Energy Conversion and Management 133 (2017) 318–331

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Coke oven gas to methanol process integrated with CO_2 recycle for high energy efficiency, economic benefits and low emissions

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ARTICLE INFO

Article history:
Received 17 September 2016
Received in revised form 2 December 2016
Accepted 3 December 2016

Keywords:
Coke oven gas
CO_2 recycle
Methanol
Dry reforming
Techno-economic assessment

ABSTRACT

A process of CO_2 recycle to supply carbon for assisting with coke oven gas to methanol process is proposed to realize clean and efficient coke oven gas utilization. Two CO_2 recycle schemes with respect to coke oven gas, namely with and without H_2 separation before reforming, are developed. It is revealed that the process with H_2 separation is more beneficial to element and energy efficiency improvement, and it also presents a better techno-economic performance in comparison with the conventional coke oven gas to methanol process. The exergy efficiency, direct CO_2 emission, and internal rate of return of the process with H_2 separation are 73.9%, 0.69 t/t-methanol, and 35.1%, respectively. This excellent performance implies that reforming technology selection, H_2 utilization efficiency, and CO_2 recycle ways have important influences on the performance of the coke oven gas to methanol process. The findings of this study represent significant progress for future improvements of the coke oven gas to methanol process, especially CO_2 conversion integrated with coke oven gas utilization in the coking industry.

1. Introduction

China has the biggest production and consumption amounts of coke around the world and they are accompanied by a large quantity of coke oven gas (COG) [1]. In 2015, the coke production in China reaches to 448 million tons [2] with co-production of approximately 210 billion m^3 of COG in China. COG mainly contains H_2 (55–60 vol.%), CH_4 (23–27 vol.%), CO (5–8 vol.%) and N_2 (3–5 vol.%) along with some impurities such as H_2S, NH_3, COS, and CS_2 [3,4]. Half of COG is burnt in the coking combustor to supply heat for coking chamber [5]. The remaining part is commonly combusted and discharged into atmosphere which is a waste of the valuable resource and also causes environmental pollution [6,7]. A better and widely accepted alternative for COG usage is to synthesize methanol [8,9]. Methanol is not only a platform chemical, which can be further converted into more than 20 kinds of down-stream chemicals [10,11], but also a potential liquid fuel [12,13] that can be applied for methanol automobiles. George Olah's proposition "methanol economy", may start a new fuel era, especially in China and USA [14].

COG to methanol (CTM) is an efficient way to utilize this gas. Generally, the optimal ratio (H_2-CO_2)/(CO + CO_2) (which is defined as R), for methanol synthesis is around 2.0–2.1 [13,15]. Values below or above this ratio are inefficient for methanol synthesis [16]. However, the R value in COG is around 5.2–6.0. Hence, COG reforming is necessary to convert the inert CH_4 component and to adjust the R value [17]. The partial oxidation reforming (POR) is adopted industrially and it is mainly divided into two types: non catalytic partial oxidation reforming (NCPOR) and catalytic partial oxidation reforming (CPOR). Both technologies can realize the adjustment of the R; however, the value is still above the suitable value of 2.0 (2.3 for NCPOR and 2.5 for CPOR) [5]. So, carbon supplementary is proposed to reduce the R value. An addition of gasification sub-system is often used as carbon supplementary because the coal gasified gas (CGG) has a high content of carbon and lacks hydrogen [18,19]. The R value can be controlled by adjusting the ratio of CGG/COG and there are many investigations related to this topic. Similar studies with respect to polygeneration systems for co-production of methanol and power from coal and COG have been conducted [20,21]. It was found that the complementation of CGG and COG effectively improves the element and energy conversion utilization during this processing. Man et al.

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http://dx.doi.org/10.1016/j.enconman.2016.12.010
0196-8904/

Nomenclature

CTM	COG to methanol
CTMCR	COG-to-methanol with CO_2 recycle
CTMWOSC	COG-to-methanol without supplementary carbon
CTMWSC	COG-to-methanol with supplementary carbon
CWHS	COG with H_2 separation
CWOHS	COG without H_2 separation
E_{in}	the total energy input
E_o	the total energy output
EX_{in}	exergy of the total fuel input
EX_o	exergy of the total fuel output
EX_{tot}	total exergy
EX_{phy}	physical exergy
EX_{chem}	chemical exergy
$(FCH_4)_{in}$	CH_4 inflow rate of the reforming unit
$(FCO_2)_{in}$	CO_2 inflow rate of the reforming unit
$(FCH_4)_{out}$	CH_4 outflow rate of the reforming unit
$(FCO_2)_{out}$	CO_2 outflow rate of the reforming unit
K_{CO}	adsorption constant of CO, bar^{-1}
K_{CO2}	adsorption constant of CO_2, bar^{-1}
K_{H2}	adsorption constant of H_2, bar^{-1}
K_{H2O}	adsorption constant of H_2O, bar^{-1}
K_{MeOH}	adsorption constant of methanol, bar^{-1}
NCPOR	non catalytic partial oxidation reforming
YCH_4	CH_4 conversion of the system
YCO_2	CO_2 conversion of the system

Capital letters

C_{fuel}	COG cost
C_{labour}	labor cost
C_{power}	electricity cost
C_t	net cash flows of the year t
$F_{O\&M}$	fixed Operation & Maintenance cost
I_1	the equipment cost of the reference equipment
I_2	the equipment cost of the estimated equipment
Q_1	the handling scale of the reference equipment
Q_2	the handling scale of the estimated equipment

Lowercase letters

a	annual
d	day
f_{CO}	fugacity of CO in gas phase, bar
f_{CO2}	fugacity of CO_2 in gas phase, bar
f_{H2}	fugacity of H_2 in gas phase, bar
f_{H2O}	fugacity of H_2O in gas phase, bar
f_{MeOH}	fugacity of methanol in gas phase, bar
i	the discount rate, %
k_1, k_2, k_3	reaction rate constant of methanol synthesis reaction (1–3), mol/(s kg bar)
r_1, r_2, r_3	reaction rate of methanol synthesis reaction (1–3), mol/(s kg)
n	scale exponent
N	the expected plant lifetime
y	year

Greek letters

θ	the domestic factor
λ	the ratio of coke oven gas to reforming
η_1	the energy efficiency of system
η_2	the exergy efficiency of system

Acronyms

Aspen	Advanced System for Process Engineering
ASU	air separation unit
BWRS	Benedict–Webb–Rubin–Starling equation of state
CGG	coal gasified gas
COG	coke oven gas
COM	cost of methanol
Compr model	compressor/turbine
CPOR	catalytic partial oxidation reforming
CRF	capital recovery factor
DME	dimethyl ether
DRM	dry reforming
DSTWU	short-cut distillation tower
GHG	greenhouse gas
Flash model	flash tank
Heater model	heater/cooler
RGibbs	thermodynamic equilibrium reactor based on Gibbs free energy minimization
Heatx model	two-stream heat exchanger
IRR	internal rate of return
LHV	low heat value
M	million
Mcompr model	multistage compressor/turbine
MeOH	methanol
O&M	operation & maintenance
PR-BM method	Peng-Robinson equation of state with Boston–Mathias modifications
Rplug	plug flow reactor
POR	partial oxidation reforming
PSA	pressure swing adsorption
R	$(H_2\text{-}CO_2)/(CO + CO_2)$
RKS-BM	Redlich-Kwong-Soave with Boston-Mathias alpha function
RStoic	stoichiometric reactor
Sep model	multi-outlet component separator
SNG	synthetic natural gas
TCI	total capital investment
TPEC	total purchased equipment cost

[22] designed a new process of coal/COG synthesis to olefins where the energy efficiency increased by 10% in comparison to the conventional coal-to-olefins process. Additionally, a co-feed process of coal and COG to synthetic natural gas (SNG) shows that the energy efficiency is increased by 4% and CO_2 emission is reduced by 60% in comparison to the conventional coal to SNG process [23]. Several commercial plants that have applied this method proved the advantages of element and energy efficiency enhancement mentioned above [19,24]. In contrast, the addition of a supplementary carbon sub-system requires the applications of several units including gasification unit, gas cleaning unit, and others, which makes the system more complex and increase the capital investment [25].

It is noted that there are some contradictions in COG utilization. In general, a half of the generated COG is combusted for coking heat supply, therefore with some CO_2 output. The other half for methanol synthesis should involve carbon supplement for hydrogen-carbon balance, therefore with addition of carbon input. The trade-off between carbon emission and carbon supplementary can be realized by the CO_2 recycle based COG to methanol which has first been proposed by Yi et al. [26]. It was described therein [26] that part of COG from coke oven mixed with part of unreacted syngas is introduced to combustor for heat supply. About 95 vol.% of CO_2 can be easily separated from the CO_2-rich exhaust gas with low energy penalty due to oxygen-combustion in coking combustor. The separated CO_2 is recycled to supply carbon for producing