Thermodynamic Analysis and Process Simulation of Syngas Production from Methane using CoWO$_4$ as Oxygen Carrier

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Abstract— **For the production of synthesis gas (syngas), the partial oxidation (POX) of methane is a reaction that is more efficient than the steam reforming process (SMR), currently the dominant technology in hydrogen production. To overcome one of the most important disadvantages of POX reaction, which deals with the use of pure oxygen, a metal oxide (CoWO$_4$) is proposed as an oxygen carrier (POX-MeO). Using a thermodynamic analysis of an arrangement of two reactors, here is presented. In the first reactor POX-MeO reactions (4CH$_4$ + CoWO$_4$ = 8H$_2$ + 4CO + Co + W; 2CH$_4$ + CoWO$_4$ = 4H$_2$ + 2CO$_2$ + Co + W) and the undesirable coal formation (CH4 = C + 2H$_2$) are carried out, while in the second reactor solid products of the first reactor are combined with steam to gasify the previously deposited coal (C + H$_2$O = H$_2$ + CO; C + 2H$_2$O = 2H$_2$ + CO$_2$) and simultaneously regenerate the metal oxide to produce syngas (Co + W + 4H$_2$O = CoWO$_4$ + 4H$_2$). Then, the regenerated oxide is recycled back to the first reactor to make a continuous process. A simulation of this process in Aspen Plus was performed taking into account an initial flow rate of 4 kmol/hr of methane. Four sensitivity analyses were performed to determine optimal operating process conditions. The first one was aimed to determine the CoWO$_4$/CH$_4$ feed molar ratio to carry out the reduction of the oxygen carrier, which was 1.1:4. The second sensitivity analysis determined 800°C as the optimal operating temperature of the first reactor to produce the highest yield to syngas. The third sensitivity analysis was carried out in the second reactor studying the variation of the operating temperature at which regeneration of CoWO$_4$ occurred, being 590°C. And finally, the fourth sensitivity analysis found the molar feed of steam to complete the regeneration of CoWO$_4$. At this established conditions a 96% of methane conversion was found and the production of one gas stream of syngas and another with 100% hydrogen purity.**

Keywords— syngas; partial oxidation; CoWO$_4$; hydrogen; process simulation.
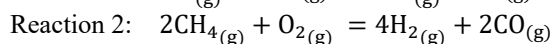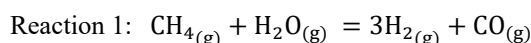
I. INTRODUCTION

Today, energy demand in the world is constantly growing, and a significant amount of this is covered by fossil fuels. Due to the reduction of these fuel reserves and the impact on the environment and health, nations worldwide are looking for alternative energy sources and sustainable raw materials [1].

In recent decades, there has been a great interest in hydrogen as a raw material for a variety of processes, for example, in ammonia synthesis, pharmaceutical manufacture, production of hydrogen peroxide and the electronics and petrochemical industries [1, 2]. Of comparable importance to hydrogen, the mixture of hydrogen and carbon monoxide (H$_2$ + CO), commonly called synthesis gas or syngas [3-5] is a valuable raw material for various industrial applications.

In principle, syngas may be generated from any hydrocarbon feedstocks [5]. However, in most applications, natural gas is the predominant raw material [3].

The steam reforming of methane (SMR, reaction 1) is the dominant technology for the production of syngas [6-9]. However, it has been suggested that the partial oxidation (POX, reaction 2) for the production of syngas presents greater efficiencies than the SMR. Furthermore, POX has other advantages such as: it needs less investment and still is able to produce a syngas with a H$_2$/CO molar ratio of 2, also is based on an exothermic reaction (which infers substantial energy savings), uses small reactors and exhibits high methane conversions ($\approx$90%) and selectivities to hydrogen (94~99%). But, this process also has some disadvantages such as high operating temperatures (900~1000°C), and the need for an oxygen plant in place, which makes this a very expensive process [10].

Reaction 1: $CH_{4(g)} + H_2O_{(g)} = 3H_{2(g)} + CO_{(g)}$

Reaction 2: $2CH_{4(g)} + O_{2(g)} = 4H_{2(g)} + 2CO_{(g)}$

To solve these disadvantages research has been conducted in order to reduce production costs of syngas through POX and to lower operating temperatures. A proposed strategy is the elimination of the oxygen plant, which represents about half of the investment [10]. An example of such achievements is the use of metal oxides as oxygen carriers, based on a variation of the partial oxidation of methane to produce syngas and/or hydrogen involving two steps: first, the necessary oxygen for partial oxidation is provided by a metal oxide (MeO) containing oxygen, which is released under a reducing atmosphere to produce syngas and the reduced metal (Me) (Reaction 3); while in the second, the reduced metal is reoxidized with steam to produce hydrogen and the MeO (Reaction 4).

Reaction 3: $CH_{4(g)} + MeO = 2H_{2(g)} + CO_{(g)} + Me$

Reaction 4: $H_2O_{(g)} + Me = MeO + H_{2(g)}$
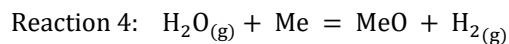
The MeO is recirculated to the initial reactor completing a full cycle, this process is called POX-MeO [4, 10]. It is important to notice that the overall reaction of this process is comparatively equal to the SMR [11].

Partial oxidation of methane under this concept was proposed by De los Rios et. al [2, 10, 12], and suggests the use of a nickel catalyst and cobalt tungstate ($CoWO_4$) as the oxygen carrier, since this material is very stable to cyclic tests subjected to partial oxidation of methane to syngas production. Reduction reactions of methane and reoxidation of the metals involved in this approach are presented in Table 1 as POX-MeO (1), POX-MeO (2) and reoxidation (3), respectively.

In any hydrocarbon combustion process undesirable coal generation is presented, in this case through the reactions 4a and 4b shown in Table 1.

This research aims to evaluate the technical feasibility of a process for the production of syngas that involves the partial oxidation of methane using $CoWO_4$ as oxygen carrier. For this work a simulation model of the process consists in two reactors, one where the partial oxidation occurs and another where the metal oxide is regenerated and the residual carbon is removed with steam.

Table 1. Chemical reactions in the proposed process.

POX-MeO (1)	$4CH_{4(g)} + CoWO_4 \rightarrow 8H_{2(g)} + 4CO_{(g)} + Co + W$
POX-MeO (2)	$CH_{4(g)} + CoWO_4 \rightarrow 2H_2O_{(g)} + CO_{2(g)} + Co + W$
Reoxidation (3)	$4H_2O_{(g)} + Co + W \rightarrow CoWO_4 + 4H_{2(g)}$
Coal Formation (Methane decomposition and Boudard reaction) (4)	(a) $CH_{4(g)} \rightarrow C + 2H_{2(g)}$ (b) $2CO_{(g)} \rightarrow C + CO_{2(g)}$
Coal gasification (5)	$C + H_2O_{(g)} \rightarrow H_{2(g)} + CO_{(g)}$
Coal gasification (6)	$C + 2H_2O_{(g)} \rightarrow 2H_{2(g)} + CO_{2(g)}$

II. METHODS

Simulation programs are useful because they allow performing material and energy balances, cost analysis, sizing estimates of equipment and process cycle time, quickly and easily [1]. In this research a process simulation is carried out in Aspen Plus, which is a simulation program that can be used for a variety of thermodynamic calculations and process analyses [13].

The Gibbs reactor system (RGibbs) can efficiently calculate the chemical equilibrium in multiphase and multistep reaction systems. To achieve this, the program finds a solution using an algorithm that minimizes the Gibbs free energy of the thermodynamic system (Gibbs free energy minimization technique) [13].
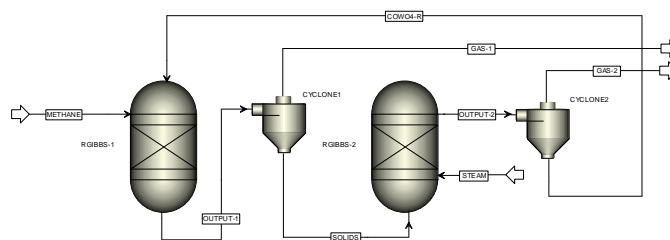

Figure 1. Process simulation flowsheet.

The process scheme shown in Figure 1, consists of two Gibbs reactors. In the first one (RGIBBS-1) the oxidation of methane in the presence of tungstate cobalt ($CoWO_4$) as oxygen carrier is carried out, while in the second reactor (RGIBBS-2) tungsten and cobalt reoxidation reactions are carried out in the presence of steam, thus regenerating cobalt tungstate and producing hydrogen, as well as removing any carbon deposits on this oxygen carrier. 4 kmol/hr of methane are fed in the first reactor. A thermodynamic system based on the Redlich-Kwong-Aspen equation of state was used in this simulation, which is aimed for processes that involve hydrocarbons and their mixtures with polar components for medium and high pressures [14].

Similarly, cyclones at the outlet of each reactor (CYCLONE1 and CYCLONE2) are used to separate the solid and gaseous products resulting from both reactors. In the case of the first separation the resulting solids (cobalt, tungsten, and a small fraction of deposited carbon) are disposed as reagents for the second reactor and the separated gas (GAS-1) constitutes the rich hydrogen product. In the second reactor, according to reactions (3), (5) and (6), the solid products, which are separated by the second cyclone comprise cobalt tungstate (COWO4-R), and this is recirculated to the first reactor, whereas the separated gas (GAS-2) is the hydrogen-rich product.

On the other hand, in this paper four sensitivity analyses were performed to determine optimal operating process conditions. The first one was aimed to determine the $CoWO_4/CH_4$ feed molar ratio to carry out the reduction of the oxygen carrier. The second sensitivity analysis will determine the optimal operating temperature of the first reactor to produce the highest yield to syngas. The third sensitivity analysis will be carried out in the second reactor aiming to study the variation of the operating temperature at which regeneration of $CoWO_4$ is expected to occurr. And finally, the fourth sensitivity analysis will find the molar feed of steam to complete the regeneration of $CoWO_4$.

III. RESULTS AND DISCUSSION

A. Sensitivity Analyses

Figure 2 (a) shows results for the first sensitivity analysis, where a minimum molar flow of 1.1 kmol/hr of $CoWO_4$ and 4 kmol/hr of methane are needed ($CoWO_4/CH_4$ molar ratio = 1.1:4) to prevent carbon deposition by methane decomposition and Boudard reactions (reactions 4a and 4b), which is of great importance, because will avoid coal gasification at RGIBBS-2. Likewise in Figure 2 (b), a considerable amount of hydrogen of

7.29 kmol/hr is produced together with small amounts of carbon dioxide and residual methane and a maximum flow of 3.6 kmol/hr of carbon monoxide, this represents a H_2/CO molar ratio of approximately 2.
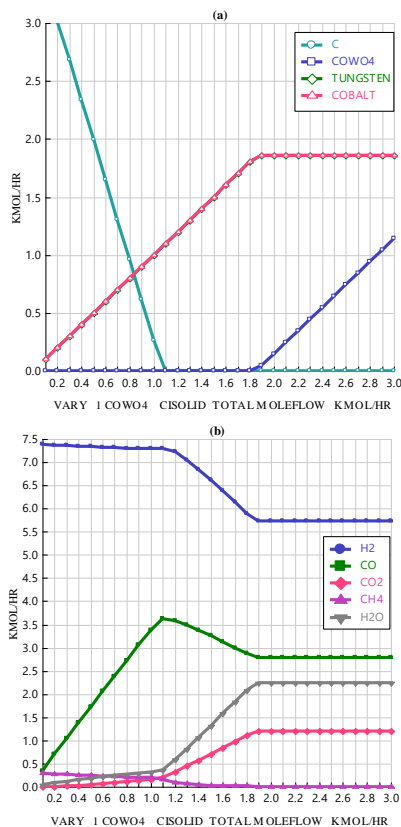

Figure 2. Sensitivity analysis of $CoWO_4$ mole inflow in the first Gibbs reactor, results of solid (a) and gas products (b).

The first sensitivity analysis is directly related to the second analysis, since the variation of the operating temperature (300 to 900°C) in RGIBBS-1 resulted in a wide range of gas equilibrium compositions. According to the results, it was found that in an approximate temperature range between 750 and 800°C the greatest amount of hydrogen is produced. Considering the increase in operating temperature, this range can be seen as a "unnecessary energy expense" compared to the hydrogen yields obtained in this temperature range, as shown in Figure 3 (b). At the same time, it can be seen in Figure 3 (a) that the possibility of carbon formation at 740°C and higher is null. For these reasons a temperature of 800°C was selected as the operating temperature of the first reactor, where the first sensitivity analysis was performed.
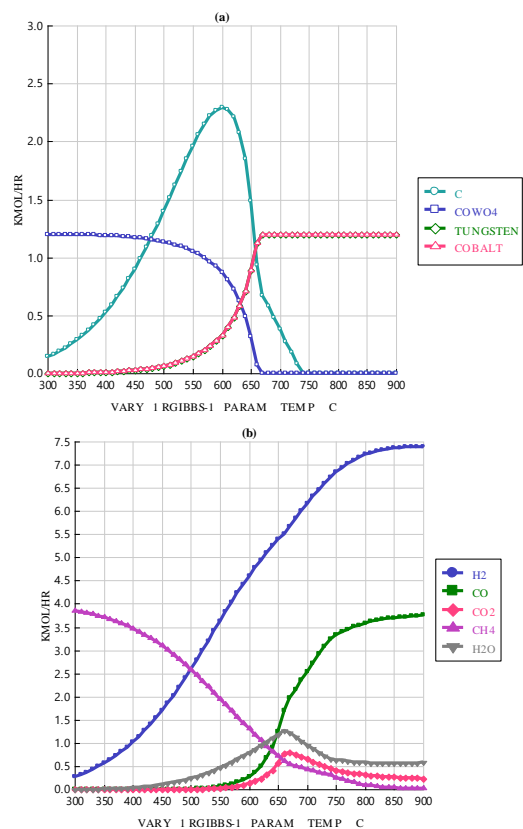

Figure 3. Sensitivity analysis of temperature in the first Gibbs reactor, results of solid (a) and gas products (b).

For the case of the sensitivity analysis in the second reactor, shown in Figure 4, it was observed that the most suitable operating temperature is 590°C, because it is the maximum temperature at which cobalt tungstate is stable together with a high hydrogen production (4.4 kmol/hr), without the formation of tungsten and cobalt (Figure 4 (a)) or the use of hydrogen to form water (Figure 4 (b)). Also, because cobalt tungstate regeneration kinetics with steam is slow at low temperatures [2]. Therefore, at a higher temperature it is possible to carry out the reaction (3), while being benefiting from faster kinetics.

At the fourth sensitivity analysis shown in Figure 5, it was found that a feed value of 5.6 kmol/hr of steam is needed in the second reactor to achieve a total regeneration of cobalt tungstate. Furthermore, this analysis shows no significant presence of carbon compounds (traces), whereby the gaseous product of this operation is only composed of hydrogen and water vapor, which in turn, by condensing water, a high purity hydrogen stream can be obtained.
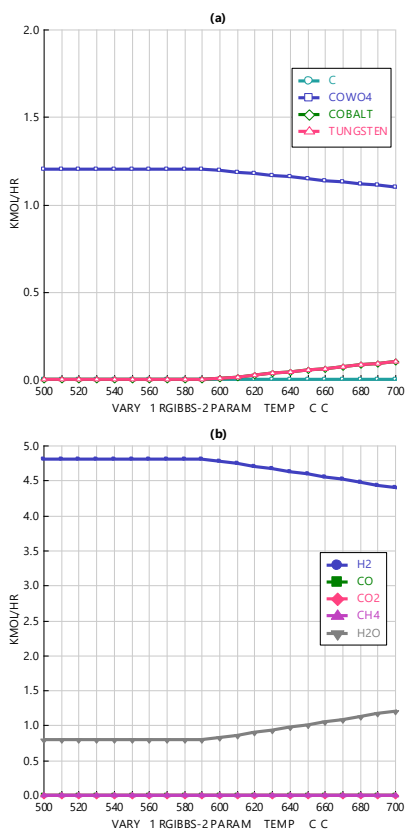
Figure 4. Sensitivity analysis of temperature in the second Gibbs reactor, results of solid (a) and gas products (b).
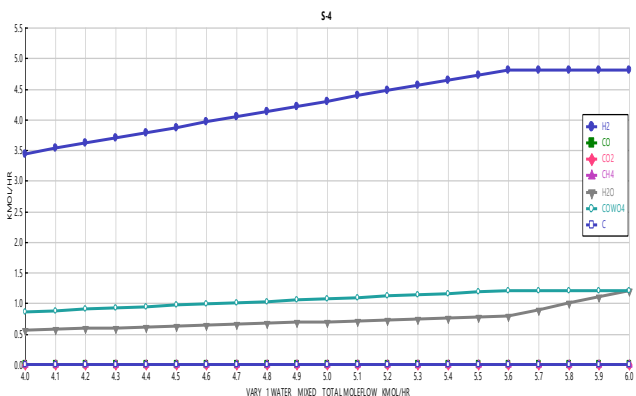

Figure 5. Sensitivity analysis of molar inflow of steam to the second reactor.

Table 2. Simulation results.

Stream ID		COWO4-R	GAS-1	GAS-2	METHANE	OUTPUT-1	OUTPUT-2	SOLIDS	STEAM
			Heat and Material Balance Table						
Temperature	C		800.0	590.0	700.0	800.0	590.0		590.0
Pressure	bar		1.013	1.013	1.013	1.013	1.013		1.013
Vapor Frac			1.000	1.000	1.000	1.000	1.000		1.000
Mole Flow	kmol/hr	0.000	11.661	5.600	4.000	11.661	5.600	0.000	5.600
Mass Flow	kg/hr	0.000	134.568	30.488	64.171	134.568	30.488	0.000	100.886
Volume Flow	cum/hr	0.000	1027.106	396.718	319.523	1027.106	396.718	0.000	396.443
Enthalpy	Gcal/hr		-0.072	-0.046	-0.036	-0.072	-0.046		-0.296
Mole Flow	kmol/hr								
CH4			0.169		4.000	0.169			
CO			3.630			3.630			
CO2			0.201			0.201			
H2			7.293	4.400		7.293	4.400		
H2O			0.368	1.200		0.368	1.200		5.600
COWO4									
COBALT									
TUNGSTEN									
C									
Mass Flow	kg/hr	337.459	134.568	30.488	64.171	401.630	367.947	267.062	100.886
Enthalpy	Gcal/hr	-0.277	-0.072	-0.046	-0.036	-0.061	-0.323	0.012	-0.296
Temperature	C	590.0				800.0	590.0	800.0	
Pressure	bar	1.013			1.013	1.013	1.013	1.013	1.013
Vapor Frac		0.000				0.000	0.000	0.000	
Mole Flow	kmol/hr	1.100	0.000	0.000	0.000	2.200	1.100	2.200	0.000
Mass Flow	kg/hr	337.459	0.000	0.000	0.000	267.062	337.459	267.062	0.000
Volume Flow	cum/hr	0.033	0.000	0.000	0.000	0.018	0.033	0.018	0.000
Enthalpy	Gcal/hr	-0.277				0.012	-0.277	0.012	
Mole Flow	kmol/hr								
CH4									
CO									
CO2									
H2									
H2O									
COWO4		1.100					1.100		
COBALT						1.100		1.100	
TUNGSTEN						1.100		1.100	
C									

Gaseous product from RGIBBS-1 (GAS-1) resulted in unreacted methane (0.04 fraction of the original feed), water vapor and carbon dioxide as byproducts. On the other hand, in the same stream, syngas of interest has a molar H_2/CO ratio of 2.01, which satisfies the relationship that has been previously reported including impurities, besides this relationship it is suitable for gas to liquid processes (GTL) [10, 15].

The established operating temperature of 800°C in the first reactor, where the partial oxidation of methane occurs, is relatively lower than those reported with other materials as oxygen carriers such as transition metal oxides (Ni, Cu, Fe and Mn), whose operating temperature conditions can be up to 1200°C [15], and this represent significant energy savings.

The solid products obtained from RGIBBS-1 (SOLIDS), consisted of a cobalt and tungsten molar ratio of 1:1 due to the reduction of the metal oxide, and these are the solids products that enter as reagents into the second reactor (RGIBBS-2) along with a stream of steam of 5.6 kmol/hr (STEAM) for the regeneration of the metal oxide.

Results from RIBBS-2, consisted in only pure cobalt tungstate (COWO4-R), which shows the complete recovery of the original oxygen carrier at a flowrate of 1.1 kmol/hr for subsequent recirculation to RGIBBS- 1, thus closing the cycle. In the case of gaseous product (GAS-2), this shows that 4.4 kmol/hr hydrogen and 1.2 kmol/hr of steam is produced, which represents a high purity hydrogen stream in the gaseous product of this operation, our main compound of interest.

Comparing the gaseous current generated in the first reactor in dry basis (65% H_2, 32% CO, 2% CO_2 and 1% CH_4) with a typical gas product from a steam reforming process (approximately 75% H_2, 12% CO, 6% CO_2, and 7% CH_4) [16], i.e. POX-MeO and SMR, it can be observed that the syngas molar ratio from the two different processes is markedly

B. Simulation

Having established the appropriate parameters for the simulation of the entire process through the sensitivity analyses, it was possible to obtain the results shown in Table 2. These results show the successful production of syngas in the first reactor with 96% conversion of methane and a full recovery of the oxygen carrier in the second reactor, leading to a direct hydrogen production.

different. Even though the H_2 mole fraction obtained in POX-MeO is smaller than the one obtained for SMR, POX-MeO generates a higher methane conversion, a syngas with less impurities with similar hydrogen contents reported in other researches.

Nevertheless, at the cyclical operating conditions suggested in the process of this study, the cyclic experimental behavior of cobalt tungstate has not been tested so far. Therefore, appropriate testing to determine the experimental viability of the proposed process in this research it is recommended as a future work.

IV. CONCLUSSIONS

A simulation of a POX-MeO process using $CoWO_4$ as oxygen carrier was performed, the advantage of this process over other previously reported research lies on the stability of cobalt tungstate to a cyclic exposure at high temperatures (800°C) and various reactive atmospheres (CH_4, H_2O, etc.).

Simulation results found optimal reaction conditions to favorably carry out the POX-MeO process. At a temperature of 800°C in the first reactor a conversion of 96% methane without carbon formation can be obtained. This in turn, benefited the second reactor performance, because only the metal oxide regeneration is achieved, together with a carbon-free hydrogen gas.

Results show that a syngas stream with a molar H_2/CO ratio of 2.01 and a high purity hydrogen in the second reactor can be obtained.

Finally, an experimental assessment of the cobalt tungstate regeneration at certain conditions in the present work is recommended, in order to evaluate the results obtained here and the viability of the process.

ACKNOWLEDGMENT

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