Replacement of catalyst may be required at these concentrations.



SPECIFICATIONS FOR PROCESS CHEMICALS AND MATERIALS

High Purity Boiler Feed Water to HP steam drum

General requirements	clear and colourless, free from dissolved matter
Conductivity at 25 °C (Note 2)	< 3 μ S/cm
pH value at 15 °C (Note 6)	> 9.5
Oxygen (O ₂) (mg/kg) (Note 5)	< 0.02
Total iron content Fe (mg/kg)	< 0.02
Total copper content Cu (mg/kg)	< 0.003
Silica (SiO ₂) (mg/kg)	< 0.05
Total carbon dioxide content (CO ₂) (mg/kg)	below detection limit
Hardness as CaCO ₃ (mg/kg)	below detection limit
KMnO ₄ consumption (mg/kg)	< 5
Oil Content (mg/kg)	below detection limit
Phosphates	See Note 4
Hydrocarbons	zero

NOTES

1. Feed water specifications and treatment methods are to be decided by the licensee/contractor. Proposed treating chemicals are to be reviewed for process compatibility.
2. With continuous sampling measured after treatment in highly acid cat ion exchanger (applied exclusively to water that is free from CO₂).
3. Boiler feed water and steam may not contain any hydrocarbons to prevent product quality degradation by contamination via the steam systems of the plant.
4. Phosphates other than Na₃PO₄ should preferably not be used in view of the possible contamination of the EO catalyst. Phosphate is a severe catalyst poison because it promotes the isomerisation reaction of EO to acetaldehyde.
5. Oxygen scavenging by hydrazine or Cor-Trol. Both scavenging agents decompose rapidly and have no influence on EO catalyst performance.
6. For pH control ammonia is preferred. Application of amines on mutual agreement to avoid deactivation of the EO catalyst performance. In case



for some reason the pH of 9.5 or higher cannot be maintained for the boiler feed water, Na_3PO_4 may be used for pH control.

Sodium Hydroxide

50 wt%

Rayon grade (0.02 % wt Cl max).

Potassium Carbonate or Hydroxide

Technical low-chloride grade (0.02 % wt Cl max).

Antifoam

For the EO absorbent and carbonate systems. BASF polyether glycol, Pluronic L101, is recommended. An equivalent viscous liquid EO or PO polyether glycol with an average MW of 3500 to 4000, free from material under 1000 MW can be used. Pour point should be above 0°C. Silicon containing antifoam should never be used, because it has a permanent negative effect on the catalyst performance.

Methane (Note 1)

Methane	min 93.0 % mol
Hydrogen (Note 2)	max 3.0 % mol
Carbon monoxide/dioxide	max 0.5 % mol
Ethane	max 0.05 % mol
C3 and heavier hydrocarbons	max 15 ppm mol
Acetylene	max 5 ppm mol
Total sulphur	max 2 mg/kg
Sulphur (after guard bed)	max 0.01 mg/kg
Methanol and other oxygenated organics	max 10 mg/kg
Water	zero
Nitrogen	max 0.84 % mol

NOTES

1. Methane from natural gas supply. It will be upgraded in OBL purification facilities. The simulations are based on a methane feed stream



composition of 99.11 % mole of methane, 0.05 % mole of ethane and 0.84 % mole of nitrogen.

2. Expected hydrogen content is zero.

Ethyl Chloride (Moderator)

Appearance	clear and free from foreign material
Purity	min 99.8 % wt
Acidity (as HCl)	max 10 mg/kg
Water	max 100 mg/kg
Non volatile residue	max 5 mg/100ml
Trichloroethylene + trichloroethane	max 50 mg/kg

For the transport of ethyl chloride (moderator) dedicated containers are required. Various options are made available by ProTank and Globe Interstar. These include 1,000 and 2,500 litres mini-tank containers and 21,000 litres tank containers. See appendix 1 for pictures of typical ethyl chloride transport containers.

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Appendix 1. Ethyl chloride (moderator) transport containers







