EKATO

Advanced Process Solutions

EKATO Gas-Liquid Reaction Technologies
气液反应技术

November 7, 2019

Hydrogenation Plant Technology
加氢装置技术

Volkmar Bösch
Process Plants Solutions

EKATO

Advanced Process Solutions

Agenda

- Industrial Hydrogenation 工业加氢
- Reactor Module
- Heating Cooling
- Hydrogen Venting & Release
- Catalyst Handling
- Catalyst Filtration
- Safety Aspects for Hydrogenation Plants

Industrial Hydrogenation – Typical Parameters and Conditions
工业加氢—典型参数和条件

EKATO

Advanced Process Solutions

Industry Segment 行业	**Products Range** 产品范围	**Quality Standards** 质量标准	**Solvents** 溶剂	**Catalyst Type** 催化剂	**Catalyst-Recycling** 催化剂回收	**Pressure range [barg]** 压力范围
Sorbitol & Polyols 多元醇	Monoplant	Food	Water	Sponge-Nickel 海绵镍	Yes	30 - 100
Oils & Fats 油脂	Narrow	ISO 9001 / Food	None	Nickel	Mainly no	4 - 10 Oil &Fat > 30 FFA
Fine Chemicals 精细化学品	Wide	ISO 9001	Various	Various	Yes	< 100
Pharma 制药	Wide	cGMP / API	Various	Various	No	< 100

Hydrogenation Plant Technology – Challenges
氢化装置技术-挑战

EKATO

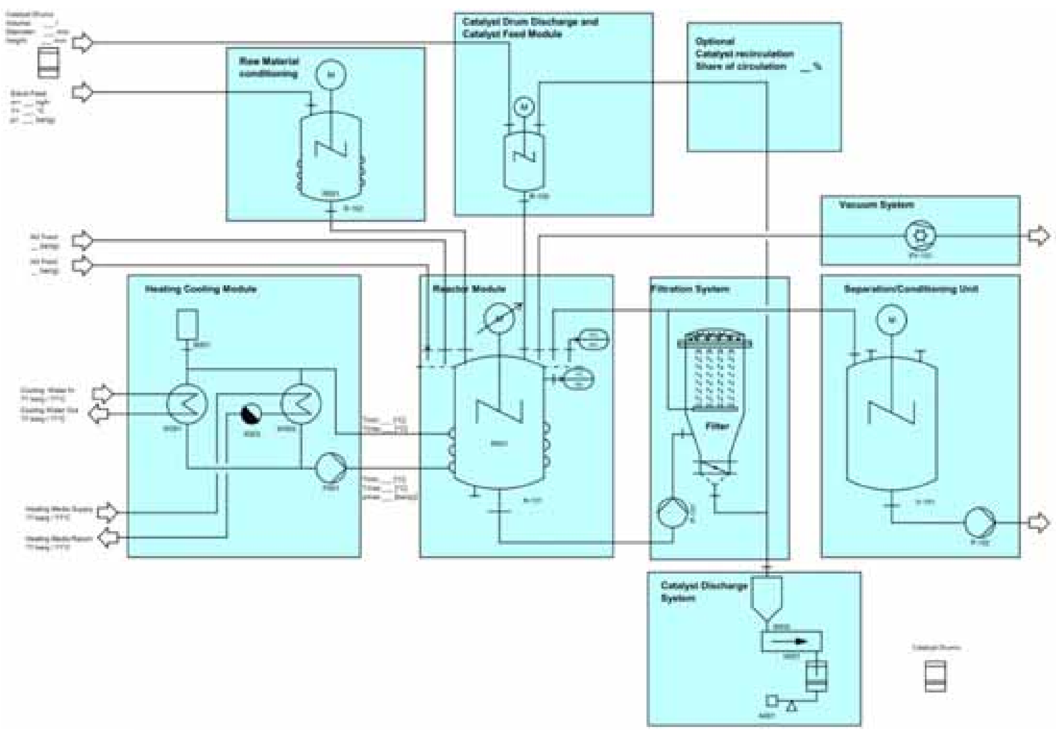
Advanced Process Solutions

- Wide range of industrial applications 广泛的工业应用
- Exothermic reaction 放热反应
- Sometimes instable intermediates 有时不稳定媒介
- Catalysts in various forms (solid, slurry, liquid)
  各种形式的催化剂（固体、浆体、液体）
- Many catalysts are pyrophoric 许多催化剂是可燃的
- Low levels of residual catalyst in product
  产品中残余催化剂含量低
- Containment and processing of Hydrogen gas
  保存和处理氢气
- Safe venting of Hydrogen 氢气安全排放
- ......

Hydrogenation Plant Overview – Batch process
加氢装置概述 — 批次工艺

EKATO

Advanced Process Solutions



Heating/Cooling-System 加热/冷却系统
- total batch time (heating/cooling batch) -总批处理时间（加热/冷却批处理）
- cooling during reaction -反应期间的冷却

Catalyst Preparation 催化剂制备
- correct catalyst handling to maintain activity -正确处理催化剂以保持活性
- correct concentration & exact dosing -正确的浓度和准确的剂量

Raw Material Preparation 原料准备
- batch time (pre-heating) -批次时间（预热）

Catalyst Filter / Recycle 催化剂过滤器/再使用
- purity of product / no catalyst -产品提纯/无催化剂
- batch consistency -批次的一致性

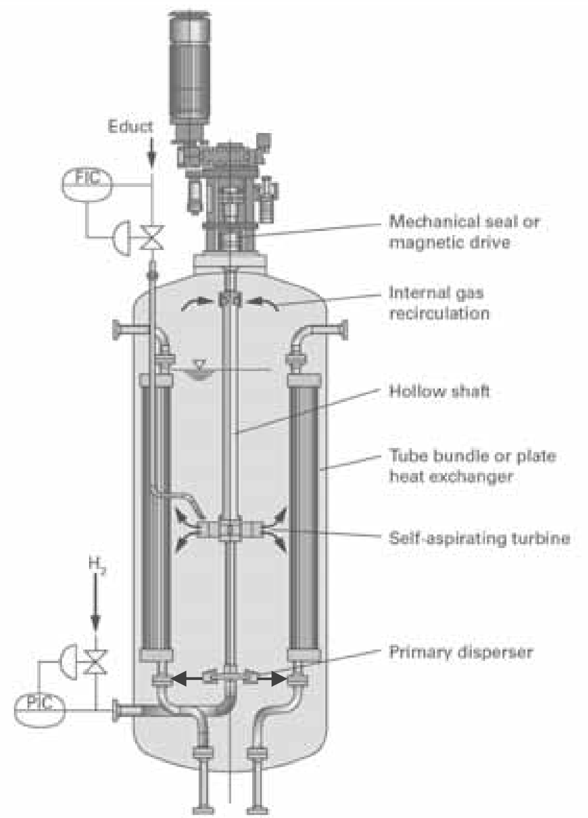
Agenda

- Industrial Hydrogenation
- Reactor Module 反应器模型
- Heating Cooling
- Hydrogen Venting & Release
- Catalyst Handling
- Catalyst Filtration
- Safety Aspects for Hydrogenation Plants

Reactor Design 反应容器设计

EKATO

Advanced Process Solutions



High Performance Hydrogenation Reactor
高性能加氢反应器

- Gas-feed into bottom of reactor 底部进气
- High gas recirculation rate 气体再循环率高
- Highest possible mass transfer 最大可能的传质
- Homogeneous process conditions 工艺过程均衡
- Compact design, no external equipment 紧凑设计，无外部设备
- Internal heat exchangers 热交换器在内部
- Safe scale-up between 5 l and 150 m^3 安全比例缩放

Hydrogen is contained inside one pressure vessel
氢气包含在同一个压力容器中

Material Selection – Hydrogen Embrittlement
材料选择 —氢脆现象

EKATO

Advanced Process Solutions

- Atomic Hydrogen may be formed on metallic surfaces 氢原子可能会在金属表面形成
- Metal hydrides may be formed (e.g. Titanium hydride) or hydrogen may be enclaved into the metal structure, weakening the material.
  可能形成金属氢化物 (如钛氢化物)或氢可能被包裹入金属结构中，削弱材料强度。
- Hydrogen atoms may gradually recombine and lead to hydrogen-induced cracking (HIC)
  氢原子可能重新结合，导致形成氢脆开裂
- Hydrogen embrittlement depends on: 氢脆取决于
  - metallic structure金属结构
  - surface quality and treatment (welding, passivation)
    表面处理（焊接、酸洗）
  - stress (pressure, temperature, alternating loads)
    应力(压力、温度、交变载荷)

Material Selection - "Rule of Thumb"
材料选择— 经验法则

EKATO

Advanced Process Solutions

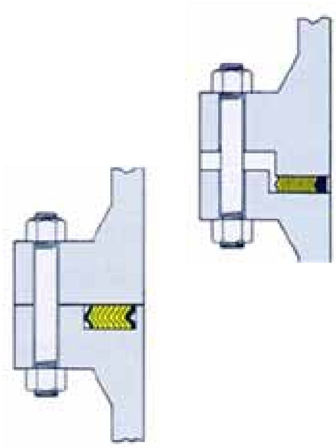
- Suitable materials are: 适用材料
  - Austenitic stainless steels (types 304, 316) 奥氏体不锈钢
  - Monel®, Hastelloy® grades or similar 镍合金
  - Aluminium and copper alloys 铝和铜合金
  - Suitable grades of carbon steel 适宜等级的碳钢
- The following materials should be avoided: 应避免以下材料
  - Ordinary carbon steel, low alloy steels 普通碳钢、低合金钢
  - Iron (also cast iron due to porosity) 铸铁
  - (pure) Nickel 纯镍
  - Copper which contains residual oxygen 含有残余氧的铜

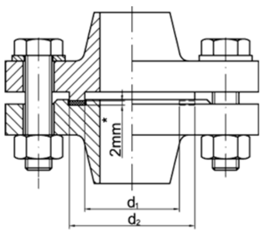
Suitability of materials also depends on process conditions, equipment fabrication and surface treatment.
材料的适宜性还取决于工艺条件、设备制造和表面处理。

Piping Connections for Hydrogen Duty
氢气管路联结

EKATO

Advanced Process Solutions





- Welded piping should be used 使用焊接管
- Flange connections should be minimized (e.g. valves and instruments with welding ends are available)
  尽量减少法兰连接（阀门仪表带焊接端头是可用的）
- For high pressures, flange connections with high integrity design should be used to prevent gasket blow-out.
  对于高压，应采用高完整性设计的法兰连接，以防止垫圈爆裂。
- Be careful with use of non-suitable screw connections, tri-clamps etc. 小心用到不合格的螺栓、接头等。
- Avoid hydrogen piping through sealed (non-vented) areas, e.g. suspended ceiling!
  避免在密封(无通风)的地方(例如吊顶)铺设氢气管道!

Dynamic Seals 动态密封

- Double / Triple acting mechanical seal design or magnetic drive system.
  双端面、三端面机械密封或磁性驱动系统
- Safety critical items: 关键安全项目
  Potential failure mechanism to be reviewed during HAZOP.
  HAZOP分析审查潜在的失效机制。
- Seal integrity to be monitored with adequate safety interlocks based on SIL-classification.
  密封完整性应根据密封等级分类，采用适当的安全联锁装置进行监控。

Use of Polymeres 聚合物的使用

© frog - Fotolia

© HSE (UK)

- H_2-Permeation into and through polymere materials can occur
  氢气可以渗透并通过聚合物材料
- Leakage through polymere walls is normally not large enough to create an explosive atmosphere on the outside.
  聚合物渗透的氢气浓度达不到产生爆炸的程度。
- Elastomeres (e.g. PTFE ® based and similar grades) are often used in installations as gaskets and sealing elements.
  弹性聚合物常用做垫圈和密封件。
- Pure PTFE gaskets are suspectible to „cold flow“ in compression
  纯聚四氟乙烯垫圈在压缩时易发生“冷流动”
- O-Rings may be susceptible to damage through “rapid gas de-compression”
  气体急速释压可能导致损害O型圈。

Source: “Elastomeric seals for rapid gas decompression applications in high pressure services“; Prepared by BHR Group Limited for the Health and Safety Executive 2006 (UK), RESEARCH REPORT 485

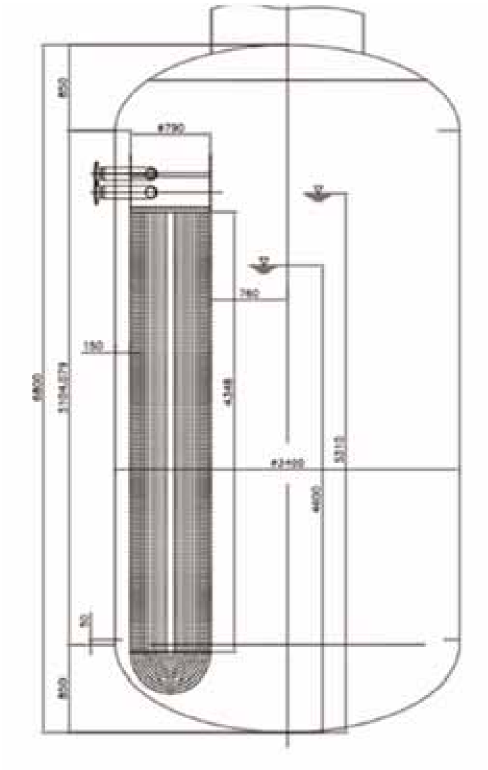
Agenda

- Industrial Hydrogenation
- Reactor Module
- Heating Cooling 热量冷却
- Hydrogen Venting & Release
- Catalyst Handling
- Catalyst Filtration
- Safety Aspects for Hydrogenation Plants

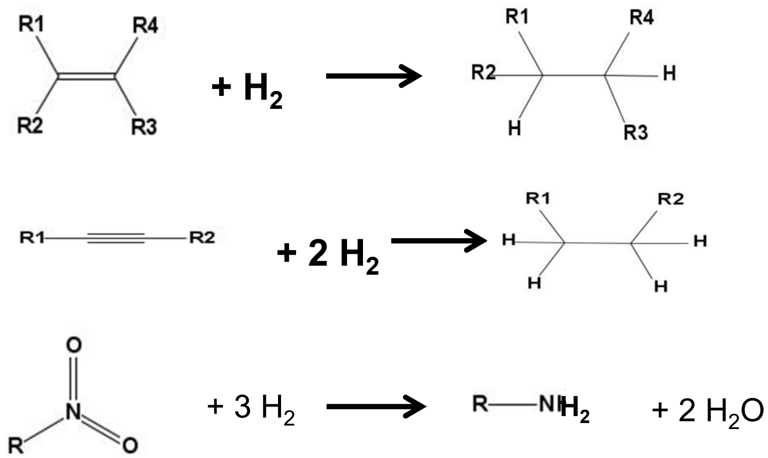
Reaction Heat 反应热量

EKATO

Advanced Process Solutions



- Hydrogenations are (highly) exothermic reactions 氢化是(高度)放热反应



Double bond: ~130 kJ/mol
双键

Triple bond: ~200 kJ/mol
三键

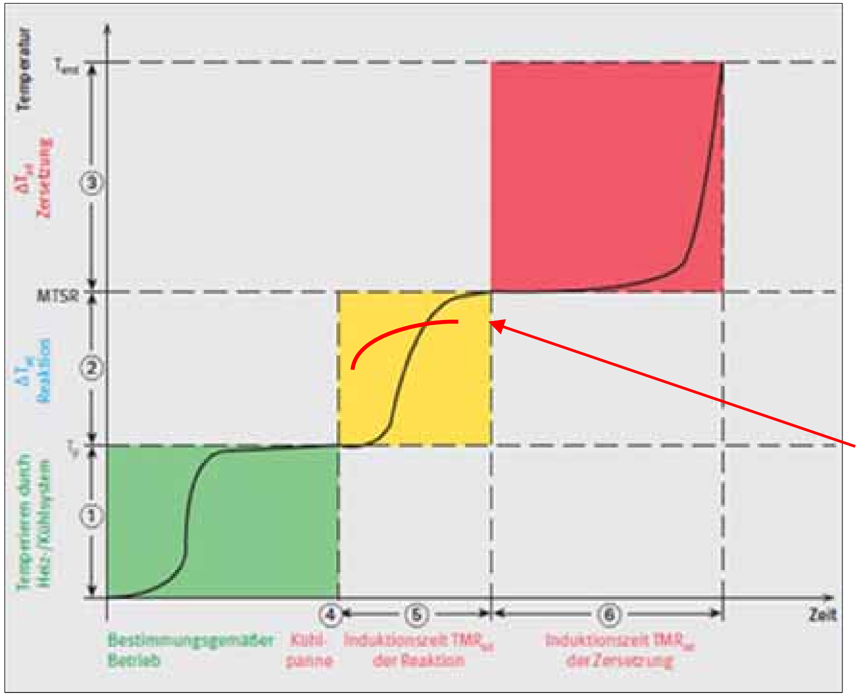
Nitro group: ~500 kJ/mol
硝基组

- Very often limited by mass transfer: catalyst concentration, agitation
  通常受传质限制:催化剂浓度、搅拌等。

Chemical Reaction – Runaway Scenario
化学反应—失控情况

EKATO

Advanced Process Solutions



© VBG DGUV Information 213-067

- High adiabatic temperature increase
  绝热温度升高
- Can lead to secondary decomposition reactions 会导致二次分解反应
- Pressure built-up possible 压力可能变化 (evaporation, gas formation 蒸发，气体形成)

- Hydrogen supply has to be cut-off 停供氢气
- Only residual hydrogen in reactor head space can react
  只有残留在反应堆顶部空间的氢才能发生反应
- Temperature increase is limited
  温度升高是有限的

Scenarios 场景

EKATO

Advanced Process Solutions

Scenario场景: Cooling Failure 冷却失败

- Reaction heat may lead to sharp temperature rise of reactor contents
  反应热可能导致反应器内物质温度急剧升高
- Adiabatic temperature increase can be very high (with Hydrogen supply ongoing)
  绝热温度可能上升的非常高（持续氢供应）
- Can potentially lead to subsequent de-composition and run-away reaction
  可能导致后续的分解反应和反应失控

➲ **High-Temperature detection with automatic Hydrogen shut-off** 高温检测，自动切断氢气

Scenario场景: Agitator Failure 搅拌器故障

- Mass transfer will be very low and catalyst will settle to the bottom
  传质会很低，催化剂会沉淀到底部
- Reaction will come to a standstill or will be very slow 反应会停滞或非常缓慢

➲ **Agitator failure not critical for Hydrogenations in most cases**
搅拌器故障在大多数情况下对加氢不重要
(beware of instable intermediates)小心不稳定的中间体

EKATO

Advanced Process Solutions

Agenda

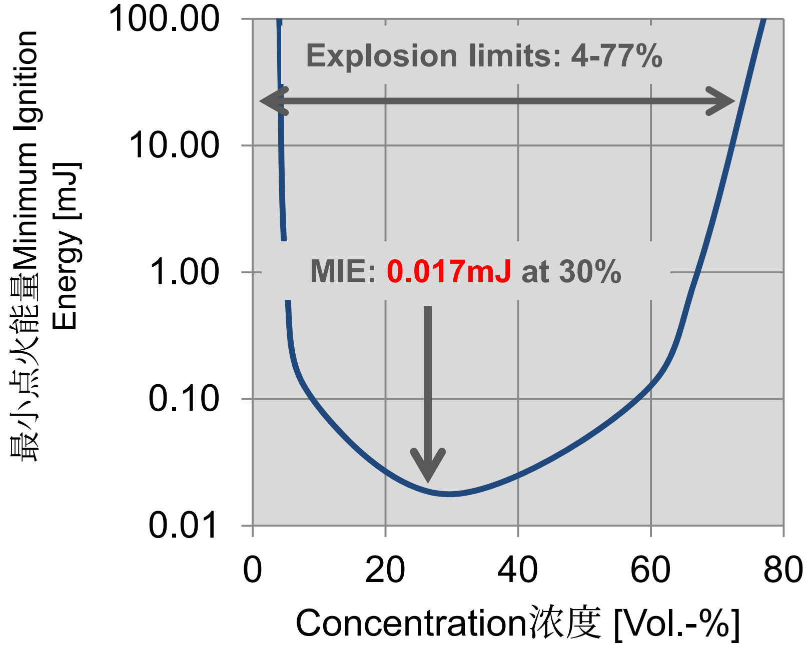
- Industrial Hydrogenation
- Reactor Module
- Heating Cooling
- Hydrogen Venting & Release 氢气排放&释放
- Catalyst Handling
- Catalyst Filtration
- Safety Aspects for Hydrogenation Plants

Flammability and Explosion Limits of Hydrogen
氢气的可燃性和爆炸极限

EKATO

Advanced Process Solutions

H2 / Air Mixture at atmospheric conditions.



- Flammability range is very wide
  可燃范围很广
- Compared to hydrocarbons, very high upper explosion limit at 77%.
  与碳氢化合物相比，爆炸上限极高，达77%。

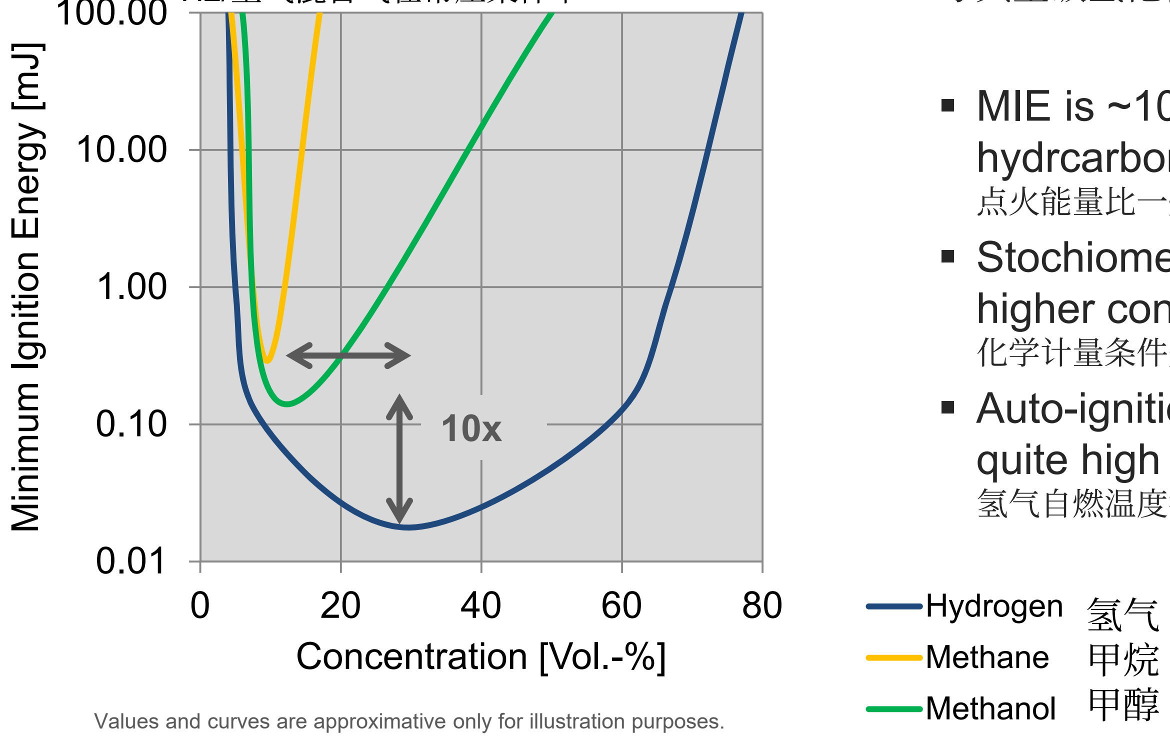
Very low minimum ignition energy (MIE) at stochiometric concentrations.
非常低 的点火能量。

Values and curves are approximative only for illustration purposes.
Source: DWV Deutscher Wasserstoff und Brennstoffzellen-Verband

Flammability and Explosion Limits of Hydrogen
氢气的可燃性和爆炸极限

EKATO

H2 / Air Mixture at atmospheric conditions.
H2/空气混合气在常压条件下



Values and curves are approximative only for illustration purposes.
Source: DWV Deutscher Wasserstoff und Brennstoffzellen-Verband

Compared to typical hydrocarbons:
与典型碳氢化合物相比

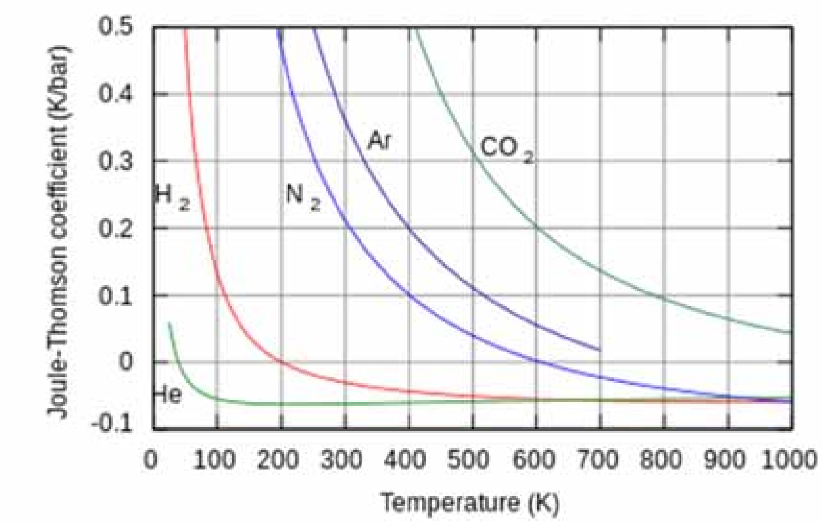
- MIE is ~10x lower than typical hydrcarbons.
  点火能量比一般碳氢化合物低约10倍
- Stochiometric conditions are at much higher concentration
  化学计量条件是在较高的浓度值。
- Auto-ignition temperature for hydrogen is quite high at 833 K (560°C).
  氢气自燃温度很高在560°C。

10x

Negative Joule-Thomson Coefficient
负的焦耳-汤姆森系数

EKATO

Advanced Process Solutions



- Hydrogen has a negative Joule-Thomson coefficient at ambient temperatures and above
  在室温及以上，氢的焦耳-汤姆逊系数为负。
- De-pressurization of compressed hydrogen may lead to warming of the gas flow (at constant enthalpy).
  压缩氢气的减压可能使氢气变暖（热焓恒定）。
- Simulation studies have shown that temperature increase will not exceed 10 K.
  模拟研究表明，升温幅度不会超过10k。
- Auto-ignition due to Joule-Thomson-Effect is not relevant if process temperature is well below auto-ignition temperatures.
  当温度远低于自燃温度时，焦耳-汤姆森效应产生的热量不会导致自燃。

Self-Ignition of Hydrogen? 氢气自燃？

EKATO

© US Department of Energy (DOE)

Hydrogen flames are almost invisible in daylight.
氢气火焰在白天几乎看不见。

- Hydrogen can easily be ignited through electrostatic charging 氢气容易因静电引发自燃
- Clean gas flows cannot be charged electrically.
  单纯的气体流动不会产生静电
- Droplet entrainment may occur during releasing hydrogen pressure and venting. This can be sufficient to ignite hydrogen.
  氢气减压和放气过程中的夹带液滴可能会引燃氢气。
- In case of a leak, pressurized hydrogen might be ignited through electrostatic charging by water droplets (air moisture), but in many cases will not.
  泄露情况下，高压氢气有可能因为空气中的水滴产生的静电自燃，但多数情况下不会发生。

Advanced Process Solutions

Considerations for Hydrogen Venting
氢气排放注意事项

EKATO

Advanced Process Solutions

- If possible, hydrogen should be vented to the atmosphere as directly as possible
  如果可能，氢气应该尽可能直接排放到大气中
- Slow and controlled de-pressurization to prevent liquid entrainment 缓慢可控的释压以避免液滴形成
- Venting should be done to a safe location and sufficiently away from other installations
  排气应该在安全的位置，并远离其他装置
- Hydrogen will go upwards and disperse quickly in the atmosphere 氢气会上升并迅速扩散在大气中
- Be aware of potential for explosive atmospheres and risk of ignition 注意爆炸和引燃的潜在危险
- Flush out hydrogen venting system with nitrogen 用氮气冲洗氢气排气系统
- Outlet pipe should be directed upwards and be fitted with a suitable flame arrestor
  管道出口应该向上开，并安装适当的阻火器

Agenda

- Industrial Hydrogenation
- Reactor Module
- Heating Cooling
- Hydrogen Venting & Release
- **Catalyst Handling 催化剂操作**
- Catalyst Filtration
- Safety Aspects for Hydrogenation Plants

Catalyst Properties 催化剂特性

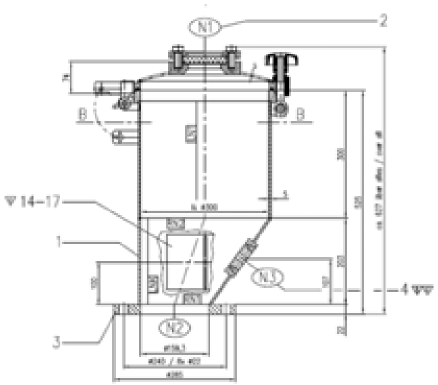


- A heterogenous catalyst is used in most cases 大多使用多相催化剂
- Can come in various forms, e.g. water slurry, pellets, dry powder
  可以有多种形态，如泥浆状、小球形、干粉等
- Physical properties relevant for plant design, e.g. particle size distribution, settling time, mechanical stability
  物理性能根据要求设计，如粒度分布、沉降时间、机械稳定性等
- Can be pyrophoric, e.g. sponge nickel when dried in air
  可能会自燃，如海绵镍在空气中
- Oxygen exposure to the catalyst during operation (dosing, filtration and reuse) should be avoided 避免催化剂接触氧气（加料、过滤和重复使用时）
- Expensive. Catalyst can be re-used many times in some processes
  价格高。催化剂在有些过程中可重复使用
- Stringent limits on residual Ni-content 严格限制残余镍含量

Catalyst Addition 催化剂添加

EKATO

Advanced Process Solutions



© Almatec

© DEC

- Safe and reliable transfer of catalyst into the process 安全可靠地将催化剂转移到生产过程中
- Air ingress into the process has to be prevented 必须防止空气进入这一过程
- Technical solution depends on catalyst properties, operational requirements and safety
  技术方案取决于催化剂的性能、操作要求和安全性
- Direct addition into the hydrogenation reactor is not recommended
  不建议直接添加

Agenda

- Industrial Hydrogenation
- Reactor Module
- Heating Cooling
- Hydrogen Venting & Release
- Catalyst Handling
- **Catalyst Filtration 催化剂过滤**
- Safety Aspects for Hydrogenation Plants

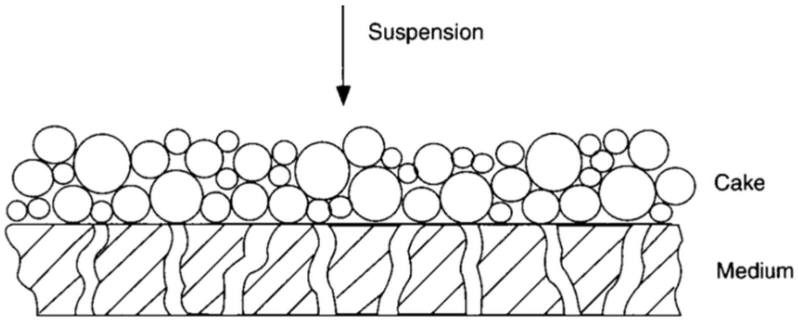
Catalyst Filtration – Factors to be considered
催化剂过滤-需要考虑的因素

EKATO

Advanced Process Solutions

- Permissible solids content in filtrate? 滤液中允许的固体含量?
- Filter aid necessary? 需添加助滤剂吗?
- Catalyst re-cycle required? 是否需要回收？
- Amount of product loss with solids discharge? 固体废物排放会造成的产品损失？
- Blockage of filter elements? 滤芯堵塞?
- Filtration flux? 过滤流量?
- Safety: Risk of oxygen ingress (wet cake, pyrophoric) 安全性：氧气进入的风险（潮湿、自燃）

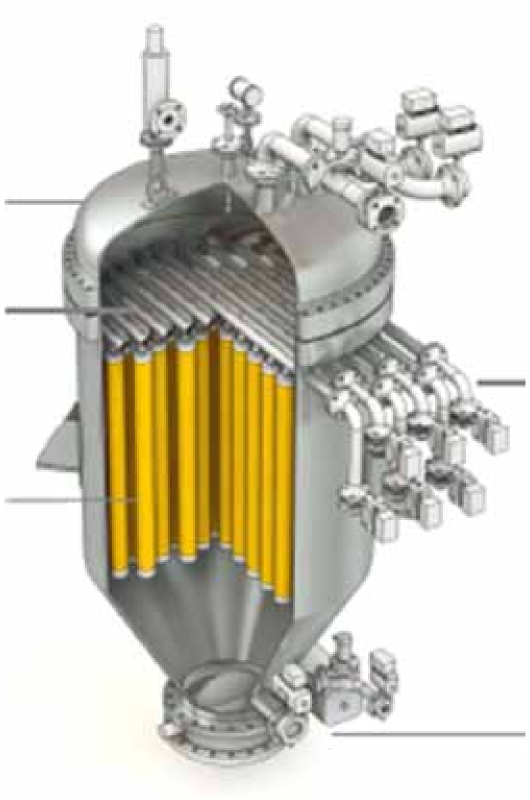
► **Filtration lab test is highly recommended**
建议进行过滤实验室测试



Catalyst Filtration 催化剂过滤

EKATO

Advanced Process Solutions



© BHS

- Different filter types can be used (e.g. candle filter, bag filter etc.) 可使用不同类型的过滤器(如烛式过滤器、袋式过滤器等)

- Batch operation or „quasi-continuous“ operation with parallel filters 批次操作或带并行滤波器的 “准连续”操作

- Solids discharge can be as slurry or wet cake 固体排放可以是泥浆状或湿饼状

- Backwash of filter elements to prevent blocking 滤芯反向冲洗，防止堵塞

- For some applications, more sophisticated options are available, e.g. in-situ filtration, continous filtration etc. 对于某些应用，有更复杂的选择，如原地过滤、连续过滤等。

EKATO

Advanced Process Solutions

Agenda

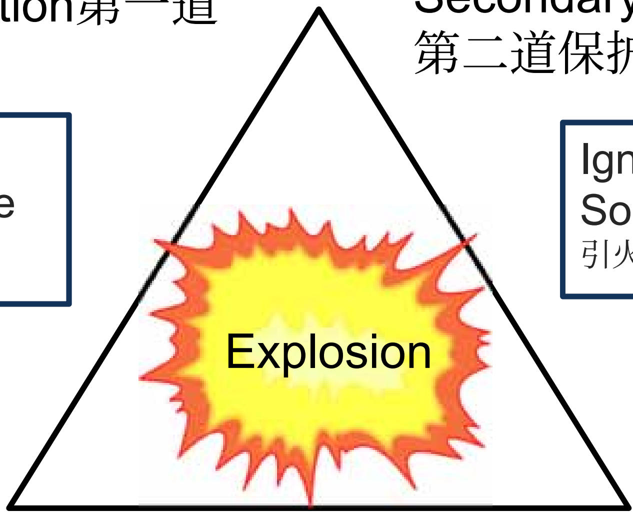
- Industrial Hydrogenation
- Reactor Module
- Heating Cooling
- Hydrogen Venting & Release
- Catalyst Handling
- Catalyst Filtration
- Safety Aspects for Hydrogenation Plants 氢气装置安全事项

Considerations for Explosion Protection
防爆注意事项

Advanced Process Solutions

Primary Protection第一道保护

Explosive Atmosphere
易爆气体环境



Combustible Material 燃料

Secondary Protection
第二道保护

Ignition Source
引火源

Tertiary Protection
第三道保护

Reduce consequences of explosion
减少爆炸的后果

Typical Protection Measures
典型防护措施

EKATO

Advanced Process Solutions

Primary Protection: Prevent explosive atmospheres
主要防护:防止爆炸性环境

▪ Inside plant equipment: 装置内设备	Inerting with Nitrogen用氮气惰化 Prevention of air ingress防止空气进入
▪ Outside plant equipment: 装置外设备	Prevention of Hydrogen leaks 防止氢泄漏 High integrity (mechanical) 完整性好（机械） Good ventilation of plant area 通风良好 Open floor design of intermediate levels 中间楼层地板开放性设计 Hydrogen detectors (with Hydrogen cut-off) 氢气探测器（带氢气断供）

Typical Protection Measures
典型防护措施

EKATO

Advanced Process Solutions

Secondary Protection: Prevent ignition 防护二：引火源

- Installation according to hazardous area classification 按危险区域等级安装
- Hydrogen is in gas group IIC 氢气放在气体区IIC
- Earthing and grounding of plant equipment 设备接地
- Minimize isolating surfaces 表面隔离

Tertiary Protection: Reduce consequences of explosion 防护三：降低爆炸后果

- Blow-off panels and roofs 嵌板和屋顶被吹掉
- Explosion-proof building design with concrete walls etc.建筑防爆设计，混凝土墙等
- Sprinklers 洒水装置
- Explosion proof pressure rating of equipment 设备防爆压力等级
  (Remark: this measure is normally not chosen for hydrogenations)注:此方法一般不用于氢化反应

EKATO

Advanced Process Solutions

Thank you for your attention!