

Conversion of refinery natural purge gases to liquid hydrocarbons in GTL loop with hydrogen-permselective membranes: An alternative to gas flaring

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ARTICLE INFO

Article history:

Received 29 January 2011

Received in revised form

24 April 2011

Accepted 25 April 2011

Available online 12 June 2011

Keywords:

Natural gas

Purged gas

CO₂ emissions

Gas flaring

GTL loop

Hydrogen-permselective membrane

ABSTRACT

One of the main issues facing mankind in this century is the global warming which is induced by the increasing concentration of carbon dioxide and other greenhouse gases in the atmosphere. A promising process for controlling the atmospheric CO₂ level is prevention of combustion in flares. In the present work, a novel GTL loop is proposed to convert the natural gas wasted by a gas refinery to higher molecular weight hydrocarbons. The process proposes an alternative method instead of conventional gas-burning flares, aims to minimize CO₂ emissions and produce liquid fuel such as gasoline. For this purpose, purged natural gas is converted to synthesis gas in a novel hydrogen-permselective membrane reactor with recycle stream and then it is converted to liquid fuel in Fischer-Tropsch membrane reactor. In this configuration, a loop is constructed by returning and mixing a portion of the product with the original feed through a recycle stream. This approach produces large amounts of higher molecular weight hydrocarbons, hydrogen production and decreases environmental impacts owing to purge gases emission. The simulation results of the aforesaid loop, show decrease in CO₂ emission rate with a value of 1/10 to that of flaring with production of 0.018 kgmol/s of hydrogen and more than 90 barrels per day of heavy fraction hydrocarbons containing gasoline and butane fraction for a specified value of (about 4 MMscfd) purge gases.

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1. Introduction

The increase in concentration of carbon dioxide and other greenhouse gases in the atmosphere since the industrial revolution have led to the serious irreversible changes in the global climate. Due to the global population growth and increase in living standards—especially in developing countries—the greenhouse gas emissions will undoubtedly increase during the next years (Rahimpour and Alizadehhesari, 2009). Therefore, the petroleum industry has struggled with how to curb the age-old practice of burning the natural gas that often comes out of the earth along with crude oil. The controversial practice called flaring is a conventional method of disposing of purge gas in refineries. This method has been the source of much controversial debate as not only does it waste a considerable amount of valuable energy but also results in severe environmental problems in the petroleum and related industries (Tolulope, 2004). The ever-increasing shortage in non-renewable fossil resources on one hand and growing environmental concerns and toughening regulations on the other make

radical changes in energy policies inevitable. Despite this, little progress has been made globally in reducing the total amount of natural gas burned off in flares. According to research by the World Bank's Global Gas Flaring Reduction Partnership (GGFR), each year the equivalent of almost one third of Europe's natural gas consumption is burned in flares, sending about 400 million tons of carbon dioxide (CO₂) into the air—roughly 1.5% of the global CO₂ emissions (Broere, 2008). Replacement by alternative methods of disposal appears to be the most plausible solution.

Recent experience at Shell illustrates the various issues that companies have to deal with as they try to put out flares. Their issue in Nigeria is to gather gas from more than 1000 wells by building gas collection facilities at the oilfields and constructing an extensive pipeline network to carry the gas to an industrial facility where it is turned into liquid for transportation (Tolulope, 2004). Among the various alternatives of combustion, there has been an increased interest in the development of gas to liquid technologies recently. Such technologies play an important role in bringing gas to markets as both fuel and/or petrochemicals (Iandoli and Kjelstrup, 2007). The process, known as GTL, was based on three steps: first, reforming of natural gas into synthesis gas (catalytic partial oxidation, steam reforming and auto-thermal reforming); Second, catalytic conversion of synthesis gas into hydrocarbons; and third,

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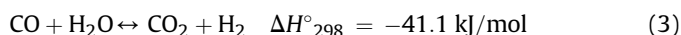
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hydro-cracking of heavy paraffinic hydrocarbons to middle distillates (Maretto and Krishna, 1999).

1.1. Production of syngas

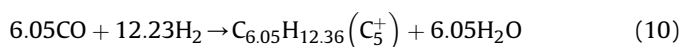
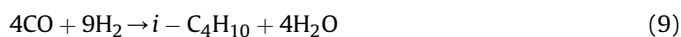
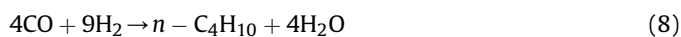
Methane steam reforming is a predominant industrial method used for syngas ($\text{CO} + \text{H}_2$) production which involves three reversible reactions: steam reforming, methane reforming and water–gas shift. The first and second reactions are highly endothermic and limited by thermodynamic equilibrium consequently these reactions are favored at high temperatures and low pressures (Yu et al., 2005; Shu et al., 1994). The third one is exothermic which has a key role to control the hydrogen to carbon monoxide ratio. In the present study, the rate expressions proposed by Xu and Froment (Xu and Froment, 1989) for the steam reforming of methane using $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst was utilized.

The following three reactions are relevant in this synthesis, Eqs. (1–3):



1.2. Fischer-Tropsch Synthesis and production of Fuel

Various studies have been carried out to improve the efficiency of FTS and its ability to generate liquid transportation fuels. Generally, the fresh feed of the Fischer-Tropsch unit consists of H_2 , CO and CO_2 that make up synthesis gas, in addition to CH_4 , C_2H_6 , C_2H_4 , C_3H_8 , $n\text{-C}_4\text{H}_{10}$, $i\text{-C}_4\text{H}_{10}$, C_5^+ and N_2 that is not incorporated in the reaction. The following eight overall reactions are relevant in the synthesis, Eqs. 4–11, which are suggested by the research institute of petroleum industry (RIPI), Iran (Marvast et al., 2005):



In Eq. (10), the heavy fraction of the product (C_5^+) is assumed as gasoline which is considered as the main product of this process and Eq. (11) is a reversible reaction known as the water–gas shift reaction.

A new kinetic model for FTS is proposed by Rongle Zhang et al. to describe the non Anderson-Schulz-Flory (ASF) product distribution. The detailed kinetic model of a Langmuir-Hinshelwood-Hougen-Watson (LHHW) type is derived for FTS and the water–gas shift (WGS) reaction with the assumption that

two elementary steps are essentially slower than others (Zhang et al., 2009). Gallucci et al. (Gallucci et al., 2008) presented co-current and counter-current modes for ethanol steam reforming in a dense Pd–Ag membrane reactor. In their work a conventional and a palladium membrane reactor packed with a CO-based catalyst was modeled and the results for both co-current and counter-current modes of operation are showed in terms of ethanol conversion and molar fraction versus temperature, pressure, the molar feed flow rate ratio and axial coordinate. Ahmadi Marvast et al. considered a water-cooled fixed bed Fischer-Tropsch reactor (Conventional Reactor) with length of 12 m (Marvast et al., 2005). In their work, they studied the effects of reactor temperature on gasoline production in an HTFT process. Forghani et al. (Forghani et al., 2009) have investigated the performance of Pd–Ag membrane reactor for Fischer-Tropsch synthesis and compared it with Conventional reactor. Their results show an improvement in the desired products' yield in addition to a slight decrease in undesired products such as carbon dioxide and light hydrocarbons. Furthermore, Unruh et al. proposed the application of hydrophilic membranes to enhance the CO_2 conversion over WGS of Fe-based catalysts to long-chain hydrocarbons (Unruh et al., 2004a,b). Yoon et al. (Koo et al., 2008) designed $\text{Ni}/\text{MgO}-\text{Al}_2\text{O}_3$ as a promising catalyst in combined steam and carbon dioxide reforming of methane (CSCRM) for the GTL process.

1.3. Pd–Ag membrane

The application of membrane technology in chemical reaction processes has recently focused on reaction systems containing hydrogen and oxygen, and is based on inorganic membranes such as Pd and ceramic membranes (Unruh et al., 2004a,b). F.C. Gielens et al. studied the permeability of H_2 -selective Pd membranes fabricated with micro system technology (Gielens et al., 2007). The stability of the membranes has been determined by experiments (Rahimpour and Asgari, 2008). Bredesen et al. investigated the hydrogen permeation and the stability of tubular palladium alloy (Pd–23%Ag) composite membranes at elevated temperatures and pressures (Gielens et al., 2007). These properties cause Pd-based membranes such as Pd–Ag membranes to be attractive to apply in petrochemical gases. The extensive literature survey of the Pd–Ag membrane can be found in previous work (Peters et al., 2008).

1.4. Farashband Gas refinery

Farashband Gas refinery placed in southern part of Iran which is planted to dehydrate the produced gas and stabilize the accompanied condensate from Aghar and Dalan gas reservoirs. Every day about 1400 million standard cubic feet (MMscf) of gas and 1500 barrels (bbl) of liquid condensate is fed to this plant where in the end, 4 MMscf of these gases are burned in flares as purge. Flaring of these gases not only wastes tons of valuable fuel but also emits a high amount of greenhouse gases such as carbon dioxide.

1.5. Objectives

In the present work, the feasibility of purge gas recovery from gas refinery is investigated with the application of a recycle stream in a GTL loop. This GTL loop is assessed through mathematical modeling for the purpose of improved selectivity of syngas production and hydrogenation in the reformer and Fischer-Tropsch reactor, respectively. Additionally, the amount of carbon dioxide emission from this process is significantly lower compared with that of flares. To approach a favorable product contribution in these reactors configuration, a portion of exit gas is returned to the reactors through a recycle stream.

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