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Research Article

Effect of the Light Alkane Content of Natural Gas on the Production of Hydrogen and Coke During the Dry Reform

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ABSTRACT

Dry reforming of ethane and propane were carried out with a nickel catalyst (3.92% by weight/γ-Al_2O_3) to characterize the effects of fed light alkanes on the reforming process of natural gas. Conversions of individual alkanes, representing 74.7% for ethane and 96.0% for propane at 1073 K, promoted hydrogen yields of 43.6% and 66.0%, respectively. The conversion (81%) of a natural gas promoted a 95% hydrogen yield, where about 20% had been obtained from the light alkanes. The reaction steps from alkane dry reforming where hydrogen was produced (alkane cracking) provided carbon formation with a yield of 23%. A kinetics evaluation, based on experimental evidence that indicated two different sets of reaction steps for both ethane and propane processes, enabled the identification of the specific reaction rates of the cracking steps for each alkane. Reaction steps in the reforming process were considered as competitive reactions and the specific cracking reaction rates of both light alkanes were used to quantify the kinetic selectivities of hydrogen, calculated as 95.42% for ethane and 76.99% for propane.

Keywords: Syngas; Ethane; Propane; Dry reforming; Hydrogen; Coke

INTRODUCTION

The development of natural gas exploration technologies follows a growing trend of demand for this raw material. Important additional sources of gas from fossil reservoirs, particularly those found with shale, charcoal and sandstone, represent a significant contribution towards meeting this demand [1]. Natural gas reform processes focused on the production of synthesis gas (syngas) and/or hydrogen are important users of this supply and have received special attention in terms of their performance [2-4]. Thus, better operating conditions, active catalysts and suitable reactors have been investigated to obtain high conversion, yield, and selectivity. The use of natural gas not viable to produce liquefied gas represents a potential means to increase hydrogen and/or syngas production [5-9]. On the other hand, the generation of carbon dioxide in different refinery operations such, as regeneration of fluid catalytic cracking units, has increased the interest of the petroleum industry in its use for natural gas conversion by reforming processes [10-12].

Continued attention has been focused on the research on different aspects of the traditional (steam reforming) and alternative (autothermic, dry, tri-reforming,..) routes for converting natural gas into syngas (CO, H_2) in order to produce hydrogen and/or liquid fuels such as hydrocarbons free sulphur as well as fuels with high cetane or octane numbers, or oxygenates compounds. In all reforming processes, attention must be paid to the compositional characteristics of the natural gas, as it contains mainly methane, but also has, depending on the origin, a significant percentage of light alkanes with higher hydrogen and carbon contents (C_2H_6,

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C_3H_8, C_4H_{10}) that can be processed to produce syngas with high H_2/CO ratio [13-15].

In the case of natural gas, as in methane reforming, reaction steps of hydrocarbon cracking provide hydrogen and carbon (coke) deposition on the catalyst [16-18]. The presence of C_2-C_3 alkanes as minor components of natural gas can increase the amounts of hydrogen and carbon, where the nature of the carbonaceous species during the reform operations can significantly affect the formation of coke. The formation of coke and its role on the catalyst activity has been investigated and compared for both hydrocarbons [19-23]. Catalytic systems of metals promoted with alkaline earth metal oxides (MgO, CaO, BaO) have been used to improve reforming and dehydrogenation activities and to prevent the formation of coke. Situations with implications for reformed natural gas products can be suggested according to the composition of the components of the gas: methane, ethane, and propane [24-26]. For example, in natural gas from different origins there can be various compositions in terms of light alkanes (CH_4, C_2H_6, C_3H_8): from Slochteren, Nederland, 81.9%, 2.7%, 0.38% vv; from Lacq, France, 69.4%, 2.80%, 1.5% vv; from Hass R'mel, Algeria, 83.5%, 7.0%, 2.0% vv; from Guamaré, Brazil, 85.5%, 8.3%, 3.1% vv. Thus, the knowledge of these compositions can already provide information on potential hydrogen yields, and on the carbon formation that can be promoter of coke formation. Different studies for various natural gas according the origin have researched the compositions with higher content in light alkanes. More recently, studies have been carried out concerning the dry reforming of NG light hydrocarbons, mainly ethane and propane [27-30]. For all these cases, the production of syngas by methane dry reforming has been considered as basis, where the reaction steps, such as methane cracking, reverse reactions of Boudouard, and water gas-shift are included. In this present work, a nickel/γ-alumina supported catalyst was formulated and employed to process light hydrocarbons (alkanes) of natural gas. The formulated catalyst had its activity tested, and its use in the processing of natural gas into syngas by dry reforming was evaluated. Considering propositions of mechanism including four step reactions for the NG light hydrocarbons (ethane, propane) a kinetic evaluation was carried out and the results were expressed in terms of conversion of reactants, product yield and selectivity, and carbon deposition.

EXPERIMENTAL

Catalyst formulation

The catalyst was prepared from nickel nitrate ($Ni(NO_3)_2.6H_2O$, Sigma) and γ-alumina (γ-Al_2O_3, Degussa) as the catalytic support. The preparation method was the incipient wetness where the impregnated solution in the support was evaporated to dryness at 393 K for 12 h, and then calcinated at 973 K in an argon flow during 5 h. In the activation step the catalyst was reduced at the same temperature, 973 K, in a hydrogen/argon (200 cm^3/min; 50/50 vv) atmosphere for 2 h.

The nickel catalyst was characterized by several methods including atomic absorption spectrophotometry (AAS, Varian AA 220 FS), B.E.T.-N_2 (ASAP 2000), Thermal Analysis (TG, DTG, DTA), X-Ray Diffraction (XRD, CuK-alpha radiation, Siemens D5000, JCPD-File n° 10-173, fiche n° 1-35-D 5, 1974), and Infrared Spectra (IRS, FTIR Brucker IFS 66).

Process evaluation

The experiments of the alkane-carbon dioxide reforming processes were carried out with the nickel catalyst (<dp>=212 µm, mcat=80.0 mg) in a fixed-bed reactor (glass reactor, Lb=12.0 cm, length; dr=6.0 mm, diameter). The reactants were fed into the reactor with the gaseous mixtures of C_2H_6:CO_2:Ar=5:20:75 v/v and C_3H_8:CO_2:Ar=2.5:22.5:75 v/v, with flow rates in the range (80-140) × 10^{-6} m^3/min. The operating flow conditions employed are presented in Table 1.

A thermal sensor and external heating provided the reactor with a controlled temperature of 1023 or 1073 K with an accuracy of ± 1 K. The gas samples of the reaction products were collected on-line from the effluent flow of the reactor. The residual reactants and the products were analyzed by a gas chromatograph (Saturn 2000, Varian), equipped with a Carbosphere 20/80 (Alltech) column and a thermal conductivity detector.

Table 1: Flow rate in the fixed bed reactor (Q). Operating conditions: 1023 K, 1073 K, 1.0 bar, 8 × 10^{-2} g catalyst. (a) ethane-CO_2, (b) propane-CO_2.

(a)				**(b)**			
Q × 10^{-6} m^3min^{-1}			**τr ($kg_{cat}s/m^3$)**	**Q × 10^{-6} m^3min^{-1}**			**τr ($kg_{cat}s/m^3$)**
C_2H_6	CO_2	Ar		C_3H_8	CO_2	Ar	
70	280	1050	3.4	35	315	1050	3.4
60	240	900	4	30	270	900	4
50	200	750	4.8	25	225	750	4.8
40	160	600	6	20	180	600	6

The conversions for ethane and propane were calculated by $Xm=10^2(Cm0–Cm)/Cm0$ where C_m is the molar concentration of the species ($m=C_2H_6$, C_3H_8). The yields of hydrogen and carbon monoxide, based on the stoichiometry of the overall reactions ($C_2H_6+CO_2 \rightarrow 2CO+(3/2)H_2$; $C_3H_8+CO_2 \rightarrow 2CO+(4/3)H_2$), were calculated as follows:

$$Y_{H_2} = \frac{C_{H_2}}{3.C^o_{C_2H_6}} \times 100;\ Y_{H_2} = \frac{C_{H_2}}{4.C^o_{C_3H_8}} \times 100;\ Y_{H_2} = \frac{C_{CO}}{2.C^o_{C_2H_6}} \times 100;\ Y_{H_2} = \frac{C_{CO}}{3.C^o_{C_3H_8}} \times 100$$

RESULTS AND DISCUSSION

Catalyst characterization

The nickel content and the surface area of the catalyst, characterized by AAS and B.E.T.-N_2, were 3.92% by weight and 1.56×10^2 m^2/g, respectively. The thermal analyses (TG, DTG, Figure 1) revealed mass losses of water (13.0%) and NO_2 (10.0%) from the impregnated precursor ($N_i(NO_3)_2.6H_2O$). The TG plot exhibited the initial calcination temperature of the precursor. The curve of differential thermal analysis (DTA) shows two endothermic peaks, which represent the processes of vaporization of water and nitrate decomposition. The maximum temperatures for water loss and nitrate decomposition were 427.9 K and 814.5 K, respectively. Losses progressed to 1273 K possibly due to NOx emissions.

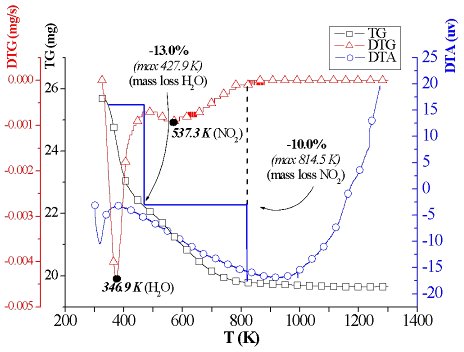

Figure 1: Thermal analyses of materials obtained during de preparation of the Ni(3.92%wt.)/γ-Al_2O_3 catalyst.

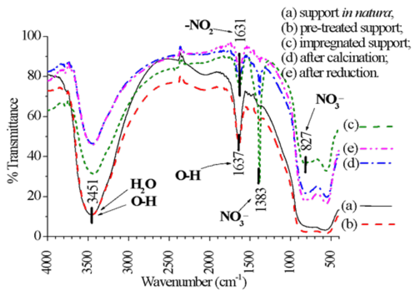

Figure 2: FTIR analyses of materials obtained during the preparation of the Ni(3.92%wt.)/γ-Al_2O_3 catalyst. (a) support (step-1) (b) pre-treated support (step-2) (c) support impregnated with precursor (step-3) (d) catalyst after calcination (step-4) (e) catalyst after reduction (step-5).

As the catalyst was being prepared, from the step of support in natura (steps-1, 2) up to the reduction, in the infrared spectra (FTIR, 2) the presences of crystalline water (3600-3100 cm^{-1}), hydrogen bonds (3600-3200 cm^{-1}, 1630-1600 cm^{-1}), and NO_2 and nitrate (1632, 1383, 827 cm^{-1}) were identified. Nitrates appear in the impregnation phase (step-3), decreasing after calcination (step-4) and practically no longer exists when the catalyst was reduced (step-5), while NO_2 groups and hydrogen bonds remain (Figure 2).

The catalyst was characterized by XRD prior and after the reaction operations. Figure 3 shows the diffracto grams of the phases present in each catalyst preparation step.

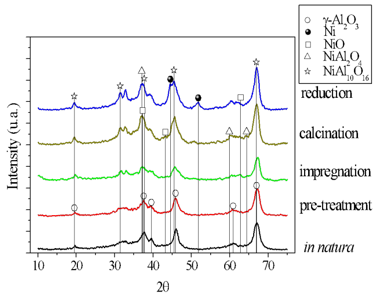

Figure 3: XRD analyses of materials obtained during the preparation of the $N_i(3.92\%wt.)/\gamma\text{-}Al_2O_3$ catalyst. (a) support in natura (step-1) (b) pre-treated support (step-2) (c) support impregnated with precursor (step-3) (d) catalyst after calcination (step-4) (e) catalyst after reduction (step-5).

The solid phases were identified as the support γ-Al_2O_3 (2θ 37.4, 45.3, 65.8, 66.6), the nickel metallic phase (2θ 44.1, 52.0, 77.5, 93.4) and traces of NiO (2θ 36.2, 43.3) in the fresh catalyst, and its forms Ni_3C (nickel carbide, 2θ 46.2) and $NiAl_2O_4$ (nickel aluminate, 2θ 44.8, 66.7) in the catalyst after reaction.

Process evaluation

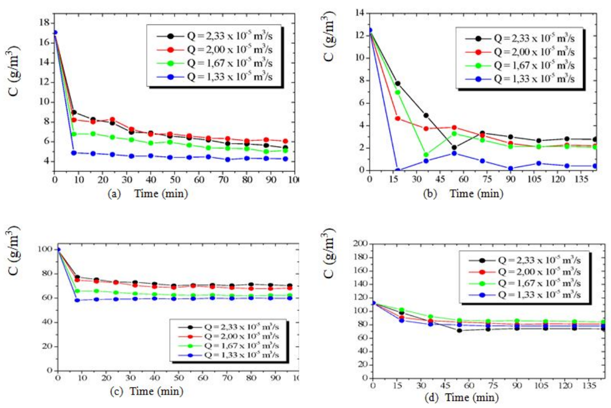

Figure 4: Concentration evolutions of the reactants in the dry reforming processes. Effect of feeding flow rate. (a) ethane, (b) propane. Conditions: cat. $N_i(3.92\%wt.)/\gamma\text{-}Al_2O_3$, 1073 K, 1.0 bar, ethane feed: $C_2H_6:CO_2:Ar=5:20:7$ vv; propane feed: $C_3H_8:CO_2:Ar=2.5:22.5:75$ vv.

The alkane-CO_2 mixtures were processed with the Ni(3.92%wt)/γ-Al_2O_3 catalyst in a continuous fixed bed reactor providing effluents composed of ethane or propane residuals and carbon dioxide, and the products carbon monoxide, hydrogen, water, methane, ethylene, propylene and carbon deposits (coke). The concentration evolutions of the reactants obtained in the operations with four different flow rates are presented (Figure 4) as a function of time. The experimental steady-state values of the concentrations were evaluated as the component concentration left unchanged over the time (90-110 min).

The experimental steady-state values of the concentrations measured in the effluent flow of the reactor enabled quantification of hydrocarbon conversions in both alkane-CO_2 processing. The highest conversions of the alkanes were obtained when a longer spacetime (6.0 $kg_{cat}s/m^3$) was employed.

The concentration evolutions of the hydrogen obtained from the processing of ethane and propane, are shown in Figure 5, while the concentration evolutions of the produced methane are presented in Figure 6.

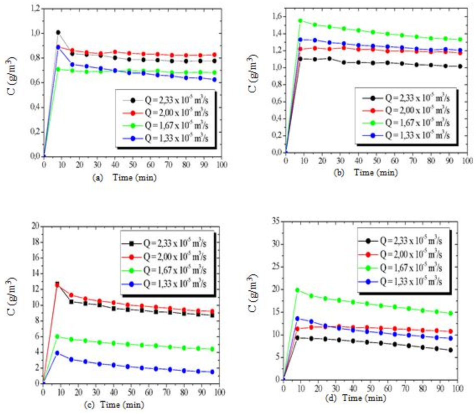

Figure 5: Concentration evolutions of hydrogen in the dry reforming processes. Effect of feeding flow rate. (a) H_2(ethane), (b) H_2(propane). Conditions: cat. N_i(3.92%wt.)/γ-Al_2O_3, 1073 K, 1.0 bar, ethane feed: C_2H_6:CO_2:Ar=5:20:7 vv; propane feed: C_3H_8:CO_2:Ar=2.5:22.5:75 vv.

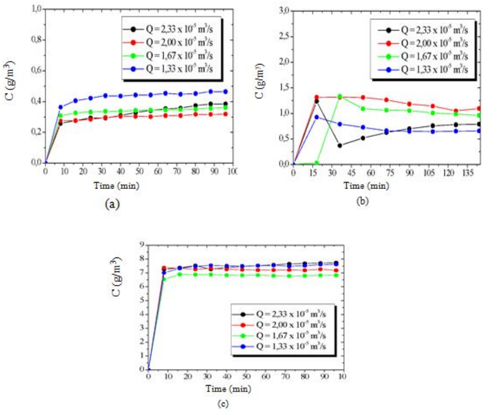

Figure 6: Concentration evolutions of methane in the dry reforming processes. Effect of feeding flow rate. (a) CH_4 (ethane), (b) CH_4 (propane). Conditions: cat. Ni(3.92%wt.)/γ-Al_2O_3, 1073 K, 1.0 bar, ethane feed: C_2H_6:CO_2:Ar=5:20:75 vv; propane feed: C_3H_8:CO_2:Ar=2.5:22.5:75 vv.

Conversions of ethane and propane reached steady-state levels of 32% and 50% at 1023 K, respectively, with higher hydrogen yields (up to 24%) from propane. However, with the 50-degree rise in operating temperature, higher conversions of both alkanes were observed (ethane 74.7%, propane 96.0%), with consequent increase of yields, reaching approximately 35% and 44%, from ethane and propane, respectively.

Modeling and kinetic evaluation

Based on the experimental evidence (Figures 4-6) for both reforming processes, according to analyses taken on line in the effluent gas of the reactor, a set of reaction steps were proposed where the major reaction steps (Table 2) were adopted for kinetic evaluation.

Table 2: Reaction steps of the alkane-CO_2 reforming processes.

Ethane-CO_2 reforming (E)	Propane-CO_2 reforming (P)	Reaction steps
$C_2H_6 \xrightarrow{k_{1E}} \mathrm{Hc} + \mathrm{H_2} + (1/2)\mathrm{C}$	$C_3H_8 \xrightarrow{k_{1P}} (1/2)\mathrm{CH_4} + 3\mathrm{H_2} + (5/2)\mathrm{C}$	Cracking of alkanes
$CO_2 + \mathrm{C} \xrightarrow{k_{2E}} 2\mathrm{CO}$	$CO_2 + \mathrm{C} \xrightarrow{k_{2P}} 2\mathrm{CO}$	Boudouard reverse reaction
$CO + H_2 \xrightarrow{k_{3E}} \mathrm{H_2O} + \mathrm{C}$	$CO_2 + 2\mathrm{H_2} \xrightarrow{k_{3P}} 2\mathrm{H_2O} + \mathrm{C}$	CO-CO_2, H_2 interactions

$Hc \xrightarrow{k_{4E}} 1.5C + 2H_2$	$(1/2)CH_4 \xrightarrow{k_{4P}} (1/2)C + H_2$	Decomposition of products (Hc, CH_4)

*C_2H_4 + CH_4 = Hc, identified as hydrocarbon (Hc).

According to the stoichiometry of the reaction steps, the rates of hydrogen and carbon production in each reform process can be formulated. The relations rjm (j=I, II, III, IV; m=ethane, propane) correspond to the rate laws of the reaction steps of the reforming processes and are expressed as follows:

- Decomposition of ethane and propane (Langmuir-Hinshelwood approach),

$$r_{1E} = \frac{k_{1E}K_{C_2H_6}C_{C_2H_6}}{1 + K_{C_2H_6}C_{C_2H_6}} \quad (1)$$

- Reverse Boudouard reactions;

$$r_{IIE} = k_{2E}C_{CO_2};\ r_{IIP} = k_{2P}C_{CO_2} \quad (2)$$

- Interactions of carbon oxides and hydrogen (Langmuir-Hinshelwood approach), considering weak adsorption of the all intermediate components (CO, CO_2, H_2, H_2O),

$$r_{IIP} = k'_{3E}C_{CO}C_{H_2}, r_{IIP} = k_{2P}C_{CO}C_{H_2}, \quad r_{IIP} = k'_{3E}C_{CO_2}C_{H_2}; k'_{3P} = C_{CO_2}C_{H_2} \quad (3)$$

Consumptions of the products (ethylene, methane; CC_2H_4+CCH_4=CHc) (Langmuir-Hinshelwood approach),

$$r_{IVE} = \frac{k_{4E}K_{Hc}C_{Hc}}{1 + K_{Hc}C_{Hc}};\ r_{IVP} = \frac{k_{4P}K_{CH_4}C_{CH_4}}{1 + K_{CH_4}C_{CH_4}} \quad (4)$$

The global reaction rates of each component (Rim; i=C2H6, C3H8, CH4, Hc, CO2, CO, H2, H2O; m=ethane, propane) were written as follows:

for ethane-CO_2 reforming:

$$R_{C_3H_8P} = -r_{IP}; R_{CH_4P} = 1/2r_{IP} - 1/2r_{IVP}; R_{CO_2P} = -r_{IIP} - r_{IIIP}; R_{H_2P} = 3r_{IP} - r_{IIIP} + r_{IVP}; R_{COE} = 2r_{IIP}$$

- for propane-CO_2 reforming:

$$R_{C_3H_8P} = -r_{IP}; R_{CH_4P} = 1/2r_{IP} - 1/2r_{IVP}; R_{CO_2P} = -r_{IIP} - r_{IIIP}; R_{H_2P} = 3r_{IP} - r_{IIIP} + r_{IVP}; R_{COE} = 2r_{IIP}$$

The evolutions of the reactor effluent concentrations were obtained from mass balances including reaction rates of the reaction steps. The resulting differential equations were expressed as–dCim/dτ+Rim=0, where τ (τ=mcat/Q, kgs/m^3) is the space time. The corresponding initial conditions (τ=$τ_0$) were expressed as follows:

$$C_{C_2H_6}(\tau_0) = C_{C_2H_60};\ C_{C_3H_8}(\tau_0) = C_{C_3H_80};\ C_{CO_2}(\tau_0) = C_{CO_20};\ C_{CO}(\tau_0) = C_{H_2}(\tau_0) = C_{H_2O}(\tau_0) = 0$$

To solve the system of differential equations the numerical method of Runge-Kutta 4th order was employed. A numerical optimization procedure was associated with the solution method where the parameter values were modified by comparing for each component (i) the calculated concentrations. $\left(C_{Th}^{im}\right)$ with the experimental $\left(C_{Exp}^{im}\right)$

ones. The optimized final values of the parameters were obtained by defining a quadratic objective function $f_o(f_o = \sum f_{oi}, f_{oi} = \sum [C_{im}^{Exp} - C_{im}^{Th}]^2)$ applied to the results obtained for all components.

Figure 7 shows calculated versus experimental effluent concentration values for the products (H_2, CO, Hc, from ethane; H_2, CO, CH_4, from propane) obtained at the two operating temperature conditions (1023 K, 1073 K). The order of magnitude of the objective functions were f_O=4.17 × 10^{-2}, and f_O=9.46 × 10^{-2}, for the results of the evaluations carried out with ethane and propane, respectively. Figures 8 and 9 shows calculated versus experimental effluent concentration values for the products (H_2, CO, Alk; H_2, CO, CH_4) obtained at the two operating temperature conditions (1023 K, 1073 K).

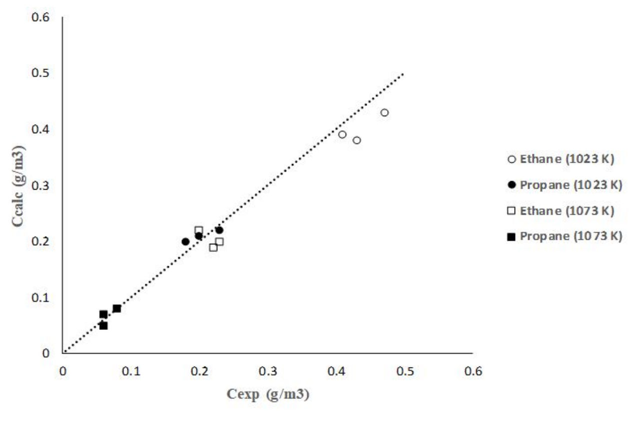

Figure 7: Reforming process ethane-CO_2 and propane-CO_2. Predicted and experimental effluent concentration of products. Conditions: Catalyst Ni(3.92%wt.)/γ-Al_2O_3, 1.0 bar.

The final values of the kinetic parameters are listed in Tables 3 and 4. The specific reaction rates for the cracking stages (I, IV) at 1073 K were of particular note in the kinetic behavior of both processes. Hydrogen production occurred through the steps I and IV with k_{1E}=2.29 × 10^{-2} mol/gcats, k_{4E}=1.11 × 10^{-3} mol/g_{cat}s for ethane dry reforming, and k_{1P}=2.40 × 10^{-3} mol/g_{cat}s k_{4P}=0.85 × 10^{-2} mol/g_{cat}s, for propane dry reforming. By these steps, carbon productions with significant reaction rates are also indicated.

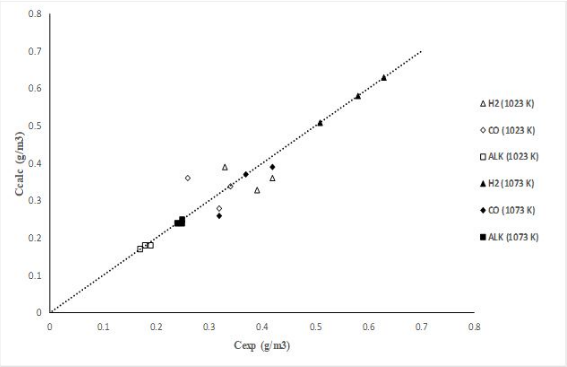

Figure 8: Calculated and experimental effluent concentration values for the products.

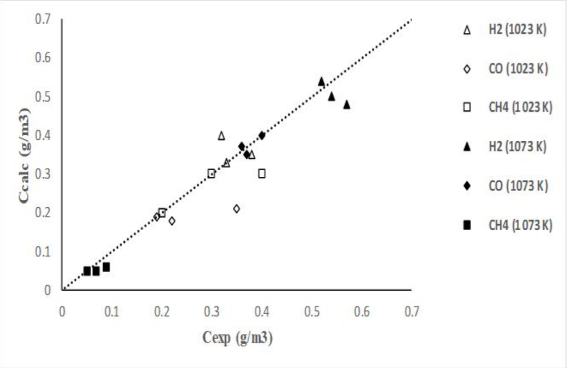

Figure 9: Calculated and experimental effluent concentration values for the products.

Table 3: Kinetic parameters of ethane-CO_2 reforming process. Effect of temperature.

Parameter	1023 K	1073 K
k_{1E} (mol/g_{cat}s)	(7.30 ± 0.11) × 10^{-4}	(2.29 ± 0.03) × 10^{-2}
k_{2E} (m^3/g_{cat}s)	(2.50 ± 0.08) × 10^{-5}	(3.06 ± 0.09) × 10^{-5}
k'_{3E} ((m^3)^2/g_{cat}smol)	(1.24 ± 0.04) × 10^{-6}	(2.81 ± 0.08) × 10^{-5}
k_{4E} (mol/g_{cat}s)	(1.69 ± 0.03) × 10^{-4}	(1.11 ± 0.02) × 10^{-3}

Considering the set of four steps for each of the alkanes as competitive reaction steps, kinetic selectivities (Sim=[kim/ Σkim] × 10^2, i=1, 2, 3, 4; m=E-ethane, P-propane) were calculated to highlight the fastest reaction steps related to the hydrogen production. For ethane dry reforming S_{1E}=95.42% and S_{4E}=4.58%, while for propane dry reforming S_{1P}=21.74% and S_{4P}=76.99%. Thus, during the operation of dry reforming of natural gas, in addition to the hydrogen obtained from methane, the alkane contributions to hydrogen production can occur mainly by the cracking of ethane (step I, ethane) and cracking of the produced methane from propane (step IV, propane).

Table 4: Kinetic parameters of propane-CO_2 reforming process. Effect of temperature. Conditions: Catalyst N_i(3.92%wt.)/γ-Al_2O_3, 1.0 bar.

Parameter	1023 K	1073 K
k_{1P} (mol/g_{cat}s)	(6.39 ± 0.10) × 10^{-4}	(0.85 ± 0.04) × 10^{-2}
k_{2P} (m3/g_{cat}s)	(2.31 ± 0.07) × 10^{-5}	(3.89 ± 0.12) × 10^{-5}
k'_{3P} ((m3)2/g_{cat}smol)	(9.17 ± 0.30) × 10^{-5}	(1.03 ± 0.03) × 10^{-4}
k_{4P} (mol/g_{cat}s)	(8.06 ± 0.12) × 10^{-3}	(2.40 ± 0.13) × 10^{-3}

The orders of magnitude of the adsorption constants of the reactants and intermediate hydrocarbons (methane, ethylene) were also estimated by the model adjustments, being in the range of order of magnitude of 0.012 to 1.11 m^3/mol. These values are considered indicators of relatively strong adsorption of these components, aspects that favor their activation on the surface of the catalyst and consequent decomposition to hydrogen.

Given the presence of alkanes (ethane, propane) in the natural gas feed, attention was paid to their contributions in the product composition according to their conversion through dry reform. Thus, two main aspects are highlighted: the additional production of hydrogen from the alkanes and the increase of coke formation, due to the production of carbon.

An evaluation based on the mechanisms indicated in Table 1 was made from the following global chemical equations:

- for the dry reforming of ethane, $C_2H_6+CO_2 \rightarrow 2H_2+2C+H_2O+CO$;

- for the dry reforming of propane, $C_3H_8+2CO_2 \rightarrow 2H_2+3C+2H_2O+2CO$

The predominant presence of methane in the natural gas indicated the need to include data concerning the dry reform of this component ($CH_4+CO_2 \rightarrow H_2+3CO + H_2O$), as collected in a previous work.

Assuming the processing of a natural gas (NG, Brazilian natural gas, Guamaré, ANP, Brazil) of composition CNG: CH_4 (85.45% vv), C_2H_6 (8.26% vv), C_3H_8 (3.06% vv), and considering the conversions reached in the present work, the yields (YH_2, YC) were obtained based on natural gas feed composition, as follows:

-for hydrogen,

$Y_{H2} = \sum_m \left(X_m \upsilon_{H2m} C_{m0} 10^2 C_{NG}^{-1}\right)$; $\upsilon_{H2-ETHANE}$, -for carbon, $\upsilon_{H2-PROPANE} = 2$

$$Y_c = \sum_m \left(X_m \upsilon_{Cm} C_{m0} 10^2 C_{NG}^{-1}\right);\ \upsilon_{c-ETHANE}, \upsilon_{c-PROPANE} = 3$$

Where Cm0 and Xm are alkane initial concentration and conversion, respectively. Table 5 lists the values of hydrogen and carbon yields.

Table 5: Evaluation of natural gas dry reforming processes. Hydrogen and carbon molar yields. Conditions: Cat. N_i (3.92% weight)/γ-Al_2O_3; 1073 K, 1.0 bar; τ=6.0 kg/m^3.

Reforming process	Xm (%)	YH_2 (%)	YC (%)
Methane-CO_2*	84.23	74.17	----
Ethane-CO_2	74.71	12.75	12.75
Propane-CO_2	96	7,14	10.71
NG	81.07	95.06	23.46
* Abreu et al.			

Natural gas rich in methane increased the production of hydrogen via dry reforming due to the contributions of the other alkanes present in the feed composition. Operating in a fixed bed reactor, additional hydrogen production was obtained in relation to that obtained from methane, whose yield was 74.61%. From the conversions of the major components of natural gas (methane, ethane, propane) it was obtained about 95% of molar hydrogen yield, where 19% were from alkanes different from methane. From these alkanes, the carbon formation was quantified as a molar yield of 23%.

In view of these results and considering the significant increased hydrogen production due to the light alkane conversions by dry reforming, an adequate supply of carbon dioxide is recommended to prolong the catalyst activity and, consequently, to allow a longer campaign time for the processing unit. In this case, carbon dioxide fed in excess, and acting mainly through the Reverse Boudouard reaction, may have reduced catalyst deactivation due to coke deposition.

CONCLUSION

The reforming of light alkanes of natural gas with carbon dioxide was carried out at 1073 K under atmospheric pressure employing a nickel catalyst (3.92%wt) supported on gamma alumina. Taking into account the individual conversions of the main components of natural gas (84.23%, methane; 74.71%, ethane; 96.00%, propane), a hydrogen molar yield of 95.06% was obtained, where the contribution of 20% was due to the light alkanes, ethane, and propane. From these alkanes, the carbon formation reported as occurring through the cracking reactions of the dry reform, was quantified, reaching a molar yield of 23%.

Reaction steps in the reforming process were considered as competitive reactions and the specific cracking reaction rates of both light alkanes were used to quantify the kinetic selectivities of hydrogen, calculated as 95.42% for ethane and 76.99% for propane.

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