

## Kinetics and Modelling Study of The Catalytic Reaction of Methane and Hydrogen Sulphide Over Mo/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> Catalyst

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### ABSTRACT

Catalytic steam reforming is a widely used method today either to produce hydrogen or to give syngas as the first step for the conversion of methane into liquid fuels through the Fischer-Tropsch synthesis.

The reforming of CH<sub>4</sub> by H<sub>2</sub>S can be considered as an alternative route to produce hydrogen from methane. With this process, the removal of H<sub>2</sub>S in natural gas streams is no longer necessary and sulfur, usually considered as a strong pollutant on liquid fuels in refineries, is used as a reagent in H<sub>2</sub>S form of hydrodesulphurization processes. This alternative produces hydrogen, a valuable chemical and clean energy source, as the principal product and carbon disulphide as a secondary petrochemical.

The open literature concerning the kinetic study of the methane-hydrogen sulphide reaction is very poor. In this research the reaction of CH<sub>4</sub> and H<sub>2</sub>S over zirconia catalyst modified with lanthanum oxide impregnated with molybdenum has been studied in a fixed bed tubular reactor varying the inlet CH<sub>4</sub> flow rate over a temperatures range of 1023 – 1323 K and feed molar ratio CH<sub>4</sub>:H<sub>2</sub>S of 1:12. The Langmuir-Hinshelwood theory has been used to analyze kinetic models. Model discrimination has been performed and the kinetic parameters and adsorption constants calculated.

Finally, the simulation process of reforming CH<sub>4</sub> by H<sub>2</sub>S has been developed in which separation of the produced hydrogen and no reacted H<sub>2</sub>S involves absorption through diethanolamine. A tubular reactor from kinetic parameters was dimensioned. Aspen Plus ® 11.1 and Hysys V.8 simulation software was used. Preliminary results showed a high purity H<sub>2</sub> can be produced by this route.

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*Keywords: reforming, hydrogen, kinetics*



## 1. Introduction

Hydrogen, in addition to be used as essential in the industry of petroleum for obtaining improved fuels, is considered an attractive energy supply because it can be burned like gasoline and natural gas, or converted to electricity without any carbon emissions at the point of use [1]. Its main advantage is that its combustion produces only water, which means that does not emit greenhouse gases, such as fossil fuels and biomass. This makes it particularly appropriate to replace the petroleum-based products.

Catalytic reforming of  $\text{CH}_4$  and  $\text{H}_2\text{S}$  to produce  $\text{H}_2$  and  $\text{CS}_2$  has experimental evidence recorded by little research over the years. Mass catalysts or simple supports that have been used, given their catalytic properties, do not meet the needs of activation, selectivity or stability required for this reaction.

Recently, research has been focusing on the structure of catalysts that have characteristics that generate high potential for conversion on moderate conditions of operation and that could be the basis of an interesting option of process in the production of hydrogen. One of these catalysts is zirconia catalyst modified with lanthanum oxide impregnated with molybdenum,  $\text{Mo/La}_2\text{O}_3\text{-ZrO}_2$ , which has shown some advantages in the improvement of the properties of the catalyst [1].

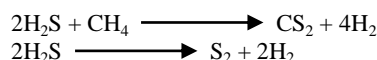
In this work, kinetics of the reactive system reforming of  $\text{CH}_4$  by  $\text{H}_2\text{S}$  using  $\text{Mo/La}_2\text{O}_3\text{-ZrO}_2$  catalyst, based on the methodology of Langmuir-Hinshelwood-Hougen-Watson was studied. Pilot plant experimental data of conversion for a range of temperatures and residence times were obtained and, by means of them, it was determined which kinetic model among several possible gave the best fit to the experimental data. The kinetic parameters and adsorption constants of the model of the best fit were obtained.

In order to observe an engineering application of the results of the project, two simulation models were created: one to propose a process flowsheet that, based on the conditions of the reaction studied, allows obtain and separate from the reaction system products with commercially acceptable purity. The other is for calculating the sizing of a tubular reactor for a given production, based on the kinetic parameters and adsorption constants calculated.

## 2. Experimental

### 2.1 Proposed kinetic mechanism and models

Catalytic reactions involved in this research work, for the kinetic study of the reforming of methane with hydrogen sulfide are as follows:



In the temperature range in which we worked, the reaction of pyrolysis of methane can be ignored [2].

The reactions of table 1 represent the mechanism proposed for this study. Writing rate expressions every step is considered as an elementary reaction; the only difference is that the concentration of the species in gas phase is replaced by its respective partial pressures.

Table 1. Steps of a Langmuir-Hinshelwood kinetics mechanism

$\text{CH}_4 + (\text{s}) \rightleftharpoons \text{CH}_2(\text{s}) + \text{H}_2$	Adsorption
$4\text{H}_2\text{S} + 4(\text{s}) \rightleftharpoons 4\text{S}(\text{s}) + 4\text{H}_2$	
$\text{CH}_2(\text{s}) + 2\text{S}(\text{s}) \rightleftharpoons \text{CS}_2(\text{s}) + \text{H}_2 + 2(\text{s})$	Surface reaction
$\text{S}(\text{s}) + \text{S}(\text{s}) \rightleftharpoons \text{S}_2(\text{s}) + (\text{s})$	
$\text{CS}_2(\text{s}) \rightleftharpoons \text{CS}_2 + (\text{s})$	Desorption
$\text{S}_2(\text{s}) \rightleftharpoons \text{S}_2 + (\text{s})$	



The expressions of rate for adsorption of methane and hydrogen sulfide are:

$$r_{AD1} = k_{A1} \left( P_{CH_4} \cdot C_V - \frac{C_{CH_2(s)}}{K_{CH_4}} \cdot P_{H_2} \right) \quad (1)$$

$$r_{AD2} = k_{A2} \left( P_{H_2S}^4 \cdot C_V^4 - \frac{C_{S(s)}^4}{K_{H_2S}} \cdot P_{H_2}^4 \right) \quad (2)$$

The expressions of rate for the step of surface reactions that produce adsorbed carbon disulfide and sulfur and hydrogen in gaseous phase are:

$$r_{s1} = k_{rs1} \left[ C_{CH_2(s)} \cdot C_{S(s)}^2 - \frac{C_{CS_2(s)} \cdot P_{H_2} \cdot C_V^2}{K_{rs1}} \right] \quad (3)$$

$$r_{s2} = k_{rs2} \left[ C_{S(s)} \cdot C_{S(s)} - \frac{C_{S_2(s)} \cdot C_V}{K_{rs2}} \right] \quad (4)$$

The expressions of rate for desorption of the carbon disulfide and sulfur are:

$$r_{D1} = k_{D1} \left( C_{CS_2(s)} - \frac{P_{CS_2} \cdot C_V}{K_{DCS_2}} \right) \quad (5)$$

$$r_{D2} = k_{D2} \left( C_{S_2(s)} - \frac{P_{S_2} \cdot C_V}{K_{DS_2}} \right) \quad (6)$$

For the mechanism postulated in the sequence given by table 1, we want to determine the limiting step of the speed. First it is supposed that one of the steps limits speed (controls rate) and then rate expressions are formulated in terms of partial pressures of the present species.

a) Assuming surface reactions is the rate controlling step.

$$r_{s1} = k_1 \left[ \frac{P_{CH_4} P_{H_2S}^2}{P_{H_2}^3} - \frac{P_{CS_2} \cdot P_{H_2}}{K_{e1}} \right] \frac{1}{Q_r^3} \quad (7)$$

$$r_{s2} = k_2 \left[ \frac{P_{H_2S}^2}{P_{H_2}^2} - \frac{P_{S_2}}{K_{e2}} \right] \frac{1}{Q_r^2} \quad (8)$$

where

$$\left[ 1 + \frac{K_{CH_4} \cdot P_{CH_4}}{P_{H_2}} + \frac{K_{H_2S} \cdot P_{H_2S}}{P_{H_2}} + K_{CS_2} \cdot P_{CS_2} + K_{S_2} \cdot P_{S_2} \right] = Q_r \quad (9)$$

b) Assuming adsorption of methane and hydrogen sulfide over the surface is the rate controlling step.

$$r_{AD1} = k_1 \left[ P_{CH_4} - \frac{P_{CS_2} \cdot P_{H_2}^2}{K_{e1}} \right] \frac{1}{Q_r} \quad (10)$$

$$r_{AD2} = k_2 \left[ P_{H_2S} - \frac{P_{S_2}^{0.5} \cdot P_{H_2}}{K_{e2}} \right] \frac{1}{Q_r} \quad (11)$$



where

$$\left[ 1 + \frac{K_{CS_2} \cdot P_{CS_2} \cdot P_{H_2} \cdot K_{rs2}}{K_{rs1} \cdot K_{S_2} \cdot P_{S_2}} + \frac{K_{S_2}^{0.5} \cdot P_{S_2}^{0.5}}{K_{rs2}^{0.5}} + K_{CS_2} \cdot P_{CS_2} + K_{S_2} \cdot P_{S_2} \right] = Q_r \quad (12)$$

c) Assuming desorption of the carbon disulfide and sulfur from the surface is the rate controlling step.

$$r_{D1} = k_1 \left[ \frac{P_{CH_4} \cdot P_{H_2S}^2}{P_{H_2}^4} - \frac{P_{CS_2}}{K_{e1}} \right] \frac{1}{Q_r} \quad (13)$$

$$r_{D2} = k_2 \left[ \frac{P_{H_2S}^2}{P_{H_2}^2} - \frac{P_{S_2}}{K_{e2}} \right] \frac{1}{Q_r} \quad (14)$$

where

$$\left[ 1 + \frac{K_{CH_4} \cdot P_{CH_4}}{P_{H_2}} + \frac{K_{H_2S} \cdot P_{H_2S}}{P_{H_2}} + \frac{K_{CH_4} \cdot P_{CH_4} \cdot K_{H_2S}^2 \cdot P_{H_2S}^2 \cdot K_{rs1}}{P_{H_2}^4} + \frac{K_{H_2S}^2 \cdot P_{H_2S}^2 \cdot K_{rs2}}{P_{H_2}^2} \right] = Q_r \quad (15)$$

## 2.2 Procedure for the analysis of the models and estimation of the kinetics parameters

A number of experimental sets were carried out in a tubular reactor varying molar feed flows with Mo/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst and operating in the temperature range: 750 - 1050 ° C. The mass of the catalyst was fixed as 3 g and the rest of operating parameters remained constant. Volumetric feed flows used are shown in table 2.

Table 2. Variation of feed flows

Volumetric feed flows		
Experimental run	CH <sub>4</sub> (L/h)	H <sub>2</sub> S (L/h)
1	0.189	2.268
2	0.236	2.83
3	0.315	3.78
4	0.4725	5.67
5	0.945	11.34

The experiments were conducted in the CGA-VI microplanta located in the "Laboratorio de evaluación en microplanta y escalamiento de catalizadores" of the Instituto Mexicano del Petróleo in Mexico D. F. The system mainly consists of three sections:

1st Feed section; consists of a control of supply of gas with mass controllers.

2<sup>a</sup> Reaction section; consists of a vertical fixed bed tubular reactor of quartz, equipped with an oven Thermolyne 11000 with internal temperature controller.

3<sup>a</sup> Identification of reaction products section; has a gas chromatograph mark Varian Star 3400 CX equipped with a capillary column HP plot - Q phase of polymer divinylbenzene with a length of 30 mm and inner diameter 530µm.

Measurement of the compositions of inlet and outlet of the reactor allowed to calculate variables to graph results. These are: the total conversion of methane ( $x_{CH_4}$ ) and the conversion of H<sub>2</sub>S to S<sub>2</sub> ( $x_{S_2}$ ) versus residence time,  $\tau$ .

$$x_{CH_4} = \frac{\text{mole of inlet } CH_4 - \text{mole of outlet } CH_4}{\text{mole de inlet } CH_4} \quad (16)$$

$$x_{S_2} = \frac{\text{mole of outlet } S_2}{\text{moles of inlet } H_2S} \quad (17)$$



$$\tau = m_{cat}/F_{CH_4}^E \quad (18)$$

$m_{cat}$  = mass of catalyst

$F_{CH_4}^E$  = molar feed plow of methane

a) Conversions were calculated: total conversion of methane and conversion of  $H_2S$  to  $S_2$  as a function of inlet and outlet moles of species. Moles were calculated by means of the experimental data of composition obtained for the different values of temperature in the range of 750°C a 1050°C and at the different values of residence times in the range of 0.5 a 1.5 kgcat.h/mole.

b) For a given temperature, through Excel, constants were calculated fitting polynomial function to the experimental data curves conversion versus residence time ( $\tau$ ),

$$x_{CH_4} = a_0 + a_1\tau + a_2\tau^2 + a_3\tau^3 \quad (19)$$

and

$$x_{S_2} = b_0 + b_1\tau + b_2\tau^2 + b_3\tau^3 \quad (20)$$

c) By means of the equations

$$r_{CH_4} = \frac{\partial x_{CH_4}}{\partial \tau} = a_1 + 2a_2\tau + 3a_3\tau^2 \quad (21)$$

and

$$r_{S_2} = \frac{\partial x_{S_2}}{\partial \tau} = b_1 + 2b_2\tau + 3b_3\tau^2 \quad (22)$$

A table of values of reaction rate versus residence time was obtained for each temperature.

d) Since

$$r_{CH_4} = r_{s1}$$

and

$$r_{S_2} = r_{s2}$$

We have now the information needed to calculate the values of the kinetic rate constants  $k_1$  and  $k_2$ , as well as the values of the constants of adsorption equilibrium  $K_{CH_4}$ ,  $K_{H_2S}$ ,  $K_{CS_2}$  and  $K_{S_2}$ , through an iterative calculation procedure, assuming that they depend only on the temperature. Computer program Polymath was used; this program lets you know so well is the fitting that makes the model to the experimental data and, as a consequence, compare models.

e) Based on the results obtained in the last step for the best model, pre-exponential factors of reaction rate,  $A_j$ , where  $j = 1, 2$  and pre-exponential factors of adsorption,  $A_{adi}$ , where  $i = CH_4, H_2S, CS_2, S_2$ , are calculated. Also activation energies,  $E_j$ , and adsorption enthalpies,  $\Delta H_i$  are obtained in the same calculation. For these calculations, values of  $k_j$  vs  $T$  and  $K_{adi}$  vs  $T$ , obtained in the last step are used, as well as the well-known equations

$$\ln k_j = \ln A_j - \frac{E_j}{R} \left( \frac{1}{T} \right) \quad (23)$$

$$\ln K_{adi} = \ln A_{adi} - \frac{\Delta H_i}{R} \left( \frac{1}{T} \right) \quad (24)$$

A graph  $\ln k_j$  o  $\ln K_{adi}$  as a function of  $(1/T)$  is built, according to we are calculating [3].



### 2.3 Process flowsheet

The proposed process flowsheet was created with the support of process Simulator Aspen plus and has as basic initial part a stoichiometric reactor, *Rstoic*, in which occur the following reactions:



at 950° C, 1 atmosphere of pressure and with a feed molar relationship of  $\text{H}_2\text{S}/\text{CH}_4 = 12$ . Fractional conversions of 0.99 and 0.28 were given as data, respectively.

### 2.4 Sizing of a tubular reactor

The size of a reactor for the rates of reactants used in process flowsheet of the last section was calculated for a catalytic reactor using, process simulator Hysys V8.4 and *Plug flow reactor model*.

## 3. Results and discussion

### 3.1 Kinetic study of the reactive system

Plots of conversion versus residence time are shown as figure 1 y 2.

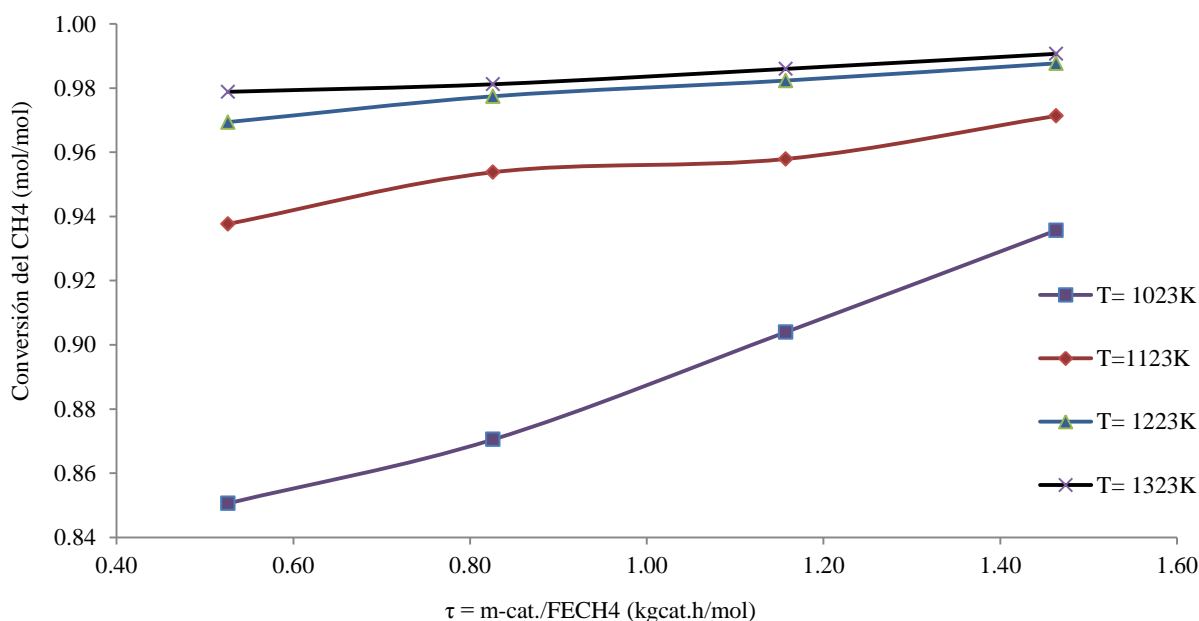


Figure 1 Total conversion of  $\text{CH}_4$  vs residence time at different temperatures, with a feed relation of  $\text{CH}_4:\text{H}_2\text{S}$  (1:12) and  $\text{Mo/La}_2\text{O}_3\text{-ZrO}_2$  as catalyst.



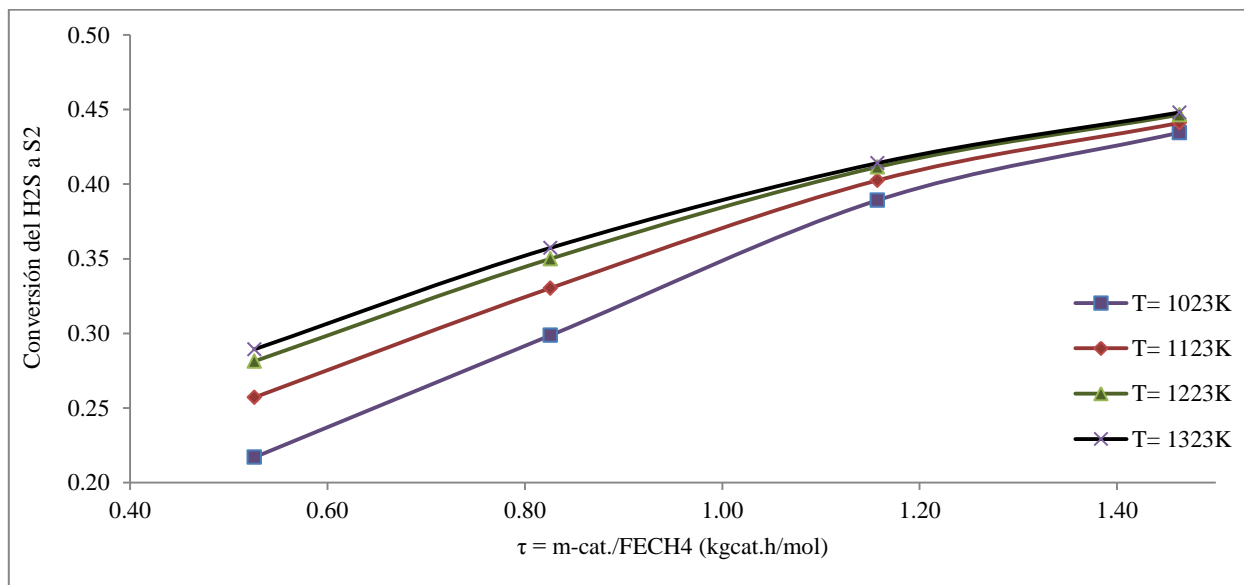


Figure 2 Total conversion of  $\text{H}_2\text{S}$  a  $\text{S}_2$  vs residence time at different temperatures, with a feed relation of  $\text{CH}_4:\text{H}_2\text{S}$  (1:12) and  $\text{Mo/La}_2\text{O}_3\text{-ZrO}_2$  as catalyst.

For each temperature, at a given value of  $\tau$  the reaction rates  $r_{\text{CH}_4}$  y  $r_{\text{S}_2}$  were calculated with the corresponding quadratic equations. Partial pressures of the species at the given  $\tau$  value were calculated with the equation  $P_i = (n_i / n_T)P$  were  $n_i$  are moles of specie  $i$  y  $n_T$  are total moles. Both,  $n_i$  y  $n_T$ , were calculated as a function of the fractional conversions  $x_{\text{CH}_4}$  y  $x_{\text{S}_2}$  at the given value of  $\tau$ .

The next step was proving the proposed kinetic models because we already had a table of reaction rate versus residence time and versus  $P_i$ , for each temperature.

The values of kinetic constants  $k_1$  y  $k_2$  as well as the values of the adsorption constants  $K_{\text{CH}_4}$ ,  $K_{\text{H}_2\text{S}}$ ,  $K_{\text{CS}_2}$  y  $K_{\text{S}_2}$ , were solved for each proposed kinetic model, by means of the software Polymath using the Levenberg-Marquardt (LM) algorithm for non-linear regression. Values of the results of variance and Rmsd (Root mean square deviation) are shown in table 3. These indicators were used for comparison of various models representing the same dependent variable and thus be able to make a discrimination among them. The model with the smaller variance and Rmsd represents data with more accuracy.

For the present study, the surface reaction model generates smaller values of indicators. There is a good concordance, which implies that the proposed mechanism could be correct and the controlling step of the speed is the surface reaction.

Table 3 Variances and Rmsd of solved models, using the Levenberg-Marquardt algorithm

Temperature K	Surface reaction		Adsorption		Desorption	
	Variance	Rmsd	Variance	Rmsd	Variance	Rmsd
1023	0.5141	0.1179	0.2160	0.0765	<b>0.0290</b>	<b>0.0281</b>
1123	<b>0.0426</b>	<b>0.0340</b>	12.010	0.5762	0.0885	0.0489
1223	<b>0.1588</b>	<b>0.0650</b>	0.5994	0.1273	0.1634	0.0665
1323	<b>0.0055</b>	<b>0.0122</b>	0.0170	0.0215	0.2147	0.0762



Once it was concluded which was the kinetic model that better fit the experimental data, we have the kinetic constants and equilibrium adsorption constants. In table 4 can be observed the values of the kinetic constants  $k_1$  y  $k_2$  and equilibrium adsorption constants  $K_{CS_2}$  y  $K_{S_2}$ ,  $K_{CH_4}$ ,  $K_{H_2S}$  obtained, taking the surface reactions as the rate controlling step.

Table 4 Values of the kinetic constants and equilibrium adsorption constants as a function of temperature.

Constants	Temperature (K)			
	1023	1123	1223	1323
$k_1$	139.66	244.56	550.27	581.42
$k_2$	267.40	329.53	586.82	588.82
$K_{CS_2}$	71.27	33.29	7.88	6.90
$K_{S_2}$	6.05	11.00	4.05	3.50
$K_{CH_4}$	102.00	102.00	102.00	102.00
$K_{H_2S}$	2.83	3.73	1.62	1.50

Finally, pre-exponential factors, activation energies and adsorption enthalpies were calculated. Results are shown in table 5.

Table 5 Kinetic parameters and adsorption constants.

Reaction	A(mol/kgcat.h)	E(J/mol)
R1	129,832.44	57,910.73
R2	13,164.78	33,326.42

Specie	Aad (bar <sup>-1</sup> )	ΔH (J/mol)
CS <sub>2</sub>	0.00095	-95,656.41
S <sub>2</sub>	0.3063	-27,968.97
CH <sub>4</sub>	101.99 bar	-0.5285
H <sub>2</sub> S	0.1012 bar	-29,961.71

### 3.2 Process flowsheet

Results of variables in the important currents of input and output of the proposed flowsheet are observed in table 6:





Table 6 Results of the main streams of the flowsheet.

Component	CH <sub>4</sub>	H <sub>2</sub> S	H <sub>2</sub>	CS <sub>2</sub>	S <sub>2</sub>
Molar flow (kmol/h)	100.0	690.0	890.9	94.5	485.3
Molar fraction	1.0	1.0	0.996	0.993	0.992
Temperature (°C)	25.0	25.0	26.3	46.4	150.0
Pressure (at.)	1.0	1.0	10.0	1.0	1.0
Vapor fraction	1.0	1.0	1.0	0.0	0.0

It can be observed high purity in all products and significant production of hydrogen, since it is produced in both reactions.

### 3.3 Sizing of a tubular reactor

Figure 3 shows the variation of the flows of the components versus length of the reactor calculated with the hysys simulator. It can be observed that all flows reach stabilization on three meters of length.

The size of the tubular reactor is:

Diameter: 30 cm

Length: 3 meters

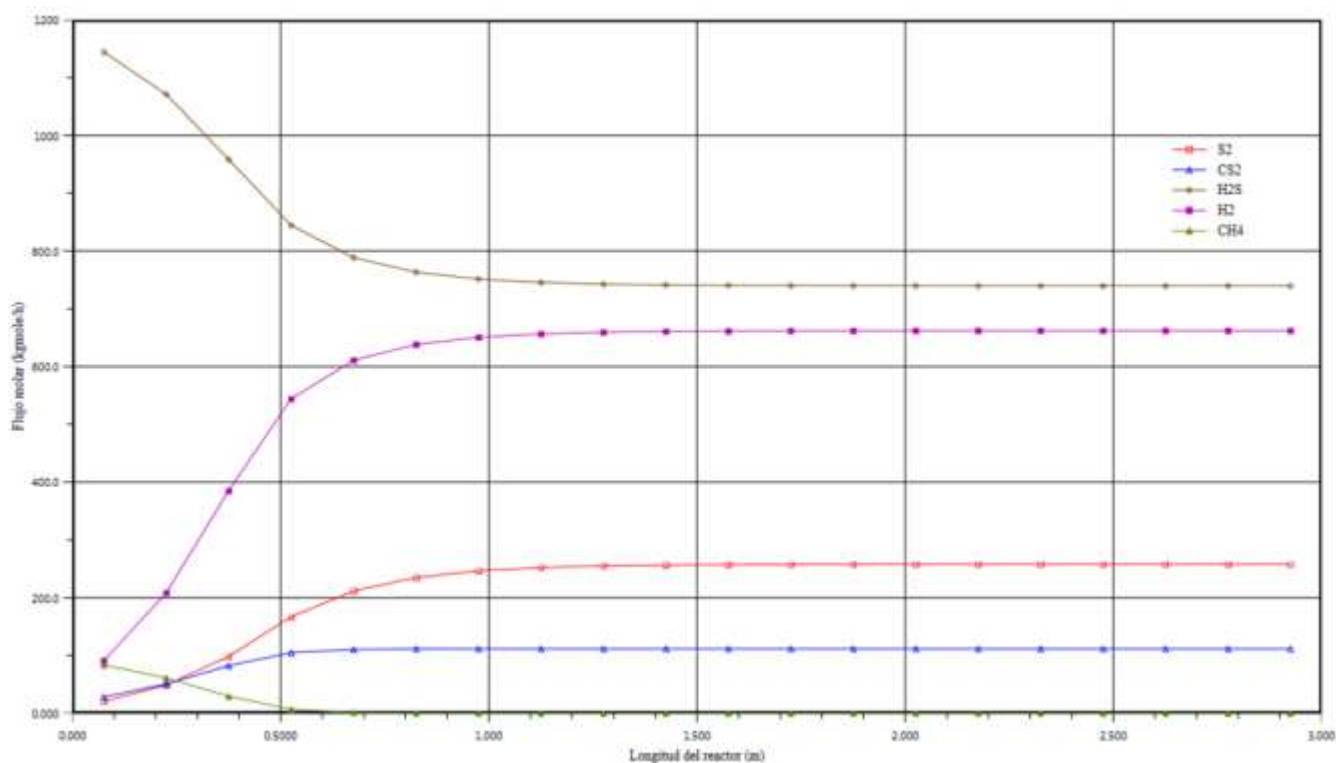


Figure 3 Variation of the flows of the components of the reforming of CH<sub>4</sub> with H<sub>2</sub>S as a function on the length of the reactor.



#### 4. Summary and perspectives

One could conclude that the best of the proposed models is that considered surface reaction as controlling rate step. Values of the kinetic parameters and the adsorption constants were obtained as a result of the regression analysis.

Build the process flowsheet with the Aspen Plus Simulator, it was observed that it is possible to get and separate the three products of the reactive system with high purities and controlling the purity of the main product based on a separation of hydrogen sulfide by absorption in diethanolamine.

The size of the basic equipment of the process, which is the tubular reactor, is reasonable: three meters in length and 30 centimeters in diameter.

#### Acknowledgements

We gratefully acknowledge the financial support of this work by Instituto Mexicano del Petróleo.

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