Minimization of Exergy Destruction Costs for the Production of Hydrogen from Methane Cracking

Federico Gutiérrez, Federico Méndez.

Abstract— **In the present work, the conservation principles (energy and species) and the second law of thermodynamics are used to determine the generated entropy in a thermochemical reactor that produces hydrogen from the thermal cracking of methane. The developed model is coupled to a genetic algorithm code to minimize the entropy. Finally, the minimum generated entropy is related with the exergy destruction costs through a thermoeconomic cost balance and the Gouy-Stodola theorem.**

Index Terms— **Entropy generated, genetic algorithms, hydrogen, methane.**

I. INTRODUCTION

The extensive use of fossil fuels has produced unfavorable phenomena as pollution or global warming. The methane thermal cracking is a promising clean process to produce hydrogen and carbon black with the benefit of low green house gas emissions. Here, the thermal cracking process is induced by a uniform solar thermal energy and with zero CO_2 emissions occur during the process [1]. The overall reaction can be described as,

$$CH_4 \rightarrow C + 2H_2 \quad . \tag{1}$$

On the other hand, exergy is an appropriate concept for assigning costs to the interactions that the system experiences with its surroundings. A pure thermodynamic analysis must reveal the main sources of irreversibility; however, in practical cases is necessary to know the inefficiency costs. Therefore, a complete analysis that takes into account the exergy costs must include thermodynamic and economic point of views. Exergy destruction is related directly with entropy generation ($\dot{S}_{gen}$) through the Gouy – Stodola theorem [2],

$$\dot{W}_{lost} = \dot{E}_D = T_d \dot{S}_{gen}, \tag{2}$$

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here T_d is the dead state temperature. Work lost ($\dot{W}_{lost}$) or exergy destroyed ($\dot{E}_D$) depends on the nature of process and it accounts the inherent irreversibilities of a system.
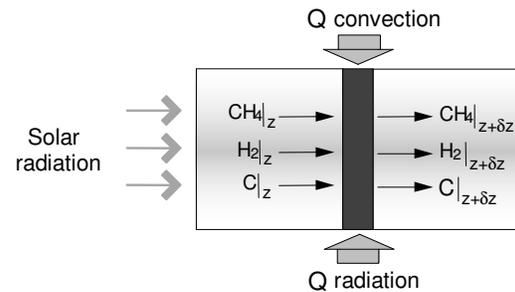

Fig. 1. Reactor scheme

II. ANALYSIS

The entropy generation for the thermal cracking of methane is analyzed by proposing a one-dimensional tubular reactor model. Inside the reactor is continuously circulating a mixture of methane gas and carbon particles, the last ones with the aim of enhance the radiative heat transfer to the gas. For simplicity, both phases are considered at the same temperature. Fig. 1 shows the physical model of the solar reactor.

A. Energy balance

Applying an energy balance to the solar reactor leads to [3],

$$\frac{F_M^0}{v_g} \frac{\partial T}{\partial t} \left(C_{p_M}(1 - X) + 2C_{p_{H_2}} X + C_{pc} \left(\frac{F_C^0}{F_M^0} + X \right) \right)$$
$$+ \frac{F_M^0}{v_g} \frac{\partial X}{\partial t} \left(-H_M + 2H_{H_2} + H_C \right)$$
$$= -F_M^0 \frac{\partial T}{\partial z} \left(C_{p_M}(1 - X) + 2C_{p_{H_2}} X + C_{pc} \left(\frac{F_C^0}{F_M^0} + X \right) \right)$$
$$- F_M^0 \frac{\partial X}{\partial z} \left(-H_M + 2H_{H_2} + H_C \right)$$
$$+ h_w \pi d(T_w - T) + \frac{\varepsilon_c \sigma F_C^0 M_{wc} a_c}{v_g V_c \rho_c} \left(1 + \frac{F_M^0}{F_C^0} X \right) (T_w^4 - T^4), \tag{3}$$

here F_i^0 represents the entrance molar flow rate of the specie i (i = methane, carbon or hydrogen), v_g is the velocity of the mixture, C_{p_i} is the specific heat, H_i is the absolute enthalpy, h_w is the convective coefficient, d is the diameter

of the reactor, ε_c is the emissivity coefficient, σ Boltzmann constant, M_{wc} is the molecular weight of carbon, a_c and V_c is the area and volume of a carbon particle, respectively. ρ_c is the carbon density, t is time, z is the longitudinal coordinate of the reactor, T_w is the wall temperature, T is the mixture temperature, and X is the conversion of methane to hydrogen and carbon. In the above (3), we assume a uniform pressure inside of the reactor and the thermal diffusive effects are neglected.

B. Species conservation balance

Applying the mass conservation principle to the methane, we obtain [4], [5]:

$$\frac{\partial X}{\partial t} + v_g \frac{\partial X}{\partial z} = K_0 \exp\left(-\frac{E_a}{RT}\right)(1-X) \quad . \tag{4}$$

Here K_0 is the frequency factor, E_a is the activation energy and R is the universal gas constant.

C. Entropy generation

Applying an entropy generation analysis to the tubular reactor (see [4] and [6]) leads to:

$$\dot{S}_g' = \left(h_w(T_w - T) + \frac{\varepsilon_c \sigma M_{wc} F_C^0 a_c}{\pi d v_g V_c \rho_c}(T_w^4 - T^4)\right)\frac{A}{T^2}\frac{\partial T}{\partial z}$$
$$+ \frac{A}{T}\left[(H_M - 2H_{H_2} - H_C) - T(S_M - 2S_{H_2} - S_C)\right]r_M \quad . \tag{5}$$

$\dot{S}_g'$ is the entropy generation rate per unit length, A is the transversal area of the reactor, S_i is the absolute entropy, and r_M is the reaction rate.

III. NON DIMENSIONAL ANALYSIS

We can use the following dimensionless variables:

$$\theta = \frac{T}{T_w}, \tag{6}$$
$$\zeta = \frac{z}{L}, \tag{7}$$
$$\tau = \frac{t}{t_0}, \tag{8}$$
$$\Phi = \frac{\dot{S}_g}{\dot{S}_0}, \tag{9}$$

where L is the length of the reactor, t_0 is a reference operation time and $\dot{S}_0$ is a reference entropy defined lines below. Therefore, applying the previously dimensionless variables, the energy equation transforms

$$\alpha_1(1 + \beta_1 X)\left(\alpha_4 \frac{\partial \theta}{\partial \tau} + \frac{\partial \theta}{\partial \zeta}\right)$$
$$= (1 - \beta_2 \theta)\left(\alpha_4 \frac{\partial X}{\partial \tau} + \frac{\partial X}{\partial \zeta}\right)$$
$$+ \alpha_2(1 - \theta) + \alpha_3(1 - \alpha_0 X)[1 - \theta^4]. \tag{10}$$

Here, the definitions of the dimensionless parameters and representative values were directly taken from [3], [7]-[9] (see the Appendix for more details):

$$\alpha_0 = \frac{F_M^0}{F_C^0} \approx 0.5650. \tag{11}$$
$$\alpha_1 = \frac{T_w A_1}{A_2} \approx 2.59308. \tag{12}$$
$$\alpha_2 = \frac{\pi d L h_w T_w}{F_M^0 A_2} \approx 1.848874. \tag{13}$$
$$\alpha_3 = \frac{\varepsilon_c \sigma L M_{wc} a_c T_w^4}{v_g V_c \rho_c A_2 \alpha_0} \approx 1.0. \tag{14}$$
$$\alpha_4 = \frac{L}{v_g t_0} \approx 3.01731 \times 10^{-5}. \tag{15}$$
$$\beta_1 = \frac{B_1}{A_1} \approx 0.092375. \tag{16}$$
$$\beta_2 = \frac{B_1 T_w}{A_2} \approx 0.239536. \tag{17}$$

The supporting parameters are,

$$A_1 = C_{p_M} + C_{p_C}\frac{F_C^0}{F_M^0}. \tag{18}$$
$$A_2 = h_{Mf}^0 + B_1 T_0. \tag{19}$$
$$B_1 = C_{p_C} - C_{p_M} + 2C_{p_{H_2}}. \tag{20}$$

T_0 is the entrance temperature of methane and carbon particles, and h_{Mf}^0 is the formation enthalpy of methane. Applying the dimensionless variables to the species conservation balance, we have

$$\alpha_4 \frac{\partial X}{\partial \tau} + \frac{\partial X}{\partial \zeta} = -\epsilon_1 \exp(-\epsilon_w) \exp\left(\frac{\epsilon_w(\theta-1)}{\theta}\right)(1-X). \tag{21}$$

The dimensionless parameters, definitions and representative values are,

$$\epsilon_w = \frac{E_a}{RT_w} \approx 16.376283. \tag{22}$$

$$\epsilon_1 = \frac{LK_0}{v_g}\left(\frac{F_M^0}{v_g A}\right) \approx 1.732986 \times 10^{10}. \tag{23}$$

Similarly, the entropy generation equation is transformed to

$$\frac{\partial \dot{\Phi}}{\partial \zeta} = \gamma_1 \frac{1-\theta}{\theta^2}\frac{\partial \theta}{\partial \zeta} + \gamma_2(1+\alpha_0 X)\frac{1-\theta^4}{\theta^2}\frac{\partial \theta}{\partial \zeta}$$
$$+ \left[1 + \frac{\gamma_a}{\theta} + \gamma_b \ln \theta\right] \exp\left(\frac{\epsilon_w(\theta-1)}{\theta}\right)(1-X) \quad . \tag{24}$$

Also, the dimensionless parameters and representative values are:

$$\gamma_1 = \frac{A h_w}{\dot{S}_0} \approx 1.395833 \times 10^{-5}. \tag{25}$$
$$\gamma_2 = \frac{\varepsilon_c \sigma M_{wc} a_c A F_C^0 T_w^3}{\pi d v_g V_c \rho_c \dot{S}_0} \approx 7.549639 \times 10^{-6}. \tag{26}$$
$$\beta_w = \frac{T_w}{T_0} \approx 6.161669. \tag{27}$$
$$\gamma_a = \frac{A A_2}{A_4 T_w} \approx 0.404252. \tag{28}$$
$$\gamma_b = \frac{A B_1}{A_4} \approx 0.096833. \tag{29}$$

where the parameters A_3 and A_4 are defined as:

$$A_3 = S_M^0 - 2S_{H_2}^0 - S_C^0 + R \ln(n_C n_{H_2}^2). \tag{30}$$
$$A_4 = A B_1 \ln \beta_w - \frac{A A_2 \beta_2}{T_w} - A A_3. \tag{31}$$

and the reference entropy generation is,

$$\dot{S}_o = LA_4K_0 \left(\frac{F_M^0}{v_gA}\right) exp(-\epsilon_w) \approx 208.8219 \ \frac{W}{K}. \qquad (32)$$

IV. MAGNITUDE ORDER ANALYSIS

From the magnitude order of the non-dimensional parameters, we appreciate the fact that α_4, γ_1, and γ_2 are very small compared the unity. α_4 has a direct impact in the dynamics behavior of the model, because it allows to assume that the reactor can be treated as a quasi-steady. On the other hand, the entropy generations due to convection (γ_1) and radiation (γ_2) are very small compared with unity. This conclusion was observed previously in [10], who stated that the chemical reactions are the most important source of irreversibility compared to other heat transfer mechanisms. Discarding these terms, the model of the reactor can be simplified to the following system:

Energy balance:

$$\alpha_1(1 + \beta_1X)\frac{\partial \theta}{\partial \zeta} = (1 - \beta_2\theta)\frac{\partial X}{\partial \zeta}$$
$$+\alpha_2(1 - \theta) + \alpha_3(1 + \alpha_0X)[1 - \theta^4]. \qquad (33)$$

Species:

$$\frac{\partial X}{\partial \zeta} = \epsilon_1 \exp(-\epsilon_w) \exp\left(\frac{\epsilon_w(\theta-1)}{\theta}\right)(1 - X). \qquad (34)$$

Entropy generation:

$$\frac{\partial \Phi}{\partial \zeta} = \left(1 + \frac{\gamma_a}{\theta} + \gamma_b ln \ \theta\right) \exp\left(\frac{\epsilon_w(\theta-1)}{\theta}\right)(1 - X) \ . \qquad (35)$$

V. SIMULATION

The solution of the model allows us to identify the behavior of the main variables of the system as temperature, conversion, and entropy generation along the solar reactor. The simulations were performed employing the indicated values at the non-dimensional analysis. Fig. 2 shows the temperature increases as a consequence of convection, radiation, and reaction effects. The conversion takes places within a slender region of the reactor (fig. 3), when the mixture (methane, hydrogen, and carbon particles) reaches a sufficient temperature to initiate the conversion.
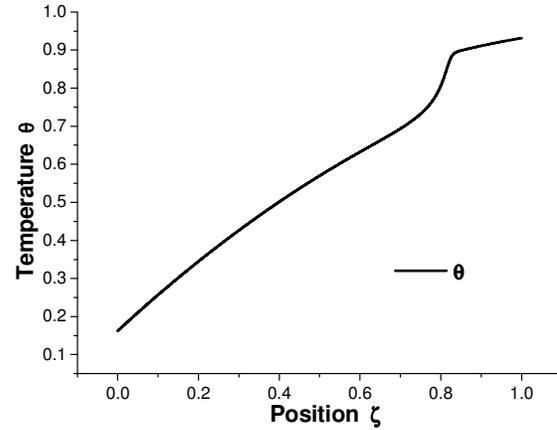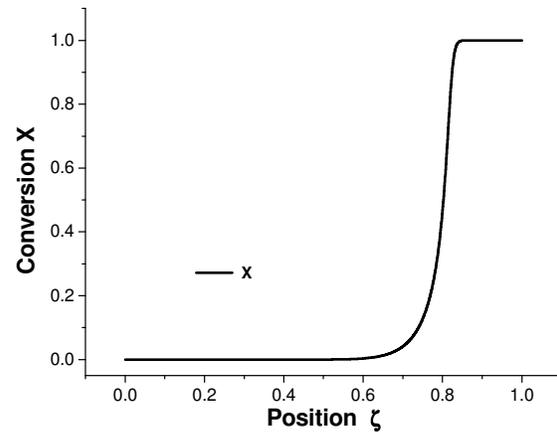

Fig. 2. Temperature θ - position ζ.

Fig. 3. Conversion X - position ζ.

The adimensional entropy generation (fig. 4) reveals that the generation takes place inside a small region of the reactor, and it depends on the reaction. In particular, the entropy generation achieved by this simulation is $\Phi = 0.00111$.

VI. OPTIMIZATION: ENTROPY MINIMIZATION.

The objective function in minimizing is the global entropy generation, defined by the following relationship

$$\dot{\Phi} = \int_0^1 \frac{\partial \Phi}{\partial \zeta} \partial \zeta \ . \qquad (36)$$

However, the entropy generation is subject to two restrictions: the energy and species balances given by (33) and (34). In addition, we consider a minimal conversion of 70% for the methane, i.e. $X \geq 0.7$. If the conversion is less than 0.7, the entropy generation is penalized with a large value of $\dot{\Phi}$, ($\dot{\Phi} = 1$). The objective function and restrictions are coupled to a genetic algorithm (GA) code, developed by Carroll [11]. The optimization aim is to find the most favorable adimensional parameters set.
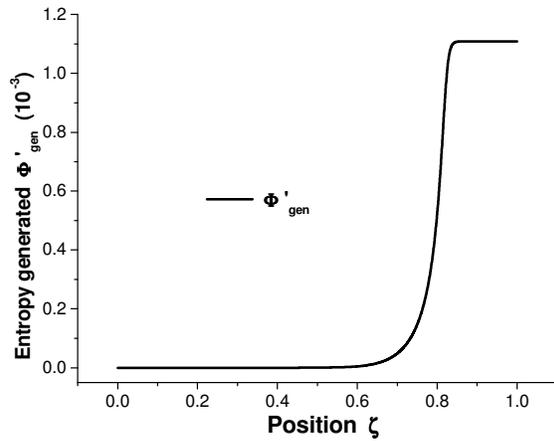
Fig. 4. Entropy generation $\dot{\Phi}$ - position ζ.

Table I. Parameter domains.

Minimum	Parameter	Maximum
0.2825	α_0	0.8475
1.2965	α_1	3.8896
0.9244	α_2	2.7733
0.5	α_3	1.5
1.2323	β_w	7.3940

Traditional optimization methods depend on the gradient of the objective function and restrictions. The classical criterion in obtaining the optimization is reduced to find those points for which the derivative of the objective function is zero. Meanwhile, GA uses random choice as a tool to guide the optimization process. GA works to coded parameters instead of the parameters themselves; evaluating them directly with the objective function [12].

The parameters to optimize are shown on table I, including the search domain for each parameter. The extreme values for each parameter of this table are calculated taking into account a perturbation of ±50% for each representative value. The above criterion was applied for all parameters of the table I, except the corresponding extreme values of β_w. For this parameter, we use a lower limit of 80%, under the reference value and the upper limit is 20% above the representative value [13]. The parameters used in the genetic algorithm code are displayed on table II.

Employing the genetic algorithm subroutine developed by Carroll [11] and coupling the non-dimensional simplified model of the reactor, together with the objective function and restrictions, leads to a value of the minimum entropy generation given by $\dot{\Phi} = 0.7986 \times 10^{-3}$. Considering a conversion of 70%, this entropy is 28% less than the presented on the simulation. The optimal adimensional parameters set is displayed at table III.

VII. EXERGY DESTRUCTION COSTS.

The physical entropy generation can be estimated from (9), replacing the minimum non-dimensional entropy previously founded and the reference entropy generation,

$$\dot{S}_{gen} = 0.166767021 \qquad (W/K). \qquad (37)$$

Choosing a dead state temperature equals to the entrance temperature $(T_d = T_o)$, then the exergy destruction leads directly from (2) to,

$$\dot{E}_D = 49.6966 \qquad (W) . \qquad (38)$$

Table II. Genetic algorithm parameters.

Parameter	Value
Population number	50
Generations	50
Crossover probability	0.8
Creep mutation	0.04
Jump mutation	0.05
Initial random number seed for the GA run	-1000

Table III. Optimal parameters set.

Parameter	Optimal value
α_0	0.6743
α_1	3.8290
α_2	2.1464
α_3	1.3177
β_w	6.7169

this is the minimum exergy destruction created by the dissociation of methane thorough the reactor. On the other hand, we can apply an exergy costs analysis to the reactor [2],

$$c_{P,i}\dot{E}_{F,i} = c_{F,i}\dot{E}_{F,i} + \dot{Z}_i + \dot{C}_{D,i}, \qquad (39)$$

in this expression there are no costs associated with the exergy losses with the surroundings, because the reactor was considered adiabatic. Moreover $c_{P,i}$, $c_{F,i}$ are the exergy cost of products (hydrogen and carbon) and the exergy of fuel (methane), $\dot{Z}_i$ is the cost associated with investment, operating and maintenance per unit time of reactor ($/s), $\dot{C}_{D,i}$ is the exergy destruction cost rate ($/s).

The exergy costs associated to the fuel, products, investment, operating, and maintenance, depend on market conditions; however, the exergy destruction cost rate is reduced when the entropy generation is minimized. The exergy destruction cost rate is defined as [2],

$$\dot{C}_{D,i} = c_{F,i}\dot{E}_{D,i} \qquad \left(\dot{E}_{P,i} \text{ fixed}\right), \qquad (40)$$

or

$$\dot{C}_{D,i} = c_{P,i}\dot{E}_{D,i} \qquad \left(\dot{E}_{F,i} \text{ fixed}\right), \qquad (41)$$

these expressions represent the lower and upper exergy destruction rate cost limits, where the actual cost is found between these limits. We can estimate the exergy cost of the fuel (methane) from the natural gas cost [14],

$$c_{CH_4} = 5.212973 \qquad (\$/GJ), \qquad (42)$$

and we calculate the exergy cost of product from the exergy costs of hydrogen and carbon by means of

$$c_{F,i} = 2c_{H_2} + c_C \quad ; \tag{43}$$

we have considered this expression to calculate the exergy cost of product, because the dissociation of one mol of methane produces two moles of hydrogen and one of carbon. We have estimated the exergy costs of hydrogen and carbon from their market value [15], [16],

$$c_{H_2} = 10.425947 \quad (\$/GJ), \tag{44}$$
$$c_C = 1.952496 \quad (\$/GJ), \tag{45}$$

then the exergy cost of product is,

$$c_{F,i} = 22.804390 \quad (\$/GJ). \tag{46}$$

By means of exergy costs of product and fuel, we have calculated, in addition the lower and upper limits of exergy destruction rate costs, which are,

$$\dot{C}_D\big|_F = 2.590671x10^{-7} \quad (\$/s), \tag{47}$$
$$\dot{C}_D\big|_P = 1.133300x10^{-6} \quad (\$/s). \tag{48}$$

Both limits indicate the magnitude order of the costs due to the dissipative effects inherent to the dissociation process. These low cost limits are a direct result of the entropy generation minimization analysis.

VIII. CONCLUSION

In the present study, we use the entropy generation minimization as a powerful tool to reduce the costs associated with the irreversibilities of the system, through an exergy destruction cost analysis. Although the costs of fuel and product depend on market conditions, the reduction on the dissipative effects were treated with the aid of the second law of thermodynamics. The above is a direct result of that the generated entropy by the reaction inside the reactor was reduced 28%, by means of genetic algorithms as minimization technique. This reduction has a direct impact in the life time costs of the reactor as is illustrated by the exergy costs balance.

APPENDIX

t_0	1	Hr
Dimensions		
A	$7.85398x10^{-5}$	m^2
d	0.01	m
L	0.1	m
Flow		
F_C	0.00263158	mol/s
F_M	0.00148684	mol/s
v_g	0.461631	m/s
Thermodynamic properties		

C_{p_C}	21.553714	J/mol·K
$C_{p_{H_2}}$	30.218734	J/mol·K
C_{p_M}	71.83176	J/mol·K
ρ_M	0.65614528	Kg/m³
ρ_{H_2}	0.08245568	Kg/m³
ρ_C	2270	Kg/m³
M_{w_C}	0.012	Kg/mol
$M_{w_{H_2}}$	0.002	Kg/mol
M_{w_M}	0.016	Kg/mol
μ_{H_2}	$2.0592x10^{-5}$	Kg/m·s
μ_M	$2.7639x10^{-5}$	Kg/m·s
Pr_{H_2}	0.7278934	
Pr_M	0.7424366	
K_{H_2}	0.4279438	W/m·K
K_M	0.16758566	W/m·K
S_M^0	186.23514	J/mol·K
$S_{H_2}^0$	130.636688	J/mol·K
S_C^0	5.688774	J/mol·K
h_{fM}^0	74850	J/mol·K
h_w	37.11246018	W/m²·K
S_0	208.8219	W/K
Reaction		
a	1	
E_a	250000	J/mol
K_0	8.0×10^{10}	s⁻¹
R	8.314	J/mol·K
n_M	1	
n_{H_2}	0.66666667	
n_C	0.33333333	
Radiation		
ε_c	1	
σ	5.67×10^{-8}	W/m²·K⁴
a_c	3.1×10^{-8}	m²
V_c	5.2×10^{-13}	m³

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