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Modeling hydrogen production in a catalytic-inert packed bed reactor by rich combustion of heavy fuel oil



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ABSTRACT

This work presents simulation results for the production of hydrogen by the rich combustion of heavy fuel oil in a dual zone packed bed reactor. The first zone provides catalyticthermal cracking of the fuel and is followed by a second zone for partial oxidation reforming of the cracked products. The kinetic model for the heavy fuel oil reactions in the catalytic zone uses decalin as a model compound. The partial oxidation reforming zone uses model compounds for the product groups formed from decalin cracking, and uncracked decalin. The hybrid reactor model is compared to results from a model of an inert (noncatalytic) porous media reactor. The work considers equivalence ratios from 1 to 2, filtration velocities between 15.0 and 65.5 cm/s, heat loss from 10 to 108% and particle diameter between 3 and 7 mm, and evaluates their effect on conversion. The simulations with the hybrid reactor model, in slightly rich conditions (equivalence ratio = 1.3) and constant filtration velocity of 19.3 cm/s deliver maximum hydrogen production for an optimal length of the intermediate zone. Considering this optimization: the total energy conversion efficiencies improve with the increase of the equivalence ratio due to the presence of hydrocarbon species generated by the cracking process. It is observed that the hybrid reactor model makes a better use of vaporized fuel, compared to a model for an inert packed bed reactor, when the deposits of carbonaceous material in the latter exceed 7.4%.

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Introduction

Hydrogen can be produced from many different sources by various methods. Some example technologies are: thermochemical splitting of water, catalytic steam reforming of mixtures of bioglycerine and bioethanol, biomass fermentation, biophotolysis of water, low temperature catalytic gasification of fowl manure, electrochemical oxidation of urea and photocatalytic decomposition of H_2S [1]. In particular, hydrogen production from heavy hydrocarbons can be carried out by catalytic steam reforming, catalytic partial oxidation

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and autothermal reforming. At present, catalytic hydrocarbon reforming is the best-developed and most economical technique for hydrogen production [2]. It has also been possible to produce hydrogen through combustion in porous media using different configurations and fuels [3–9].

Porous combustion technology is a novel energy utilization process, environmentally benign, and efficient, located at the forefront of modern technological developments [10]. It corresponds to non-catalytic combustion with propagating wavelike high-temperature zones, which are established by heat recirculation within the porous bed (filtration combustion) and shows reaction fronts inside a porous matrix characterized by rapid exothermic reactions influenced by large interfacial heat transfer [11]. In particular, conversion to syngas has been successfully realized with liquid fuels by filtration reactors and other types of heat-recirculating reactors [8].

Recent studies of filtration combustion of liquid fuels to syngas have considered different kinetic approaches, with either overall or detailed mechanisms for specific model compounds. An experimental and numerical study of conversion of liquid heptane to syngas through non-catalytic combustion in a packed bed of alumina pellets used a mechanism of intermediate complexity for the computational results, composed of 107 species and 723 reactions to describe the high temperature oxidation and pyrolysis of *n*-heptane, iso-octane, and their mixtures [11,12]. The comparison of experimental and numerical results showed good agreement only for equivalence ratios less than 2.0, and between 2.0 and 3.0 numerical simulations gave significantly higher hydrocarbon than those measured in experiments. Another work on partial oxidation of diesel fuel in a porous reactor for the production of syngas used n-heptane as a diesel surrogate fuel. For these numerical investigations, the comprehensive mechanism of Curran et al. [13] was used in equilibrium and kinetic analyses. The results showed that the deviation between the measured and equilibrium concentrations were large for an excess air ratio lower than 0.45 due to the formation of CH₄, C₂H₂, soot, and other hydrocarbons, compared to the equilibrium H₂ and CO concentrations calculated using n-heptane surrogated fuel [14]. Recently, the work of Gómez et al. [15] on filtration combustion modeling of HFO to syngas production used the overall chemical kinetics model for partial oxidation of methane in inert porous media [16,17] and water gas shift reaction under non-catalytic conditions [18], combined with stoichiometric, chemical and physical properties for decalin as a model compound. Their numerical results showed a good agreement with experimental exhaust concentrations of H₂, and positive effects of the equivalence ratio (φ) and filtration velocity (v_{filt}) increase and heat losses reduction on the fuel conversion to H₂.

Decalin is widely used as a model compound for mixtures of commercial fuels such as diesel, jet fuel, and heavy fuel oil [19–22]. Decalin is a two-fused ring cycloparaffin and a model compound for bicyclic naphthenes found in jet fuels and coal-, oil-shale-, oil-sand derived fuels, and it is also a potential endothermic fuel for hypersonic flight [23]. Furthermore, it has structural proximity to the average chemical species that can be found in a typical heavy fuel oil [24]. Also, decalin is a possible compound representative of cyclo-alkanes present in diesel fuel [19]. It has been used in mixtures as a surrogate for low-sulfur JP-8 in a study of autothermal reforming, with good correlation, in a three-component mixture of *n*-dodecane/ decalin/toluene [20]. To emulate the fuel properties affecting the spray development and gas phase ignition of a conventional jet fuel, a mixture of *n*-dodecane/iso-cetane/decalin/ toluene was used. The results showed good agreement for liquid density and volatility, important properties for spray predictions under engine conditions [21]. In regard to the combustion of HFO, it has been found that a mixture of composition methylnaphthalene/decalin/cyclohexane/*n*-hexadecane is a promising surrogate of this fuel [22].

Concerning the production of synthesis gas from HFO using an inert porous medium reactor, practical experience indicates that a carbonaceous residue is formed in the packed bed, giving a lower efficiency [25]. An alternative to achieve a better fuel efficiency is to use a packed bed reactor of two zones in series, in which the first zone contains a packing of zeolite catalyst, performing a catalytic-thermal cracking of the premix rich air-fuel, which has previously been vaporized in an initial inert hot zone. The products from the cracking, along with excess fuel, can be processed in the second zone with an inert packed bed, where they are subjected to partial oxidation.

With regard to the catalytic cracking of HFO on zeolitic catalysts, Otterstedt et al. [26] studied the effect of added alumina to the matrices of cracking catalysts containing different types of zeolite Y on their cracking performance when processing a heavy vacuum gas oil feed (HVGO) and #6 Fuel Oil. The temperature of the reactor for fuel oil was 560 °C. They mentioned that #6 Fuel Oil was a considerably more difficult feed to crack, and concluded that for this feed, the alumina addition resulted in a higher conversion at the same catalyst to oil ratio, independent of the type of zeolite. This higher conversion was accompanied by a greater selectivity for coke and a lower selectivity for gasoline.

Since the results of modeling of filtration combustion of HFO using decalin as model compound were consistent with experiments [15], it is proposed to use decalin for modeling the catalytic cracking of the fuel. The study of Al-Sabawi and de Lasa [27] on the cracking of decalin on zeolites in industrial FCC conditions provides kinetic information that can be used to approximate the kinetic behavior of the reactive process in the first zone of the combined reactor. They found that decalin undergoes reactions such as ring opening, protolytic cracking, isomerization, hydrogen transfer and transalkylation. They proposed a heterogeneous kinetic model for decalin conversion that included thermal effects, adsorption and intrinsic catalytic reaction phenomena. It was determined that hydrogen transfer reactions were more pronounced and selectively favored against other reactions at lower reaction temperatures, while ring-opening and cracking reactions predominated at higher reaction temperatures.

This paper reports a modeling approach (named here as *Model C–I*) proposed for a catalytic-inert combined reactor used for the processing of #6 Fuel Oil in a packed-bed reactor using decalin as a model compound. Although this process has been proposed for the steam reforming of methane, it has not been discussed for the case of valorized liquid fuels. In the following, we first describe the mathematical model, and then some simulation results and discussion.

Physical and mathematical description

Model overview

Fig. 1 shows a diagram of the catalytic-inert packed bed reactor. A homogeneous pre-heated fuel-air mixture enters the cylindrical packed bed reactor. The first zone, L_1 , contains inert media, which ensures total vaporization of the atomized fuel and hot air mixture coming from the premixing chamber [7,28]. Zone L_2 is the catalytic cracking section. The final zone, L_3 , is an inert section in which the partial oxidation of the products of the catalytic cracking occurs. There is no cracking in zone L_3 . To represent the physical aspects that are associated with the transport phenomena occurring within the reactor, the following assumptions were made.

- (1) Prior to the injection of HFO, the solid and fluid phases are preheated to the temperature profile established from combustion of liquefied petroleum gas (LPG) obtained as in Ref. [15]. The compositions are uniform in the computational domain. Thermal and mass fluxes are null at the end of L_3 zone.
- (2) The fraction of L_1 length where the fluid mixture is in gas phase is established based on the thermal profile from LPG combustion and the boiling temperatures of both the model compound and the real liquid fuel (HFO). It assumes instantaneous phase change, which is reasonable based on the timescale at the process.
- (3) In the L₂ zone, the gas phase reactants diffuse from the fluid bulk to the catalytic surface where they are adsorbed and react.
- (4) The three modes of heat transfer (conduction, convection and radiation) all contribute to the heat transport inside the reactor.
- (5) The gas and solid are not in local thermal equilibrium. Therefore, an energy balance was written for each phase.



Fig. 1 – Schematic of the reactor.

- (6) Radiation in the gas phase is assumed to be negligible compared to the radiation among solid surfaces.
- (7) The model considers that the thermophysical properties of the gaseous species and of the solid are function of the temperature; however, other properties of the solid phase such as density and emissivity are assumed to be constant values.
- (8) The effectiveness factor was approximated using a generalized Thiele modulus for an isothermal reaction of first order.
- (9) The catalytic zone is considered to be formed by porous alumina spheres, superficially coated with zeolites (*zeolityc coating*). In these conditions, the mass of alumina is much greater than that of zeolites, therefore the physical properties of the packed bed in L_2 zone were taken as those at alumina.

A computational model was developed for each of the three zones. The model for zone L_1 was the same as described in Gómez et al. [15] but without homogeneous chemical reactions. Zone L₂ is the catalytic cracking section. The modeling approach for this zone is an extension of the model proposed by Gómez et al. [15]. The extension requires an additional mass balance equation for the solid catalysts, as well as mass transfer between the fluid and solid phases. The final zone, L₃, is an inert section in which the partial oxidation of the products of the catalytic cracking occurs. There is no cracking in zone L₃. The L₃ zone used the model of Gómez et al. [15] with specific chemical kinetics for the different species present in this location (cracking products and fuel not cracked). In the following sections a brief description of the model is given. The reader should refer to reference [15] and also to the supplementary information where the complete model equations are given.

In brief, the model solves momentum, mass and energy balance equations. The momentum balance for the fluid phase has the form of the volume averaged Navier-Stokes equation [29]. Separate mass and energy balances were written for the fluid and solid phases, and the domain is assumed to be axi-symmetric. Thus the model is a heterogeneous model in two space dimensions.

To characterize the operational behavior of the process, calculate the hydrogen and carbon monoxide yields and the syngas energy conversion efficiency. A methodology based on the work of Dixon et al. [11], Smith et al. [8] and Toledo et al. [25] was used. Decalin was used as a model compound, whose molecular formula is $C_{10}H_{18}$. Then, the calculation of the H_2 simulated yield (sim), is given by the expression:

$$\eta_{\rm H_2} = 100 \cdot \left[\frac{2 \cdot N_{\rm H_{2,sim}}}{N_{\rm H} \cdot N_{\rm C_{10} H_{18}}} \right]$$
(1)

Similarly the simulated CO yield is defined with the relationship:

$$\eta_{\rm CO} = 100 \cdot \left[\frac{N_{\rm CO_{sim}}}{N_{\rm C} \cdot N_{\rm C_{10}H_{18}}} \right] \tag{2}$$

where $N_{\rm H_{2,sim}}$, $N_{CO_{sim}}$ and $N_{C_{10}H_{18}}$ are molar flows; $N_{\rm H}=18$ and $N_{C}=10$ for decalin.

The syngas energy conversion efficiency (only H_2 and CO) compares the chemical energy content available as syngas to the bound chemical energy in the fuel, and is evaluated according to:

$$\eta_{energy,sim} = 100 \cdot \left[\frac{m_{\rm H_{2sim}} \cdot \rm{LHV}_{\rm H_2} + m_{\rm CO_{sim}} \cdot \rm{LHV}_{\rm CO}}{m_{\rm C_{10}H_{18}} \cdot \rm{LHV}_{\rm C_{10}H_{18}}} \right]$$
(3)

where $\eta_{energy,sim}$ represents the simulated syngas energy conversion efficiency. $m_{\rm H_{2,sim}}$ and $m_{\rm CO_{sim}}$ are mass flows. LHV_{H2} = 120, LHV_{C0} = 10.1 and LHV_{C10H18} = 42.7 correspond to lower heating values in MJ/kg.

Kinetic mechanisms of decalin and cracking products

Modeling of catalytic and thermal cracking kinetic

Gudiyella et al. [22] suggested that a good surrogate for HFO is a mixture of composition methylnaphthalene/decalin/cyclohexane/n-hexadecane, however, no work on kinetic modeling of catalytic cracking on zeolites is reported for this mixture. Therefore, we used the kinetic information of pure decalin cracking on zeolites under industrial FCC operations conditions, based on the study of Al-Sabawi and de Lasa [27], to approximate the catalytic L_2 zone.

Al-Sabawi and de Lasa [27] reported complete kinetic information for catalytic conversion on a standard FCC catalyst called CAT-LC (large crystallite), which was selected as a representative catalyst of the L_2 zone. Table 1 shows the properties of the CAT-LC catalyst. The preparation of both FCC catalysts and their characterization for acidity, structural properties and reactivity can be found in Tonetto et al. [30].

For modeling purposes, reaction products formed from decalin conversion were classified into five groups [27]:

- i CPO: olefins that come from the ring-opening and cracking of a decalin molecule. These consist of unsaturated C_{10} monocyclic naphthenes (RON).
- ii CPP: saturated C_{10} monocyclic naphthenes as well as naphthenes and paraffins with a smaller number of carbons than decalin produced via hydrogen transfer reactions involving CPO compounds.
- iii ISO: include all C₁₀ bicyclical structures.
- iv AP: consist of all C_{10} bicyclic naphtheno-aromatics and aromatics as well as ROA species.
- v HP: consist of all naphthenic and aromatic species having more than 10 carbon atoms.

Table 1 — Properties of FCC catalyst called CAT-LC. Modified from Al-Sabawi and de Lasa [27].		
Property	Value	
Zeolite content (%)	29	
Unit cell size (Å)	24.28	
BET surface area (m²/g)	197	
External surface area (m²/g)	20	
Crystallite size (μm)	0.9	
Crystallite density (kg/m³)	825	
Brønsted/Lewis sites ratio to 100 °C	1	

These five groups are produced by catalytic cracking and/or thermal cracking according to conversion models of Al-Sabawi and de Lasa [27], shown in Figs. 2 and 3.

The intrinsic kinetic constants k_i change with the reactor temperature T_f , following a re-parameterized Arrhenius-type equation:

$$\mathbf{k}_{i} = \mathbf{k}_{i0} \exp\left(\frac{-E_{i}}{R_{g}} \left(\frac{1}{T_{f}} - \frac{1}{T_{AV}}\right)\right)$$
(4)

 E_i represents the energy of activation, k_{i0} the pre-exponential factor, and T_{AV} the centering temperature defined as the average temperature used in the reaction experiments (500 °C). The adsorption constants of the species *j* were evaluated using the expression:

$$K_j = K_{j0} \exp\left(\frac{-\Delta H_j}{R_g T_f}\right)$$
(5)

 K_{j0} is the pre-exponential factor with units of m³/(kg of catalyst) and $(-\Delta H_j)$ is the heat of adsorption in J/mol. The classification CP includes all compounds of the groups CPO and CPP.

The model presented in Fig. 2 considers the primary reactions of decalin, including: (1) ring opening/protolytic cracking, (2) isomerization, (3) hydrogen transfer, and (4) transalkylation/alkylation. The reactions (1) and (2) are modeled by first order kinetics since these types of reactions are uni-molecular; the reactions (3) and (4) are modeled by kinetic of second order, because two adsorbed molecules are involved in these mechanisms [27].

Al-Sabawi and de Lasa [27] determined via thermal cracking of decalin that the majority of the products were formed via ring opening/cracking and isomerization, which are represented in the model of Fig. 3. The kinetics in this latest case are first order. In addition, they consider a Lang-muir-Hinshelwood (L-H) representation for the adsorption of species on the active sites of the catalyst, and that the ideal gas law applies. Finally, the model ignores the deactivation of the catalyst by deposition of coke on the surface of the catalyst.

Based on the kinetics developed by Al-Sabawi and Lasa [27], which correspond to Eqs. (7), (12), (14), (16), (18) and (20) of their work, and the simplification of the L-H representation indicated by the authors, the following kinetic expressions are proposed for the heterogeneous reactions occurring in the solid phase of the L_2 zone:



Fig. 2 – Model of decalin catalytic conversion (from Ref. [27]).





$$\left(-R_{C_{10}H_{18}} \right)_{S} = \frac{\rho_{f}}{\rho_{s}} \left\{ \frac{\rho_{cr} \left[K_{C_{10}H_{18}}(k_{1}+k_{2})w_{C_{10}H_{18}} + \frac{\rho_{cr}K_{C_{10}H_{18}}K_{CPO}(k_{3}+k_{4})w_{C_{10}H_{18}}w_{CPO} \right] + \left(k_{T1} + k_{T2} \right) w_{C_{10}H_{18}} + \frac{\rho_{cr}K_{C_{10}H_{18}}K_{CPO}(k_{3}+k_{4})w_{C_{10}H_{18}}w_{CPO} \right]}{\left(1 + \rho_{cr}K_{CPO}w_{CPO} \right)^{2}} \right] \right\}$$

$$(-R_{CPO})_{S} = \frac{\rho_{f}}{\rho_{s}} \left\{ \begin{array}{l} \rho_{cr} \left[\nu_{CPO} K_{C_{10}H_{18}} k_{1} w_{C_{10}H_{18}} - \frac{\rho_{cr} K_{C_{10}H_{18}} K_{CPO}(k_{3} + k_{4}) w_{C_{10}H_{18}} w_{CPO}}{(1 + \rho_{cr} K_{CPO} w_{CPO})^{2}} \right] \right\}$$

$$(7)$$

$$(-R_{\rm ISO})_{\rm S} = \frac{\rho_f}{\rho_{\rm s}} \left\{ \rho_{\rm Cr} \nu_{\rm ISO} K_{\rm C_{10}H_{18}} k_2 w_{\rm C_{10}H_{18}} + \nu_{\rm CPO} k_{\rm T2} w_{\rm C_{10}H_{18}} \right\}$$
(8)

$$(-R_{CPP})_{S} = \frac{\rho_{f}}{\rho_{s}} \left\{ \frac{\rho_{cr}^{2} \nu_{CPP} K_{C_{10}H_{18}} K_{CPO}}{\left(1 + \rho_{cr} K_{CPO} w_{CPO}\right)^{2}} \cdot k_{3} w_{C_{10}H_{18}} w_{CPO} \right\}$$
(9)

$$(-R_{AP})_{S} = \frac{\rho_{f}}{\rho_{s}} \left\{ \frac{\rho_{cr}^{2} \nu_{AP} K_{C_{10}H_{18}} K_{CPO}}{(1 + \rho_{cr} K_{CPO} w_{CPO})^{2}} \cdot k_{3} w_{C_{10}H_{18}} w_{CPO} \right\}$$
(10)

$$(-R_{\rm HP})_{\rm S} = \frac{\rho_f}{\rho_{\rm S}} \left\{ \frac{\rho_{\rm cr}^2 \nu_{\rm HP} K_{\rm C_{10}H_{18}} K_{\rm CPO}}{\left(1 + \rho_{\rm cr} K_{\rm CPO} w_{\rm CPO}\right)^2} \cdot k_4 w_{\rm C_{10}H_{18}} w_{\rm CPO} \right\}$$
(11)

The rate constants and adsorption equilibrium constants are expressed in Arrhenius forms, using Eqs. (4) and (5) respectively. Furthermore, note:

$$\begin{split} \nu_{\text{CPO}} &= \frac{M_{\text{CPO}}}{M_{\text{C}_{10}\text{H}_{18}}}, \nu_{\text{ISO}} = \frac{M_{\text{ISO}}}{M_{\text{C}_{10}\text{H}_{18}}}, \nu_{\text{CPP}} = \frac{M_{\text{CPP}}}{M_{\text{C}_{10}\text{H}_{18}}}, \nu_{\text{AP}} = \frac{M_{\text{AP}}}{M_{\text{C}_{10}\text{H}_{18}}} \text{and } \nu_{\text{HP}} \\ &= \frac{M_{\text{HP}}}{M_{\text{C}_{10}\text{H}_{18}}} \end{split}$$

 ν is a ratio of molecular weights.

According to the above, with rich conditions of model fuel, decalin cracking generates a mixture of the product groups (CPO, CPP, ISO, AP and HP), plus un-cracked decalin, which forms the inlet to the L_3 zone. In this zone of inert porous medium they are subjected to POR, to produce syngas. The present model considers each of these product groups in terms of a selected representative or model compound, for which is defined a mechanism of POR. The criterion of selection of the compound of each group is based on the yield and selectivity observed in Table 2 from Al-Sabawi and de Lasa work, and indications of these authors for CPO in the same publication [27]. These chemical species are shown in Table 2.

Modeling of POR kinetics

The kinetic mechanism of decalin POR described in Gómez et al. [15] was used to represent the kinetic behavior in homogenous phase of the decalin fraction not cracked in zone L_2 and thus present in zone L_3 . As there are no existing global kinetic models of partial oxidation and steam reforming for C1 to C5 species in an inert porous media reactor, we approximate their POR kinetic behavior with the kinetic information for methane along with the one of water gas shift reaction kinetics under non-catalytic conditions, as described in Ref. [15]. The details of the POR kinetic description are given in the supplementary information.

Table 2 – Representative compounds of the decalin cracking.		
Group	Compound (C)	
СРО	cyclohexene (C1)	
CPP	n-butane (C2)	
ISO	trans-decalin (C3)	
AP	naphthalene (C4)	
HP	methyl-naphthalene (C5)	

(6)

Numerical solution

Model solution and parameters

The mathematical model of the reactor was implemented and solved using COMSOL Multiphysics version 5.0. Grid refinement studies were performed to verify a mesh independent solution as described in Gómez el al [15]. The final mesh used 5830 elements (base case). The model parameters that allow characterizing the heterogeneous reactive processes in the L_2 zone are given in the supplementary information. They correspond to heat of adsorption and adsorption constants for decalin over CAT-LC, kinetic parameters for decalin thermal conversion, and intrinsic kinetic parameters for decalin catalytic conversion.

The reaction heat associated with decalin cracking was approximated from values corresponding to the catalytic cracking of gas oil [31], and the value is 6.986×10^4 J/mol. The porosity of the catalyst was 0.5 [32].

The physical and kinetic parameters of the homogeneous reactions in zones L_1 and L_3 were taken from Tables 2 and 3 in Gómez et al. [15]. For purposes of comparison between Model C–I and the model developed by Gómez et al. [15], named here as Model I, the sampling point and time are fixed (4 cm from the outlet, 960 s after the injection of FO 6), and the initial thermal profile in L_3 zone. In zones L_1 and L_2 the initial thermal profiles are flat and equal to 500.15 K and 823.15 K respectively. With regard to the latter, the first temperature ensures thermal evaporation conditions of the model compound (decalin) and the 1 s corresponds to the catalytic cracking temperature which gives the highest conversion of decalin, according to the study of Al-Sabawi and de Lasa [27].

The base case of Model C–I comprised a hybrid porous media reactor of length 49.21 cm ($L_1 = 7.5$ cm, $L_2 = 14.21$ cm and $L_3 = 27.5$ cm), which corresponds to a length to diameter ratio for the catalytic zone of $L_2/D_{Ti} = 1$ [33]. In addition, it is considered that the fraction of L_1 , necessary for the phase change of the fuel is of negligible length, since the initial temperatures throughout this zone are assumed to be greater than the boiling temperature of the model fuel; then, L_1 is

included in the computational domain, because in this section the reactant mixture would be in gaseous phase. In this analysis, the POR homogeneous reactions of decalin and of the cracking products can occur in the L_2 and L_3 zones, given the initial thermal conditions in those zones. In L_1 , which has low initial temperatures (lower than the autoignition temperature), it is assumed that homogeneous reactions do not occur, and corresponds to a section where the different profiles of the state variables are developed (species concentrations, velocity, and temperatures), prior to entering the L_2 zone.

Simulations of Model I and Model C-I were performed, under similar process conditions (operational and geometric), to determine whether the C-I process offers an improvement in HFO processing in terms of product yields (H₂, CO) and energy conversion efficiencies.

Results and discussion

Base case of model C-I

Fig. 4 presents simulation results for the base case of Model C-I at the time of gas sampling. Fig. 4a shows that the temperature profiles of both solid and fluid phases coincide, a result similar to that obtained with Model I (see Fig. 5C and D in Ref. [15]). The homogeneous reaction zone exhibits a maximum in the overall reaction heat immediately downstream of the catalytic zone L_2 . This reaction heat produced by decalin and cracking products POR in gaseous phase is accompanied by an abrupt decrease in decalin and oxygen mass fractions and the generation of syngas (Fig. 4b).

The behavior of the species concentrations in the catalytic solid phase (Fig. 4c and d) is as expected. Decalin is consumed within the intermediate zone, a process controlled by the variable magnitude of the effectiveness factor, and cracking products increase in this zone, as the reaction front progresses downstream. In the initial thermal conditions of L_2 zone, the greatest product of cracking in the catalytic solid phase corresponds to cyclohexene, a result that coincides with that reported by Al-Sabawi and Lasa [27].

Table 3 – Comparison of mass fractions of the gas phase species for the sampling point, obtained through simulation with Model I (base case: $\phi = 1.3$, $v_{filt} = 19.3$ cm/s) and Model C–I (base case: $\phi = 1.3$, $L_2/D_{Ti} = 1$, $v_{filt} = 19.3$ cm/s).					
Gas	Mass fraction Model I (wet basis)	Mass fraction Model I (dry basis)	Mass fraction Model C—I (wet basis)	Mass fraction Model C–I (dry basis)	
C ₁₀ H ₁₈	0.0058	0.0062	0.0020	0.0022	
O ₂	$2.3442 imes 10^{-9}$	$2.4941 imes 10^{-9}$	1.5464×10^{-9}	$1.6532 imes 10^{-9}$	
H ₂	0.0071	0.0075	0.0055	0.0058	
N ₂	0.6433	0.6844	0.6588	0.7044	
CO	0.0873	0.0929	0.0693	0.0741	
CO ₂	0.1964	0.2090	0.1917	0.2050	
C ₄ H ₁₀	-	-	8.5024×10^{-4}	$9.0900 imes10^{-4}$	
C ₆ H ₁₀	-	-	0.0012	0.0013	
C ₁₀ H ₈	_	-	0.0019	0.0020	
t-C ₁₀ H ₁₈	-	-	0.0020	0.0022	
$C_{11}H_{10}$	-	-	0.0021	0.0022	
H ₂ O	0.0601	-	0.0646	-	
\sum	1	1	1	1	



Fig. 4 – Axial variations by simulation in exhaust gas sampling, t = 5080 s: gas phase (a and b); solid phase (c and d). ($\phi = 1.3$, L₂/D_{Ti} = 1).



Comparison between models with respect to the exhaust gas

Table 3 shows a comparison between Model I and Model C-I considering base cases. The gas phase mass fractions of Model I correspond to the second and third columns of Table 5 in Gómez et al. [15].

Considering the dry basis results, a higher conversion of decalin and oxygen is obtained in the case of the hybrid reactor. Compared to Model I, H₂ and CO productions are reduced by 22.67% and 20.24%, respectively. This is explained by the presence of non-converted catalytic-thermal cracking species in the inert zone L₃, mostly represented by cyclohexene, naphthalene, trans-decalin and methyl-naphthalene (0.77%). Furthermore, there is an increase in the water production. By comparing the local values of the inverse kinetic constants of steam reforming (k_{-3}) and the Water gas shift reaction (k_{-4}) of both models, a slight increase is observed for the hybrid reactor (+0.33% and +0.27%, respectively). The

latter would explain the larger mass fraction of water obtained by the Model C-I, at the sampling point.

On the other hand, the presence of unreacted cracking hydrocarbon species in the L_3 zone suggests the possibility of increasing syngas production by separating the exhaust stream from the hybrid reactor into two streams (S). The first containing the H₂ and CO produced (3), and the second containing the other species (4). This latter stream, which contains the cracking products, could be pre-mixed with air under rich conditions (5), and then fed into a second inert porous media reactor, allowing increased total syngas production (7). Fig. 5 shows this configuration.

Analysis of the length of the catalytic bed

The variation of length of zone L_2 in Model C-I was studied for zone L_2 . This zone is the main difference with Model I. In this analysis L_1 and L_3 were of fixed and equal lengths and the same as the base case. The criterion for establishing the length of L₂ necessary for the analysis of subsequent effects was the best result of H₂ production (dry basis mass fraction). The range L₂/D_{Ti} = 0.125 and L₂/D_{Ti} = 1, which interval has been considered in hybrid reactor research [33], was studied. In general, the simulation results of the Model C–I for the L₂/D_{Ti} > 1 range show that H₂ production decreases compared to L₂/ $D_{Ti} \leq 1$, so they were not included in this study.

Fig. 6 shows how the H₂ production and the maximum axial temperature vary with the L_2/D_{Ti} ratio. A constant combustion temperature was observed over the entire range. On the other hand, H₂ production increases when the length of the catalytic zone is smaller than the diameter of the porous bed (L_2/D_{Ti} <1), with values greater than the base case of $L_2/D_{Ti} = 1$, but always lower than the base case in *Model I* (Table 3). The maximum in the mass fraction ($w_{H_2} = 0.0062$) occurs at $L_2/D_{Ti} = 0.25$. The latter result corresponds to a length of the catalytic zone equal to 3.55 cm, which was used in the analysis of the next two sections.

Effects on energy conversion efficiency and product yields

The previous simulation results show that, under comparable conditions, the hybrid reactor does not generate a higher



Fig. 6 – L_2/D_{Ti} ratio on the combustion temperature and H_2 production. ($\phi = 1.3$, $v_{filt} = 19.3$ cm/s).

production of H₂ and CO with respect to the inert porous media reactor. However, the presence of hydrocarbon species (C₄H₁₀, C₆H₁₀, etc.) in the exhaust gases produced by catalyticthermal cracking reactions allows additional energy inputs, which is an advantage over *Model I*. To evaluate these additional energy inputs, a total energy conversion efficiency, defined as $\eta_{totalE,sim}$ can be estimated. The evaluation of the behavior of MPI reactors in rich filtration combustion was performed using this efficiency indicator, which shows orders of magnitude, for example 82% ($\varphi = 2.8$) in experiments with *n*-heptane [11], and 61% ($\varphi = 3.15$) with Jet-A [8]. The calculation is performed here using the following expression:

$$\eta_{\text{totalE,sim}} = 100 \cdot \left[\frac{\sum_{i} \dot{m}_{i,\text{sim}} \cdot \text{LHV}}{\dot{m}_{C_{10}H_{18}} \cdot \text{LHV}_{C_{10}H_{18}}} \right]$$
(12)

where $i=H_2$, CO, and hydrocarbon species; $\dot{m_i}$ corresponds to the mass flow of species i. The lower heating values of the cracking products in MJ/kg, are as follows: $LHV_{C_4H_{10}}=45.8$, $LHV_{C_6H_{10}}=43.4$, $LHV_{C_{10}H_8}=39.5$, $LHV_{t-C_{10}H_{18}}=42.9$ and $LHV_{C_{11}H_{10}}=39.8$. These values were obtained using methodology from Poling et al. [34].

The following simulation results with the Model C–I describe the effects of the equivalence ratio, filtration velocity, heat loss and particle diameter of the packed bed, on syngas and total energy conversion efficiencies (Eqs. (3) and (12), respectively), and also on the H_2 and CO yields (Eqs. (1) and (2), respectively), at the sampling point. In addition, results are included with Model I for comparative purposes.

Fig. 7 shows the effect of the equivalence ratio (v_{filt} = 19.3 cm/s). It is observed that between equivalence ratio of one and two, the total energy conversion efficiency of the Model *C*–*I* exceeds the syngas energy conversion efficiency to Model *I*, with a maximum difference at $\varphi = 2.0$ (Fig. 7a). When comparing the syngas conversion efficiencies of both modeling approaches, the result of Model *I* is higher throughout the range of φ . A similar situation occurs with H₂ and CO yields (Fig. 7b). On the other hand, of the efficiencies and the respective yields converge in stoichiometric or slightly rich input conditions ($\varphi < 1.1$). This indicates that, at this feed limit for both reactors, the Model *C*–*I* of the hybrid reactor converges to Model *I* of the inert reactor, therefore, the catalytic-thermal cracking zone has a neutral effect with



Fig. 7 – Effect of equivalence ratio on: a) syngas and total energy conversion efficiencies; b) H₂ and CO yields.



Fig. 8 – Effect of filtration velocity on: A) syngas and total energy conversion efficiencies; B) H₂ and CO yields. ($\phi = 1.6$).



Fig. 9 – Effect of heat loss on: a) syngas and total energy conversion efficiencies; b) H₂ and CO yields. (ϕ = 1.6; v_{filt} = 20.0 cm/s).

respect to H₂ and CO production. Furthermore, the products of cracking do not generate a significant contribution in the total energetic conversion.

Fig. 8 analyzes the effect of the filtration velocity at $\varphi = 1.6$, an inlet condition that shows significant differences between the two modeling approaches. The syngas and total energy conversion efficiencies of the Model C–I, as shown in Fig. 8a, show a decreasing trend with the increase of the filtration velocity, contrary to the syngas energy conversion efficiency of the Model I. Likewise, the H₂ and CO yields show trends contrary to Model I. Around $v_{filt} = 20.0$ cm/s the best result in conversion efficiency of the Model C–I is generated, $\eta_{totalE.sim} = 57.19\%$.

The effects of heat loss and particle diameter of the packed bed are analyzed for $\varphi = 1.6$ and $v_{filt} = 20.0$ cm/s. Fig. 9 shows that a decrease in heat loss increases the syngas energy conversion efficiencies of both models, as well as the total energy conversion efficiency of *Model C*–*I*. With respect to syngas energy conversion efficiencies, *Model I* gives a greater magnitude throughout the analyzed interval. However, $\eta_{totalE,sim}$



Fig. 10 – Effect of particle diameter of the packed bed on: a) syngas and total energy conversion efficiencies; b) H_2 and CO yields. ($\phi = 1.6$; $v_{filt} = 20.0$ cm/s).



Fig. 11 – Effect of the reduction of φ by formation of carbonaceous residue on the production of syngas.

surpasses to $\eta_{energy,sim}$ of Model I, given the significant energy input of the hydrocarbon species from catalytic-thermal cracking reactions. On the other hand, it is observed that the H₂ and CO yields of Model I exceed the corresponding ones of Model C–I, and they are increasing with the decrease of heat loss.

Fig. 10 shows that the syngas energy conversion efficiencies and the H_2 and CO yields of both models are insensitive to the change in particle diameter of packed bed in the range 3 and 7 mm. However, the total energy conversion efficiency of *Model* C–I shows a slight increase with the increase of the particle diameter. In addition, the magnitudes of efficiencies and yields, when compared among models, maintain the same trends observed in this section.

The results obtained here with the Model C–I suggest that the presence of an intermediate catalytic zone, in its application to rich filtration combustion of heavy fuel oil, would favor the total energetic conversion, and its exhaust products could increase the syngas yield, when they are being processed in a second MPI unit in serial, as shown in Fig. 5.

Comparative analysis by simulation of the impact of the formation of carbonaceous material in inert porous bed reactor

In this section, we analyze the effect that the formation of carbonaceous material inside the inert porous media reactor would have. Experimentation has shown that it occurs in rich filtration combustion of HFO [25]. Smith et al. [8] state that high molecular weight fuels are prone to soot formation, and that the material deposited on the porous medium consists of large hydrocarbons, condensed hydrocarbons and solid carbon. It is expected that the formation of this residue on the inert packed bed of the reactor will result in a lower production of syngas. To consider this impact, it is proposed to transform the generation of carbonaceous residual to a decrease of φ in zone L₂ of Model I, and to assign this value to the inlet condition in this section (computation domain). It should be noted that all the analysis that include Model I in previous sections consider that ϕ of the fuel mixture at inlet in zone L_1 is the same as that of inlet in zone L_2 .

The results of rich filtration combustion of kerosene Jet-A [8], indicate that up to 40% of the carbon entering the reactor is deposited on the porous medium ($\varphi = 3.15$). In particular, for the range $\varphi = 1.0$ to $\varphi = 1.5$ their results show that these deposits could reach close to 20% (Fig. 3 in Ref. [8]). We compare the base case of *Model I* ($\varphi = 1.3$, $v_{filt} = 19.3$ cm/s), assigning a decreased φ in the inlet condition of zone L_2 , between $\varphi = 1.3$ (deposit, 0%) and $\varphi = 1.04$ (deposit, 20%). The H₂ and CO productions in this range are compared with those of the optimal case of *Model C*–I ($\varphi = 1.3$, $L_2/D_{Ti} = 0.25$, $v_{filt} = 19.3$ cm/s).

Fig. 11 shows that at $\varphi = 1.2$ (deposit, 7.4%) for inlet to the zone L_2 of Model I, generates a syngas production of the same order of magnitude as Model C–I. With carbon deposits on the porous media greater than 7.4% ($\varphi < 1.2$), the optimal case of Model C–I is a better alternative in H₂ and CO production. If the worst condition of Model I (deposit, 20%) is considered, with respect to the Model C–I, H₂ yield, CO yield and energy conversion efficiency to syngas, decrease by 34.5%, 26.5% and 30.4%, respectively. For deposits lower than 7.4% ($\varphi > 1.2$), the H₂ and CO productions of Model I improve with respect to the optimal of the hybrid model.

Conclusions

This paper has reported the results of a computational investigation of the production of hydrogen from heavy fuel oil in a hybrid catalytic/non-catalytic reactor. This model, called C–I for catalytic/inert is an extension of the inert only (I) model under rich inlet conditions ($\varphi > 1.1$). The model of the hybrid reactor developed here shows that in rich conditions the total energetic conversion increases due to the presence of hydrocarbon species generated by the catalytic-thermal cracking process. In addition, given the presence of non-converted hydrocarbon species in the exhaust gases from the catalytic portion the syngas yield will increase when processing this stream in series in a second inert porous media reactor.

The present results justify the idea of inserting a catalyticthermal cracking zone in an inert porous media reactor for rich filtration combustion of vaporized HFO. Then, a hybrid reactor with two reactive zones in series, cracking followed by POR, would be a better alternative to an inert porous media reactor with deposits of carbonaceous material that exceed 7.4%.

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Nomenclature

D _{Ti}	Internal diameter of the reactor defined at interface		
	bed packed-insulation, m		
Ei	Activation energy, J/mol		
$(-\Delta H_j)$	Heat of adsorption, J/mol		
Kj	Adsorption equilibrium constant		
K _{j0}	Pre-exponential factor, m³/(kg catalyst)		
k _i	Rate constant, various units		
k _{i0}	Pre-exponential factor, various units		
М	Molecular mass, g/mol		
ṁ	Mass flow rate, kg/s		
Ņ	Molar flow rate, mol/s		
$(-R_i)_{\text{S}}$	Rate of disappearance of species i at conditions at		
	catalyst external surface, kg _i /(kg•s)		
R_g	Universal gas constant, 8.314 J/(mol·K)		
Т	Temperature, K		
T_{AV}	Average temperature (500 °C)		
w_i	Mass fraction of component i, kg_i/kg		
Greek sy	mbols		
$\eta_{ m H_2}$	Yield of H2		
$\eta_{\rm CO}$	Yield of CO		
η_{energy}	Syngas energy conversion efficiency		
ρ	Density, kg/m ³		
$ ho_{ m cr}$	Crystallite density, kg/m ³		
φ	Equivalence ratio		

v Ratio of molecular weights

Subscripts

- 0 Inlet
- E Efficiency
- f Fluid
- h Homogeneous reaction
- i,j Species
- m Mixture, mass transfer
- s Solid

Abbreviations

- AP Aromatic products
- CAT-LC Catalyst prepared with large zeolite crystallites
- CP Cracking products
- CPO Cracking products-olefins
- CPP Cracking products-paraffins
- FCC Fluid catalytic cracking
- FO 6 #6 Fuel Oil
- HFO Heavy fuel oil

- HP Heavy products
- ISO Isomers
- LHV Lower heating value
- LPG Liquified petroleum gas
- POR Partial oxidation reforming
- RON Ring-opened products (naphthenes)
- ROA Ring-opened products (aromatics)

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.ijhydene.2017.12.056.

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