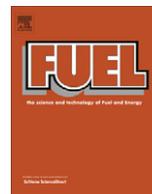




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Feasibility study for mega plant construction of synthesis gas to produce ammonia and methanol

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HIGHLIGHTS

- ▶ Best operational parameters to operate the ATR are obtained.
- ▶ When air is fed, parameters are 0.575 O₂/C, 1.5 H₂/CO, 600.15 K and 0.34 CO₂/C.
- ▶ The H₂/CO ratio is favored with high steam concentration in the feed.
- ▶ Good conversion and yield are obtained when CO₂ is introduced in the feed.
- ▶ Process without natural gas oven produce 9787 MM N m³/year of synthesis gas.

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ABSTRACT

This paper presents a feasibility analysis for the autothermal reforming (ATR) of methane in a fixed bed for syngas production to manufacture ammonia and methanol. The hydrocarbon feed stream of methane (in the presence or absence of ethane) are representative of the natural gas reserves recently found in the North East of Venezuela (Güiría). A packed bed reactor is modeled using published kinetics for steam reforming, catalytic partial oxidation, gas shift and carbon dioxide reforming. A set of optimum operating parameters are obtained to guarantee an ATR process using air instead of oxygen in the feed at an inlet fixed oxygen/carbon ratio of 0.575, water/carbon ratio of 1.5 and carbon dioxide/carbon ratio of 0.34 an inlet temperature of 600.15 K. These provide a 98% methane conversion with a syngas product ratio of three necessary for ammonia and methanol production. Two different processes are analyzed with the same autothermal reforming system, the first process is based on patented large scale technologies (Lurgi, Haldor Topsøe) [1,2], the second process eliminate the oven and differ in the placing of the heat exchanger to reach the desired product conditions for subsequent treatment to obtain a “dehydrated” syngas stream, preliminary feasibility analysis indicates greater saving are obtained in capital investment when air is used as oxidant instead of pure oxygen.

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1. Introduction

Historically, the synthesis gas is considered as a high value strategic mixture in natural gas reforming and as raw material in the production of a large range of intermediate and end products in the petrochemical industry. Globally, the vast majority of the produced syngas is through a steam reformation process of hydrocarbons (natural gas, naphtha, etc.) through a catalytic reaction. In the last decade, a plant could have a production capacities ranging between 2500 and 3500 million m³/year, however, newer process technology have a production capacities near 7500 MM N m³/year and even higher, these plants are known as “mega plants” with the low production cost due to their large scale and low power consumption. Scientific developments in ATR have improved the

syngas process reaching this way optimal energetic costs, making possible the large scale production know as “mega plants”, simple train with high reliability, safety and productivity [1]. The ATR process is used for methanol and ammonia production. The main licensors are Haldor Topsøe, Lurgi, ICI, Foster Wheeler.

In the 1930s SBA and BASF lead the way in ATR technology, using catalytic steam reforming after the partial oxidation, in the 1950s Topsøe and SBA used ATR for industrial synthesis gas production and afterward Topsøe alone further developed the large-scale gas to liquid plants [3–5]. Developments made in the 1990s, allow operations at low steam to carbon ratios with safe burner operation. The most recent world-scale plant has been built in Qatar, Pearl Gas-to-Liquids (GTL) plant [4], is considered the largest yet, with a capacity of more of 20,000 MM N m³/year.

This work is feasibility study of a “large scale” syngas plant that could be used primarily for ammonia and methanol production in the industrial complex, *Complejo Industrial Gran Mariscal de*

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Nomenclature

ATR	autothermal reformer (–)	R	universal constant gas (8,314) (J/mol K)
Bi_h	heat transfer biot number (–)	Re	Reynolds number (–)
Bi_m	mass transfer biot number (–)	r_i	rate of reaction i (mol/g s)
CIGMA	industrial complex “Gran Mariscal de Ayacucho” (–)	S_{CO}	selectivity towards the production of carbon monoxide (–)
C_{p_i}	heat capacity of compound i (J/mol K)	S_{H_2}	selectivity towards the production of hydrogen (–)
D	reactor diameter (m)	T	temperature (K)
F_i	molar flux of compound i (mol/s)	V	volume of reaction (m ³)
F_i^0	molar flux fed of compound i (mol/s)	X_{CH_4}	methane conversion (–)
h	convective heat transfer coefficient (W/m ² K)	Yield	reaction yield reached in the reactor (–)
IRR	internal rate of return (–)		
K_{eq}	equilibrium constant (–)	Symbols	
K_p	equilibrium constant (Pa ^{–1})	ΔH_r	reaction enthalpy (J/mol)
k_g	overall mass transfer coefficient (m/s)	ΔT	temperature difference (K)
L	reactor length (m)	η	effectiveness factor (–)
NPV	net present value (\$)	ρ	fluid density (g/m ³)
P	pressure (Pa)	ρ_b	bulk density of a catalyst bed (g/m ³)
P_i	partial pressure of compound i (Pa)		
POC	products of combustion (–)		

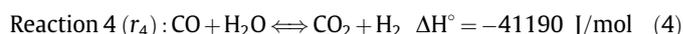
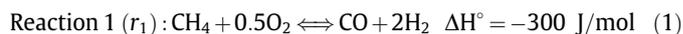
Ayacucho (CIGMA), to be located in the Peninsula Paria, Sucre State, part of the gas industrialization plan, offshore in the northeastern region of Venezuela (Güiria). The incentive is to use the large natural gas reserves, and to consolidate the integrated development of a new large-scale petrochemical complex. Data reported by the state company PDVSA is used in this simulation. Natural gas reserves in Venezuela currently stand at 151.5×10^{12} ft³ of which 90% associated gas and 10% to non-associated gas, both on-shore and offshore. Expectations are on the order of 196×10^{12} ft³ of natural gas, which outlines the excellent opportunities available for Venezuela to increase its proven gas reserves and position itself among the top countries with gas resources available for exploitation [6–8].

The overall objective of this work is to study the feasibility of developing a large scale syngas production plant (mega plant) using ATR reforming, which allows the integrated production of ammonia and methanol in CIGMA. To this end, a model is used to simulate the reactor in terms of conversion, selectivity and yield. The effect of ethane in natural gas feed composition is studied on conversion, selectivity and yield of the reaction. Maintaining constant the composition of the natural gas feed, the effect of oxidant feed ratio (oxygen or air) to the secondary reformer is evaluated. The distribution of synthesis gas products available for conversion into ammonia and/or methanol is determined. PROII is used to simulate the two proposed processes. Preliminary economic feasibility study for the two proposed process is done.

2. ATR reactor and chemical reactions

The compact ATR reactor has a burner, a combustion chamber and catalyst bed, is adiabatically operated in refractory lined pressure vessel. The turbulence within the burner provides proper mixing of the feed streams and prevents soot formation. The preheated mixture, natural gas, oxygen and steam are fed through the top of the reactor. In the upper zone, the partial oxidation reactions (Eqs. (1) and (5)) proceed, where the hydrocarbon conversion is driven by the liberated heat from methane/ethane partial oxidation reaction. Then, the mixture is passed through a catalyst bed, where the catalyst destroys any carbon formed at the top of the reactor while steam reforming (Eqs. (2) and (6)) and carbon dioxide reformation (Eq. (3)) reactions take place and the synthesis gas is further equilibrated by the water gas shift reaction (Eq. (4)) [4,5]. Thus for the simulation it is assumed that in the ATR the set of reactions occur

simultaneously, the natural gas conversion with the desired syngas composition, is a parallel exothermic partial oxidation and endothermic steam reforming, combined with water–gas shift and carbon dioxide reforming reaction in one vessel. The set of reactions that take place within the ATR with their respective heat of formation are listed below:



In Table 1, selected kinetics for the six reactions [9–11].

3. Mathematical model of the reactor

The reactor design is mainly determined by three factors: the kinetics, the size distribution of the solids catalyst, and the hydrodynamic within the reactor. The model consists of a set of equations, which seek to define the system behavior. The simplified model have the following assumptions: (1) steady state conditions, (2) adiabatic fixed bed reactor, (3) unidirectional flow, where the concentration and temperature gradients occur only in the axial direction, (4) plug flow without dispersion, (5) negligible pressure drop, (6) porous spherical catalyst particles, (7) catalyst deactivation is negligible, due to the very low hydrocarbon disintegration temperatures (primarily methane with a small amount of ethane), (8) under the chosen operating conditions, as predetermined mass Biot and mass Mears (Table 2), internal and external mass transfer limitation are negligible, (9) and no temperature gradient between the bulk and catalyst surface as indicated by heat Biot and temperature Mears (Table 2), heat transfer limitations are only within the particle. To prevent internal and external mass transfer limitations, patented technologies for mega syngas reformers report reactor volume greater than 70 m³ with length to diameter ratio (L/D) between 2.5 and 5.

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