乙烯工业 2006,18(1) 57~59
ETHYLENE INDUSTRY

变压吸附在乙烯装置氢气分离中的应用

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摘 要:介绍了变压吸附的分离原理及变压吸附技术在乙烯装置中分离氢气的应用,成功的分离出了高纯度氢气产品。

关键词:变压吸附;氢气;乙烯装置

中国石化中原石油化工有限责任公司(以下简称中原乙烯)聚乙烯、聚丙烯及乙烯装置所需氢气是经深冷分离的粗氢通过甲烷化除去一氧化碳得到的。为了满足新上碳四选择性加氢制1-丁烯的需要,需要寻找新的氢气来源,为此尝试从裂解气中进一步分离氢。

1 氢气产品原料来源

1.1 工艺流程

乙烯装置的裂解气经裂解气压缩机(GB-201)升压后,进入深冷分离系统。在深冷分离系统中,经过与冷剂换热降温,进入FA-304罐。FA-304罐中分离出的液体送入脱甲烷塔(DA-301),气相经冷箱降温进入FA-305罐。FA-305罐底分离出的液体送入DA-301塔,FA-305罐顶的气相经冷箱降温进入FA-306罐。FA-306罐分离出的液体经冷箱回收冷量后循环回裂解气压缩机,FA-306罐顶气相一部分经冷箱进FA308、FA-311。FA-311分离出的氢气用于碳二、碳三、裂解汽油加氢和其它装置使用,另一部分物料经膨胀机回收冷量后作燃料使用。这部分物料富含氢气,仅作燃料是一种浪费,若能尽一步回收氢气则能取得很好的经济效益。

氢气原料工艺流程见图1。

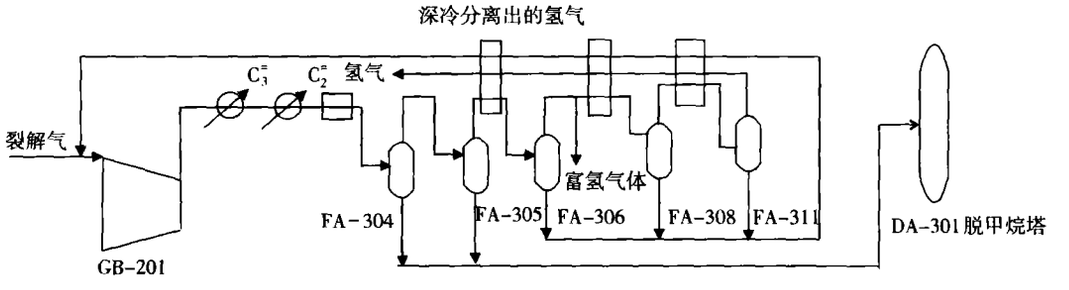

图1 氢气原料工艺流程

GB-201—裂解气压缩机;$C_3^=$—丙类冷剂;$C_2^=$—乙烯冷剂;FA-304—脱甲烷进料分离罐No.1;FA-305—脱甲烷进料分离罐No.2;FA-306—脱甲烷进料分离罐No.3;FA-308—氢气、甲烷分离罐No.1;FA-311—氢气、甲烷分离罐No.2;DA-301脱甲烷塔;氢气—此处指深冷分离出的氢气;富氢气体—用于PSA的原料

1.2 氢气原料的组成

氢气原料组成见表1。

表1 氢气原料组成

组成	H_2	CH_3	C_2H_4	CO
体积分数,%	69.34	30.23	0.29	0.14

2 氢气的分离

2.1 氢气分离方法的选择

将氢气与其它杂质分离的方法有深冷分离、

收稿日期:2005-07-23;**修改稿收到时期**:2006-03-01。

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膜分离及变压吸附分离。

2.1.1 深冷分离

中原乙烯目前采用深冷分离方法得到氢气。即将裂解气与冷剂换热，利用各物料的挥发度不同，脱除重组分得到粗氢，其组成见表2。

表2 粗氢组成

组成	H_2	CH_4	CO
摩尔分数，%	96.98	2.79	0.22

因粗氢中含有的一氧化碳是众多催化剂的毒物，故采用甲烷化的方法除去一氧化碳，最终氢气产品质量指标见表3。

表3 氢气产品质量指标

组成	H_2(摩尔分数)，%	CH_4(摩尔分数)，%	$CO+CO_2$/ $\times10^{-6}$	O_2/ $\times10^{-6}$	H_2O/ $\times10^{-6}$
	96.98	2.79	0.22	1	5

2.1.2 膜分离

膜分离的原理是：当多组分的气体混合物通过聚合物薄膜时，由于各气体组分在聚合物中的溶解扩散系数的差异，从而导致气体透过膜的渗透速率不同。在驱动力一各气体组分在膜两侧分压差的作用下，渗透速率较快的气体(如氢气、水蒸汽等)，优先透过膜并在膜的低压侧被富集。而渗透率较慢的气体(如氮、甲烷等)则在膜的高压侧滞留而被富集，从而实现氢气的分离。使用该技术得到的氢气纯度在90%～99%，氢气回收率达90%～95%，但氢气中微量杂质含量偏高。目前，膜分离氢气技术在国内已成功应用于催化重整尾气、加氢精制尾气、加氢裂化尾气和催化裂化干气等。

2.1.3 变压吸附分离

变压吸附(PSA)就是在较高压力下进行吸附，在较低压力(甚至真空状态)下使吸附的组分解吸出来。在气体提纯(提浓)过程中，每个操作过程仅需几秒或几十秒。整个操作周期在120 s左右，否则会影响装置的流量与纯度。经过处理的原料气通过具有选择吸附能力的微孔结构物质——吸附剂，使之分离得到富集的氢气。一般采用多床变压吸附工艺，以保持进料、产品气及尾气的流量。工业上通常采用4至12座吸附塔。随着吸附塔的增加，可提高氢气的回收率或增加能力，或两者同时提高。

变压吸附分离氢气有两个优点：一是杂质脱除率可满足任何要求；二是可生产高纯度的氢气，氢气产品纯度达99.99%(体积分数)以上。

通过分析对比，中原乙烯选择变压吸附分离技术分离乙烯装置裂解气中的氢气。

3 变压吸附分离氢气技术

3.1 工艺流程简介

图2为变压吸附制氢气工艺流程。

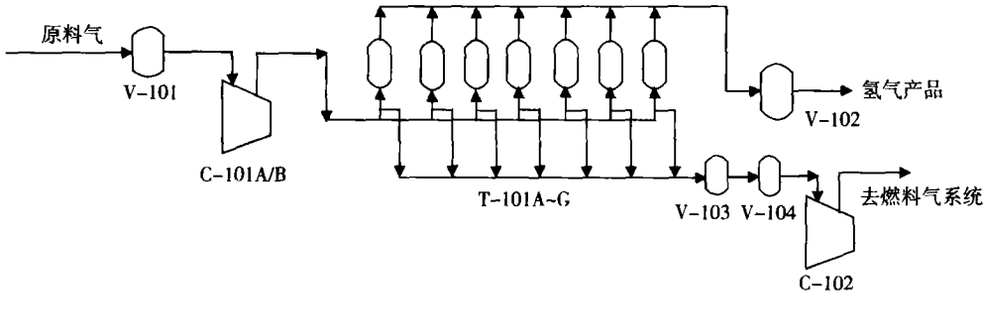

图2 变压吸附制氢气工艺流程

V-101原料气缓冲罐；V-102氢气缓冲罐；V-103解吸气缓冲罐；V-104解吸气缓合罐；C-101A/B原料气压缩机；T-101A～G吸附塔；C-102解吸气压缩机

从图2可看出，从外管网送入乙烯装置的氢气甲烷混合氢在0.22～0.28 MPa、20～40 ℃工艺状况下进入原料缓冲罐(V-101)，被原料气压缩机(C-101A/B)压缩至0.9 MPa，进入由7座吸附塔(T-101A～G)及一系列程控阀组成的变压吸附装置。

原料气在变压吸附系统内，自下而上通过其中一个正处于吸附步骤的吸附塔，经选择吸附后，产品气从吸附塔出口流出。经压力调节进入氢气

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缓冲罐(V－102)。从氢气缓冲罐出来氢气最终在 0.85 MPa 压力下送至用户。

吸附塔排出的解吸气送往解吸气缓冲罐(V－103),然后进入解吸气混合罐(V－104)。解吸气经充分混合后,此时温度 20～40 ℃,压力约 0.02 MPa,经解吸气压缩机(C－102)压缩至 0.42 MPa,送至界区作燃料。

3.2　运行方式

变压吸附装置有 3 种运行方式,其主运行方式为 7－3－2/P(7 座吸附塔,3 台同时进料,2 次均压)。当某 1 座吸附塔上的程控阀因外部元件故障导致程控阀不能开关时,可根据情况选择 6－2－2/P 和 5－1－2/P 两种运行方式运行。

3.3　自动控制系统

变压吸附装置的控制以西门子 S7－400H 可编程序控制与计算机操作界面相结合,集中显示。该系统所有的程控阀均由 PLC 系统控制。通过程控阀的切换,即可完成变压吸附整个工作状态的切换。PLC 系统根据变压吸附工艺过程,按预先设置的每个工作步骤及切换时间,使其循环切换吸附系统的程控阀门,达到提纯氢气产品的目的。

3.4　运行情况

变压吸附装置自 2004 年 8 月投入运行以来,运行平稳,氢气产品质量稳定。以 2005 年 6 月份为例见图 3～7。

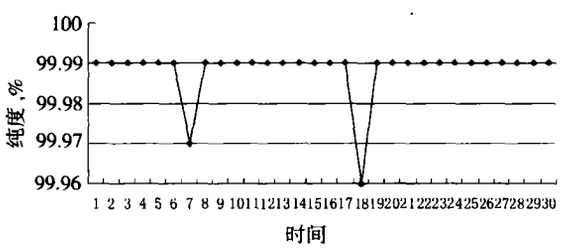


图 3　氢气产品纯度

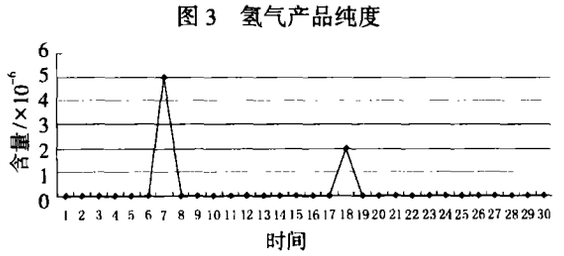


图 4　氢气产品中一氧化碳含量

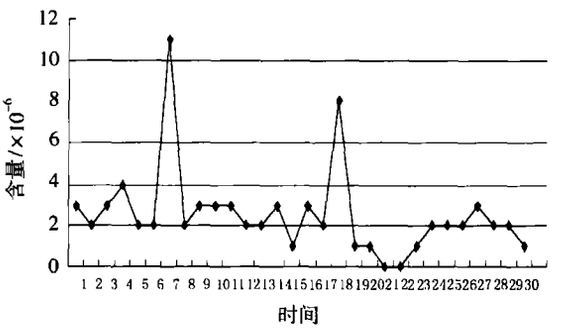


图 5　氢气产品中甲烷含量

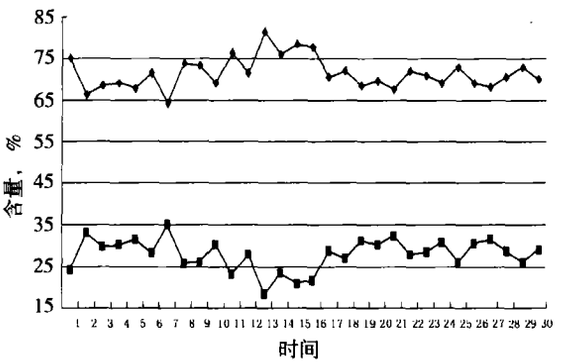
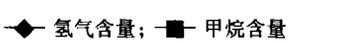


图 6　原料组成



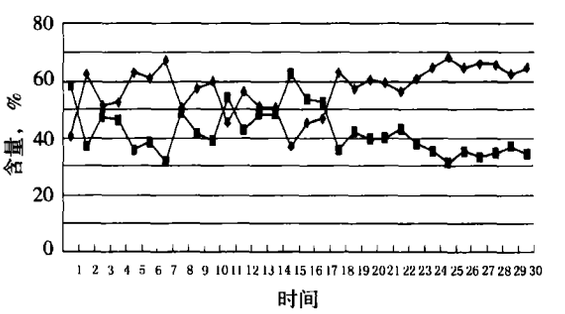
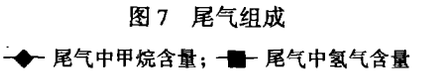


图 7　尾气组成



从图 3～7 可以看出,除个别情况出现波动外,氢气产品符合质量要求。

4　结论

中原乙烯装置采用变压吸附分离裂解气中的氢气后,其氢气产品质量稳定,杂质含量低,完全可以用于下游碳四选择性加氢,提高了企业的经济效益。

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ETHYLENE INDUSTRY
Started Publication in 1989, Quarterly. Mar. 2006 Vol. 18 No. 1 Total 65th

sures are put forward. These measures should be implemented stage by stage, in order to improve the working conditions of mechanical seal and finally prolong the service life of mechanical seal.

Keywords: Circulating pump in the 1st stage reactor, Mechanical seal, Rotary and stationary seal ring, coking, in parallel

Purification of Propane Distillate Oil, the Bottom Product of Propylene Rectifying Column

Li Yumin. Longcheng Fuel Gas Co. Ltd., P. C. 111003

Abstract: Purification process of propane distillate oil, the bottom product of propylene rectifying column in the Ethylene Works of PetroChina Liaoyang Petrochemical Company, is introduced. Green oil components in the propane distillate oil can be removed, thus improving the effect and value in use of the propane distillate oil.

Keywords: Propane distillate oil, Green oil removing process, Equipment

Summary of the Revamping of Demethanizer in Fushun

Xu Pu, Liu Xinyuan, Wang Tao, et al. Ethylene Industrial Co. Ltd. of PetroChina Fushun Branch, P. C. 113004

Abstract: This article analyzes and summarizes the operating conditions of the demethanizer after revamping, and advances measures for further optimization.

Keywords: Demethanizer, Revamp, Optimization

Application of Tertiary Refrigeration Technology in Qilu Ethylene Plant

Li Zhiting, Tang Diping, Wang Jiping. Olefin Complex of SINOPEC Qilu Company Ltd., P. C. 255411

Abstract: Lummus technology of tertiary refrigeration has been applied successfully to the expansion of ethylene plant in Qilu as its first commercial application. This paper introduces the running status of Qilu TR system and presents some problems arise during the startup and normal operation as well as the corresponding solutions.

Keywords: Ethylene, Propylene, Methane, Tertiary refrigeration

Operation Optimization of Binary Refrigeration, Chiller and Demethanizer System

Peng Yuekun. Olefin Works of Yangzi Petrochemical Co. Ltd., P. C. 210048

Abstract: The article introduces the advantages of binary refrigeration technology and the present situation of binary refrigeration, chiller and demethanizer system, analyses the problems and the corresponding causes in binary refrigeration, chiller and demethanizer system, and advances optimization measures for these problems.

Keywords: Ethylene plant, Binary refrigeration, Chiller, Demethanizer

Technical Reconstruction of Crack Gas and Propylene Refrigeration Compressors for Safe Operation

Zhang Pinglin, Zhao Junfeng, Zhang Zhenhua. Ethylene Complex of PetroChina Dushanzi Co., P. C. 833600

Abstract: The propylene refrigeration compressor and the replaced crack gas compressor went out of order on Jan. 4th 2003 because of lubricant oil deterioration, compressor shaft seal leakage, increased bearing temperature in crack gas and propylene turbine, increased exhaust pressure in propylene turbine, speed governor vibration, and failure of timely automatic start – up of the spare oil pump, which endangered the safe and normal operation of compressors. This article analyzes the causes of the phenomenon mentioned above and summarizes the technical reconstruction measures and the effect achieved.

Keywords: Compressor, Shaft seal, Speed governor, Degree of vacuum

Analysis and Evaluation of Using Refinery Hydrocracked LPG as Ethylene Cracking Feed

Wang Qingjiang[1,2], *Tan Wei*[1], *Li Hong*[2]. 1 *School of Chemical Engineering of Tianjin University, P. C.* 300072; 2 *Olefin Division of SINOPEC Tianjin Branch, P. C.* 300271

Abstract: The cracking of refinery hydrocracked LPG in cracking furnace is tested to deal with the price rise of naphtha and develop new ethylene feed. The yield, throughput and energy consumption while using hydrocracked LPG as the cracking feed are analyzed based on the on – line and off – line data collection. Comprehensive economic benefits are also evaluated. The conditions for using hydrocracked LPG as the cracking feed are also put forward.

Keywords: Refinery hydrocracked LPG, Cracking, Economic benefit

Application of PSA in the Separation of Hydrogen in Ethylene Plant

Jiang Tao, Sun Peizhi, Li Haizhou. PetroChina Zhongyuan Petrochemical Co. Ltd., P. C. 457000

Abstract: The principle of PSA and its application in the separation of hydrogen in ethylene plant are introduced. High purity hydrogen product has been successfully separated using PSA Technique.

Keywords: PSA, Hydrogen, Ethylene plant

Technology of Producing Ethylene from FCC Dry Gas by PSA and Purification

Wang Jian, Ma Yijin, Wang Chongming. Lanzhou Petrochemical Company of PetroChina, P. C. 730060

Abstract: The technology of producing ethylene from FCC dry gas by PSA and purification as well as its industrial application in Lanzhou Petrochemical Company are Introduced. Refinery & chemical integration synergy is further developed by way of optimizing the resources allocation. Good economic benefit is achieved.

Keywords: FCC dry gas, PSA, Dry gas purification, Ethylene recov

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