

天然气制合成油介绍

钱 伯 章*

(金秋石化科技传播工作室)

钱伯章. 天然气制合成油介绍. 天然气工业, 2002; 22(4): 88~ 90

摘 要 天然气制合成油得到的柴油燃料基本不含硫和芳烃, 费—托法合成技术的进步已使天然气制合成油 (GTL) 的生产成本可与 18~ 22 美元/桶的原油价格相竞争, 因而 GTL 已成为天然气, 尤其是偏远地区天然气高效利用的一个有前景的途径。GTL 技术由合成气生产、费—托合成和产品精制三部分组成。GTL 的工艺方案有埃克森公司 AGC- 21 工艺、壳牌公司 SMDS 工艺、萨索尔公司 Synt hol 工艺、合成油公司工艺等。GTL 技术在合成气生产和费托合成方面还出现了一些新的进展。21 世纪将迎来 GTL 装置新的发展期, 在未来 15 年内, 预计 GTL 装置生产能力将增加 $(4\ 500\sim 6\ 750)\times 10^4\text{t/a}$ 。2005 年前将有 7 套 GTL 装置投运, 总能力 $880\times 10^4\text{t/a}$ 。

主题词 天然气制合成油 柴油 费—托法合成 合成气

天然气制合成油(GTL)正成为天然气高效利用的途径脱颖而出。当前, 世界炼油业正面临生产低硫和超低硫汽、柴油以满足日益苛刻的环境法规要求。例如, 欧盟柴油含硫量将从2000年350 μg/g 减小到2005年50 μg/g、2008年30 μg/g, 美国柴油含硫也将从现在500 μg/g 减小到2006年15 μg/g。通过费—托法工艺将天然气转化成合成油的柴油燃料含硫小于1 μg/g、芳烃含量小于1%(体积百分比)、十六烷值大于70, 为生产清洁燃料开辟了一条新途径。经过改进的费—托法合成技术, 采用新型钴催化剂和先进的淤浆床反应器, 使 GTL 装置投资和操作费用大大降低, GTL 的生产成本已可与 18~ 22 美元/桶的原油价格相竞争, 为建设天然气炼油厂注入了新的活力。

GTL 技术

GTL 技术可分为两大类: 直接转化和间接转化。天然气(甲烷)如可直接转化, 则可节省生产合成气的费用, 但甲烷分子很稳定, 反应需高的活化能, 而且一旦活化, 反应将难以控制。现已开发的几种直接转化工艺, 均因经济上无吸引力而尚未工业化应用。间接转化则通过生产合成气, 再经费—托法合成即可生产全成油。现代化费—托法合成技术, 基于新型钴茎催化剂的淤浆床反应器, 已成为公认的合成工艺路线。

GTL 技术由合成气生产、费—托法合成和产品精制三部分组成, 见图 1。

1. 合成气生产

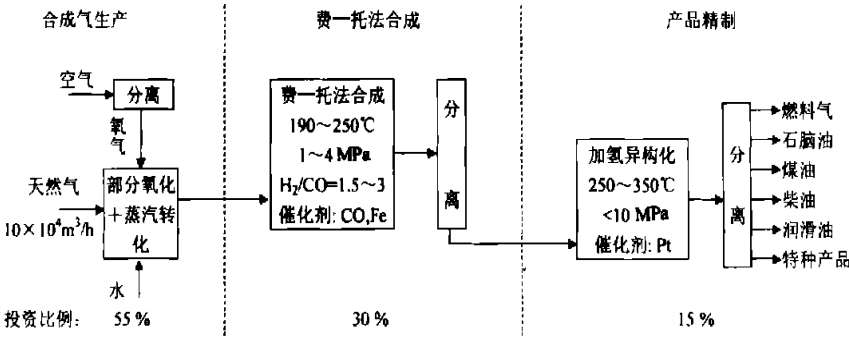


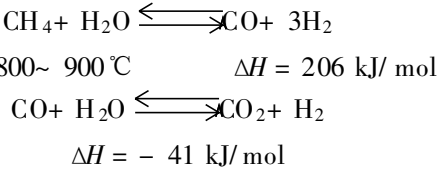
图 1 天然气制合成油(GTL)流程

* 钱伯章, 1939 年生, 高级工程师; 退休前任职于中国石化集团公司上海高桥石化公司, 曾先后发表论文 400 余篇, 著作 3 部。地址: (200127) 上海市峨山路 180 弄 15 号 908 室。电话: (021) 58700767。

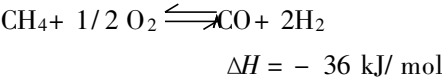
合成气生产技术有蒸汽转化、部分氧化和自然转化三种。

蒸汽转化典型的有福斯特·惠勒公司、海尔德·托普索公司、动力技术国际公司、鲁奇公司和伍德公司技术。

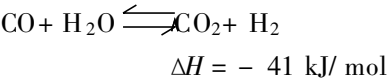
蒸汽和天然气在高温 (800~ 900 ℃) 和中压 (2 MPa) 及镍催化剂存在下反应。蒸汽转化生成合成气的 H₂/CO 比较高。反应式为:



部分氧化典型的有德士古和壳牌公司技术。天然气在很高温 (1 200~ 1 500 ℃) 和很高压力 (14 MPa 以上) 下燃烧,不使用催化剂。大规模生产时用氧气代替空气。可生成近乎理想的 H₂/CO 比例。反应式为:



自然转化典型的有鲁奇公司和海尔德·托普索公司技术。先发生部分氧化,再在催化剂床层产生蒸汽转化反应。反应式为:



不同方式生产合成气的组成见表 1。

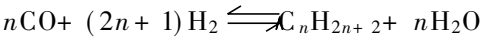
表 1 不同合成气生产方案

	H ₂ /CO	剩余 CH ₄ (%)	剩余 CO ₂ (%)
蒸汽转化	3~ 5	8~ 10	10~ 12
补加 CO ₂	2.8	7	25
部分氧化	1.8	0.2	2~ 3
自然转化	2.1	2.5	5~ 6

2. 费—托法合成

费—托法合成可将合成气转化成各种不同链长的烷烃和烯烃。当然,如果需要,也可将合成气生产其他液体产品,如甲醇、氨或二甲醚。费—托法合成的选择性见表 2。

费—托法合成典型的采用铁基或钴基催化剂。工艺过程在中温 (200~ 300 ℃) 和中压 (1~ 4 MPa) 下进行。将合成气转化为烃类的主要反应为:



费—托法合成油类似于清洁的轻质原油,见表

3。

3. 产品精制

表 2 费—托法合成的选择性 (SaSol 数据)

选择性, %	固定床反应器	淤浆床反应器
CH ₄	2.0	3.3
C ₂ ~ C ₄ 烯烃	2.1	8.2
C ₂ ~ C ₄ 烷烃	2.9	3.9
C ₅ ⁺	91.6	80.2
含氧化合物	1.4	4.4

表 3 费—托法合成油性质

	费—托法合成油	阿拉伯轻原油	布伦特原油
API 重度	46.5	32.3	38.3
硫 (μg/g)	< 10	19 000	4 000
氮 (μg/g)	< 10	1 100	1 300
倾点 (℃)	60	- 18	- 45
柴油馏分 (%)	52	46	49
重于柴油的馏分 (%)	40	42	37

费—托法合成的烃类产物有不同的链长。该混合物可作为合成原油送往炼油厂作原料加工,改质步骤可与整个 GTL 工厂组合在一起,也可不组合在一起。采用缓和加氢异构化工艺可将长链烃切断成低温性能良好的短链正构和异构烷烃,得到高质量的喷气燃料和柴油调合料。表 4 列出天然气合成油生产的柴油性质。生产的石脑油也低含硫、高含石蜡烃。虽然不是很好的汽油组分,但其高含石蜡烃是极好的石油化工原料。生产的合成石蜡,其价格高于石油石蜡,可用作特种产品。

表 4 GTL 生产的柴油性质

	GTL 柴油	欧洲 2005 年柴油规格
冷滤点 (℃)	- 18	
十六烷值	> 75	> 53
多环芳烃	< 0.1%	< 6%
硫 (μg/g)	0	< 50
密度 (g/L)	767	< 835
T ₉₅ (℃)	334	< 355

GTL 工艺方案

已推出的 GTL 工艺方案主要有埃克森公司、壳牌公司、南非合成油 (SaSol) 公司、合成石油 (Syntroleum) 公司等工艺,以下仅介绍壳牌 SMDS 工艺。

壳牌公司开发的 SMDS (壳牌中间馏分油合成) 工艺已于 1993 年在马来西亚民都鲁建成工业规模 GTL 装置,生产 56 × 10⁴ t/a 馏分油燃料、特种化学品和石蜡。进料为 Sarawak 浅海气田 2.8 × 10⁶ m³/d 天然气和 2.5 t/d 氧气,采用壳牌公司部分氧化法气化工工艺生产合成气。再采用壳牌公司金属茂催化剂,籍改进型费—托合成工艺生产重质烷烃。然后

加氢裂化生产中间馏分油。馏分油性质见表 5。

GTL 发展前景

表 5 SMDS 工艺生产的馏分油燃料性质

	石脑油	煤油	瓦斯油
密度(15℃ kg/ m ³)	690	738	780
赛氏色度(ASTM D156)	29	30	—
ASTM 色度 (ASTM 1500)	—	—	0
馏程 初馏点(℃)	43	155	201
干 点(℃)	166	191	358
硫(μg/ g)	< 3	< 10	< 15
十六烷值	—	58	75
烟点(mm)	—	> 50	—
闪点(℃)	—	42	88
芳烃(体积百分比)	0	< 0.1%	< 0.1%

21 世纪将迎来 GTL 装置的发展期,在未来 15 年内,预计 GTL 装置生产能力将增加到 4 500×10⁴~ 6 750×10⁴t/a。表 6 列出已投产和部分拟建的 GTL 装置。据统计,除中型装置外,全世界现在建和拟建的 GTL 装置至少有 10 套之多,其规模为 22.5×10⁴~ 450×10⁴t/a。建设地点包括尼日利亚、埃塞俄比亚、澳大利亚、卡塔尔、南非、印度尼西亚、埃及、委内瑞拉、特立尼达—多巴哥、波利维亚和巴布亚新几内亚。2005 年前,将有 7 套 GTL 装置投产,总能力将达 880×10⁴t/a。

表 6 投产和拟投产的天然气制冷合成油(GTL)装置

公 司	装置地点	装置能力(×10 ⁴ t/a)	现状
萨索尔(SaSol)	南非萨塞尔堡	11(煤基合成油) 675(煤基合成油)	运转 运转
萨索尔—雪佛龙,尼日利亚国家石油公司	尼日利亚 Escravos	148	2005
萨索尔、卡塔尔石油总公司	卡塔尔 Ras Laffan	90	2002
Mossgas	南非莫塞尔湾	135	运转
壳牌公司	马来西亚民都鲁 孟加拉	56 225	运转 计划
壳牌公司、伊朗国家石油公司	伊朗南 Pars	315	2005
壳牌公司、埃及石油总公司	埃及	338	2005
壳牌公司	特立尼达—多巴哥	338	2005
壳牌公司、印度尼西亚矿产能源部、 印度尼西亚石油公司	印度尼西亚	315	计划
委内瑞拉石油公司	委内瑞拉	68	2004
Rentech	美国 Commerce 城 南非	3.6~ 4.5(甲醇装置改造) 45	2002 计划
Donyl—Polo 石化公司	印度 Arunachal pradesh	1.6	建设中
埃克森	美国 Banton Rouge 美国阿拉斯加 Prudhoe 湾 卡塔尔	0.9 450 450	中型 计划 计划
合成油公司	美国 Bellingham 澳大利亚 Sweetwater	0.3 45	中型 2002
BP	阿拉斯加 Prudhoe 湾	1.3	2002
科诺科	— —	1.8 270	2002 2007

结 束 语

- 1) GTL 技术为天然气资源尤其是偏远地区天然气田的开发利用提供了有效的途径。
- 2) 我国现每年进口石油 7 000×10⁴t,石油资源的短缺已使煤代油重新提上议事日程。洁净煤技术

将成为缓解我国石油供需矛盾的主要技术途径。我国有丰富的煤炭资源,为煤炭气化和煤炭气体制合成油是洁净煤技术的一条可供选择的途径。

(收稿日期 2002- 01- 23 编辑 申红涛)

(Southwest Petroleum Institute) and Wu Yaling (Nanchong Refining Chemical Plant). *NATURAL GAS IND.* v. 22, no. 4. pp. 80 ~ 82, 7/25/2002. (ISSN1000- 0976; In Chinese)

ABSTRACT: The slug flow often occurs to the fluctuating multiphase (oil-gas-water) pipeline flowing in the desert oil-gas gathering and transportation pipeline, submarine oil-gas transmission pipeline and surface long-distance transmission pipeline, which causes the pressure drop along the pipeline to be increased and the pipeline corrosion to be augmented and even makes the pipeline showing an unsteady vibration. So, how to predict the slug flowing characteristic parameter along the pipeline is of important practical significance. A new slug flow software that has fair user interface and can be operated in the Windows system has been developed and is introduced in the paper. A calculation may be started out from either the beginning or the ending of the software which can provide three computing models for choice. By use of this software, the curves of the pressure drops, temperature drops and liquid holdup factors changing along the multiphase (oil-gas-water) pipeline may be acquired and all the slug flowing characteristic parameters may be calculated with a relatively high accuracy.

SUBJECT HEADINGS: Gathering line, Multiphase (oil-gas-water) pipeline, Slug flow, Software, Research

Yu Xichong (*Master*), born in 1973, received his Master's degree in storage-transportation engineering from the University of Petroleum, East China, in 1999. Now he is studying for his doctorate in the Southwest Petroleum Institute. Add: Nanchong, Sichuan (637001), China Tel: (0817) 2642808

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INTRODUCTION TO THE DEVELOPMENT OF GAS AIR-CONDITIONS

Wang Changqing, Long Weiding, Huang Zhizhong and Tan Hongwei (Tongji University). *NATURAL GAS IND.* v. 22, no. 4. pp. 83~ 87, 7/25/2002. (ISSN1000- 0976; In Chinese)

ABSTRACT: Along with the implementation of the west-to-east natural gas transmission engineering in China, a great deal of natural gas in the western part will be transported to the eastern economically well-developed regions, which provides a very good turning-point for developing gas air-condition techniques. The development of gas air-conditions not only is beneficial to protecting atmospherical environment and to reducing

greenhouse gas displacement but also may effectively decrease the peak-trough differences of power supply caused by electric power air-conditions, so as to raise the generating efficiency of electric power plant. The kinds and properties of the gas air-conditions and their development and utilization in Japan as well as the policies and measures adopted by the Japanese government and relevant enterprises for expanding the gas air-condition techniques are introduced in the paper. Finally it is pointed out by the authors that in combination with the west-to-east natural gas transmission engineering and by making use of the experience of developing the gas air-conditions in Japan widely applying this kind of air-condition, it is necessary to develop the gas air-condition techniques and to popularize and utilize this kind of air-condition in China.

SUBJECT HEADINGS: Gas air-condition, Performance, Development, Analysis

Wang Changqing (*Doctor*), born in 1965, is an associate professor in the Tongji University. Add: No. 71, Chifeng Road, Shanghai (200092), China Tel: (021) 65981921

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INTRODUCTION TO THE GAS-TO-LIQUIDS

Qian Bozhang (Jinqiu Petrochemical Scientific and Technological Dissemination Section). *NATURAL GAS IND.* v. 22, no. 4. pp. 88 ~ 90, 7/25/2002. (ISSN1000- 0976; In Chinese)

ABSTRACT: The diesel oil obtained from the gas-to-liquids (GTL) does not contain sulphur and aromatic hydrocarbon in the main and the progress in the synthetic technology of Fischer-Tropsch process has made the manufacturing cost of the GTL be able to compete against the crude oil price of 18~ 22 \$/bbl, therefore GTL have opened up a vast range of prospects for high effectively utilizing natural gas, especially the one at remote districts. The technology of GTL is composed of three parts, i.e. the synthetic gas production, the synthesis by Fischer-Tropsch process and the refinement of products. There are several technological plans for GTL, such as the AGC-21 technology of Exxon Co., the SMDS technology of Shell Co., the synthol technology of Sasol Co. and the technology of Synthetic Oil Co., etc.. Some new progress has been yet found in the synthetic gas production and the synthesis by Fischer-Tropsch process subordinate to the technology of GTL and a new developing stage of GTL devices will be coming on in the 21st century. In the future 15 years, it is predicted that the production capacity of GTL devices will increase to 45~ 67.5 × 10⁶t/a and seven

sets of GTL devices with total production capacity of 8.8×10^6 t/a will be put into operation before 2005.

SUBJECT HEADINGS: Gas-to-liquid, Diesel oil, Fischer-Tropsch process, Synthesis, Synthetic gas

Qiao Bozhang (senior engineer), born in 1939, held a post in the Shanghai Gaoqiao Petrochemical Co., Sinopec, before his retirement. He has published over 400 articles and three books early or late. Add: No. 15, Lane 180, Eshan Road, Shanghai (200127), P. R. China Tel: (021) 58700767

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RESEARCH ON THE PREDICTION METHOD OF FORMING NATURAL GAS HYDRATES AT HIGH PRESSURES

Li Yuxing, Zou Deyong and Feng Shuchu (University of Petroleum, Shandong). *NATURAL GAS IND.* v. 22, no. 4. pp. 91~94, 7/25/2002. (ISSN 1000-0976; In Chinese)

ABSTRACT: Along with the increase in high-pressure gas wells in exploration and development, the prediction of natural gas hydrate formation conditions is of vital importance owing to the influence of Joule-Thomson effect on gas. In light of the properties as high pressure, high velocity and complicated natural gas and formation water constituents encountered in the high-pressure gas well test and production, the formation conditions and prediction method were studied by applying thermodynamical theory and in combination with partial experimental results, then a calculation model and relevant software were developed for judging and preventing the hydrates from being formed in high-pressure testing system. In the paper, on the basis of introducing hydrate formation conditions and calculation method, the results are examined by applying the experimental data. With a smaller error, this method may be used for the calculation with a pressure of higher than 100 MPa.

SUBJECT HEADINGS: High pressure, Natural gas, Hydrate, Forming, Condition, Prediction, Method

Li Yuxing (associate Professor), born in 1970, graduated in storage-transportation engineering at the University of Petroleum, North China, in 1992 and received a Ph.D from the University of Petroleum, Beijing, in 1997. Now he is engaged in teaching and research on the hydrate, natural gas transportation, gas-liquid mixed flow and gathering & transferring pipe network optimization, etc.. Add: Dongying, Shandong (257062), P. R. China Tel: (0546) 8391089

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PROGRESS IN ADSORBED NATURAL GAS TECHNOLOGY IN CHINA*

Chen Jinfu, Qu Mei and Xu Wendong (Environmental Engineering Research and Development Center, University of Petroleum, Beijing). *NATURAL GAS IND.* v. 22, no. 4. pp. 95~97, 7/25/2002. (ISSN 1000-0976; In Chinese)

ABSTRACT: With the further implementation of "West-East Transmission Project", coal or oil replaced by gas has been regarded as the best measures taken on to solve the problems of city environmental protection in East China and to blaze a new path to rescue us from the crisis of oil resource. Due to the low density of volume energy, Adsorbed Natural Gas (ANG), as a promising technology for natural gas storage, encourages widely use of natural gas especially in vehicles. It is well introduced how ANG has been developed in China in these days; some results from careful studies and research are presented here which include the principle and characteristics of ANG, microstructure and performance of adsorbents, ANG vehicle tests and so on. The study also shows that ANG will be applied in various ways and in many areas such as natural gas vehicles, natural gas peaking, domestic gas instead of LPG, gas storage and transportation With pipeless network, as well as environmental protection and national defence.

SUBJECT HEADINGS: Natural gas, Adsorbent, Adsorbance, Storage of natural gas, Adsorbent natural gas, Storage equipments

Chen Jinfu (associate professor with a Ph. D), born in 1964, is mainly engaged in study and teaching on adsorbent (storage) natural gas and chemical storage of hydrogen energy. Add: Shuiku Rd., Changping, Beijing (102200), P. R. China Tel: (010) 89733637 E-mail: cjf64@sina.com

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RESEARCH ON CONDENSING TYPE GAS WATER-HEATER

Tan Shunmin, Luo Xiancheng and Zheng Liping (Chongqing University). *NATURAL GAS IND.* v. 22, no. 4. pp. 98~101, 7/25/2002. (ISSN 1000-0976; In Chinese)

ABSTRACT: Through the theoretical and experimental research on condensing type gas water-heater, it is proved that its